Tensor Properties of Solids

Phenomenological Development of the Tensor Properties of Crystals

Tensor Properties of Solids: Phenomenological Development of the Tensor Properties of Crystals
Richard F. Tinder

www.morganclaypool.com

ISBN: 1598293486 paperback
ISBN: 9781598293487 paperback

ISBN: 1598293494 ebook
ISBN: 9781598293494 ebook

DOI: 10.2200/S00057ED1V01Y200712ENG04
DOI: 10.2200/S00058ED1V01Y200712ENG05

A Publication in the Morgan & Claypool Publishers series

SYNTHESIS LECTURES ON ENGINEERING # 4

Lecture #4

Series ISSN
ISSN 1939-5221 print
ISSN 1939-523X electronic

Tensor Properties of Solids

Phenomenological Development of the Tensor Properties of Crystals

Richard F. Tinder
Washington State University

SYNTHESIS LECTURES ON ENGINEERING # 4

MORGAN & CLAYPOOL PUBLISHERS

ABSTRACT

Tensor Properties of Solids presents the phenomenological development of solid state properties represented as matter tensors in two parts: Part I on equilibrium tensor properties and Part II on transport tensor properties.

Part I begins with an introduction to tensor notation, transformations, algebra, and calculus together with the matrix representations. Crystallography, as it relates to tensor properties of crystals, completes the background treatment. A generalized treatment of solid-state equilibrium thermodynamics leads to the systematic correlation of equilibrium tensor properties. This is followed by developments covering first-, second-, third-, and higher-order tensor effects. Included are the generalized compliance and rigidity matrices for first-order tensor properties, Maxwell relations, effect of measurement conditions, and the dependent coupled effects and use of interaction diagrams. Part I concludes with the second- and higher-order effects, including numerous optical tensor properties.

Part II presents the driving forces and fluxes for the well-known proper conductivities. An introduction to irreversible thermodynamics includes the concepts of microscopic reversibility, Onsager's reciprocity principle, entropy density production, and the proper choice of the transport parameters. This is followed by the force–flux equations for electronic charge and heat flow and the relationships between the proper conductivities and phenomenological coefficients. The thermoelectric effects in solids are discussed and extended to the piezothermoelectric and piezoresistance tensor effects. The subjects of thermomagnetic, galvanomagnetic, and thermogalvanomagnetic effects are developed together with other higher-order magnetotransport property tensors.

A glossary of terms, expressions and symbols are provided at the end of the text, and end-of-chapter problems are provided on request. Endnotes provide the necessary references for further reading.

KEYWORDS

tensor properties, crystals, thermodynamics, equilibrium, transport

Preface

An exhaustive in-depth treatment of the tensor properties of crystals would be a daunting task and would require several books on the subject, each of which would be of considerable length. This would require each property, experimentally known to exist or predicted by theory, to be developed from first principles at the atomic or quantum mechanical level. This is not what this text is about. We purport to develop the physical properties of solids (actually crystals) from the thermodynamic and tensorial points of view, which, if done correctly, provide a valuable introduction to a multitude of physical properties. The phenomenological development used in this text permits a thermodynamic basis for property definitions that is inviolate or nearly so. However, it is correct to say that many of the matter tensor properties defined in this way may not have been studied previously to establish their relative importance.

This text is designed to be used as a one-semester or two-quarter course in the subject matter. It also serves as a valuable source of information for practicing engineers and scientists in related fields. Although the text provides the necessary background in tensor analysis, the readership is expected to have some knowledge of calculus and matrix algebra. An understanding of basic vector analysis is also deemed helpful. The necessary information regarding crystallography and point groups as they relate to this text is provided as background material in the text.

The contents of this text are based on the author's notes used for a graduate course taught over several years at Washington State University to graduate students and second-semester seniors in the areas of material science, electrical and mechanical engineering, physics, and chemical physics. An instructor of a course in this subject matter is provided ample opportunity to limit, alter, or expound on any part of the text material as needed to satisfy the course description and needs of the students. Extensive glossaries of terms, expressions, and symbols at the end of the text aid in the learning process.

As with any text dealing with complex subject matter, there will undoubtedly be found typos and errors that were overlooked by the author. Hopefully, these have been kept to a minimum. However, should any be found by the instructor or readers, the author would appreciate knowing of them so that corrections can be made. The author may be contacted at the following e-mail address: rtinder@eecs.wsu.edu.

Acknowledgments

The author is deeply indebted to the many senior and graduate students for their countless questions, comments, arguments, and suggestions given during the many years that the contents of this text were used as notes in the conduct of the author's graduate course taught at Washington State University. As most professors know, students can and do provide the most candid and critical assessments of material presented in a given course. The author also acknowledges the suggestions and contributions of Prof. Elias (Lee) Stefanakos to the subject matter presented in this text, in particular, to the optical effects presented in Chapter 7. Dr. Stefanakos is director of the Clean Energy Research Center at the University of South Florida.

Gratefully acknowledged is the encouragement and helpful suggestions offered by Joel Claypool, publisher of Morgan & Claypool Publishers. Finally and most importantly, the author acknowledges the support, care, and understanding of his loving wife, his best friend and confidante, Gloria.

Contents

PART I

Equilibrium Tensor Properties of Solids

CHAPTER 1

Introduction

1.1 DEFINITION OF A TENSOR PROPERTY

A property, as defined in this text, is a coefficient that linearly relates an intensive (or cause) parameter to an extensive (or effect) parameter. When the intensive and extensive parameters are tensor variables, the property is also a tensor quantity. One way of expressing this is

$$\begin{pmatrix}\text{Effect}\\ \text{Tensor}\\ \text{Parameter}\end{pmatrix} = \begin{pmatrix}\text{Tensor}\\ \text{Property}\\ \text{Coefficient}\end{pmatrix}\begin{pmatrix}\text{Cause}\\ \text{Tensor}\\ \text{Parameter}\end{pmatrix} \tag{1.1}$$

or its inverse, which places the inverse of the tensor property coefficient on the left-hand side of the equation.

The particular tensor property will have a definite physical significance and will be represented by a fixed number of components depending on the nature and tensor character of the intensive and extensive parameters that it relates. One physical significance of the property coefficient may be given as the rate of change of one parameter with respect to the other as implied by Eq. (1.1).

One or both of the parameters that define the property coefficient will usually be a field tensor such as stress or strain, electric or magnetic field strength, or temperature (a scalar). The extent to which a property of a crystal exists with respect to the application of a given field depends on the electronic and subatomic structure of the atoms and on the manner in which they are arranged in the lattice.

Shown in Table 1.1 are four typical examples of properties of crystals that are directly related by cause and effect tensor parameter. Here, the pyroelectric coefficient p_i is a vector–scalar tensor property, hence, a vector, that relates the change in polarization δP_i with a change in temperature δT. The thermal expansion coefficient α_{ij} is a tensor–scalar tensor property of tensor rank 2 that relates a change in strain ε_{ij} with a change in temperature δT. The piezoelectric coefficient d_{ijk} is a vector–tensor property of tensor rank 3 that relates the polarization P_i to the stress tensor σ_{jk}. Finally, the elastic compliance coefficient s_{ijkl} is a tensor–tensor property of rank 4 that relates the stress σ_{ij} to

TABLE 1.1: Typical examples of properties of crystals that are directly related by cause and effect tensor parameters

EFFECT TENSOR PARAMETER	CAUSE TENSOR PARAMETER	PROPERTY NAME	TENSOR EQUATION	TENSOR RANK OF COEFFICIENT
δP_i	δT	Pyroelectricity	$\delta P_i = p_i \delta T$	First (p_i)
$\delta \varepsilon_{ij}$	δT	Thermal expansion	$\delta \varepsilon_{ij} = \alpha_{ij} \delta T$	Second (α_{ij})
P_i	σ_{ij}	Piezoelectricity	$P_i = d_{ijk} \sigma_{jk}$	Third (d_{ijk})
ε_{ij}	σ_{kl}	Elasticity	$\varepsilon_{ij} = s_{ijkl} \sigma_{kl}$	Fourth (s_{ijkl})

Shown are the tensor parameters, property to which they are applicable, and the tensor equations and tensor rank for the property coefficients.

the strain ε_{kl} (Hooke's law). Thus, it is seen that the tensor rank of a property coefficient is the sum of the tensor ranks of the parameters that it relates. Note that all tensor property coefficients given in Table 1.1 are examples of equilibrium properties. A well-known example of a nonequilibrium or transport property is resistivity ρ_{ij}, a second-rank tensor that relates electric field strength E_i to the current density J_j according to $E_i = \rho_{ij} J_j$, which, of course, is the tensor representation of Ohm's law. The distinction between equilibrium and nonequilibrium transport properties will be made clear in the section that follows, together with Parts I and II of this text.

1.2 CONCEPTS OF EQUILIBRIUM AND REVERSIBILITY

The properties of interest to Part I of this text are those that can be represented by tensors and described with reference to equilibrium states and thermodynamically reversible changes in crystals. Consider a thought experiment on any closed system (e.g., a crystal) in which all imaginable physically measurable quantities are accurately recorded as a function of time. If it is found that all processes, defined by the physically measurable quantities, are macroscopically time independent, *thermodynamic equilibrium* is said to exist. This requires, for example, the absence of the transport of heat (or entropy), charge, and mass and that all parts of the system be mechanically in static equilibrium. Thus, thermodynamic equilibrium prevails if the system under consideration is in thermal, electrical, magnetic, mechanical, and chemical equilibrium. Thermodynamic equilibrium does permit microscopic fluctuations to occur on the atomic level as long as they are random and do not produce measurable time-dependent changes in the physical state of the system.

Properties of crystals that represent time-independent processes are called *equilibrium properties*. Such properties can adequately be described phenomenologically by using equilibrium thermodynamics, that is, thermostatics. Properties that represent time-dependent or spontaneous processes are called nonequilibrium or transport properties. Such properties can be described only by use of the thermodynamics of irreversible processes, a subject that is covered in Part II of this text.

The concept of thermodynamic reversibility is intimately connected with the concept of equilibrium. The term *reversible* applies to a process within a system that has been displaced from equilibrium only to an infinitesimal extent. Therefore, a reversible process may be defined as the hypothetical passage of the system through a series of equilibrium states so close together that they are nearly indistinguishable. Such a process is reversed by an appropriate infinitesimal change of the physical conditions imposed on the system. Actually, no ongoing process is reversible in the strict sense of the word. However, if the conditions to be imposed on the system are applied infinitesimally fast, then, within experimental error, the process may be considered reversible. A reversible process is usually considered to be a linear process over an infinitesimal change in cause and effect parameters. However, a reversible process may be nonlinear, provided that the infinitesimal changes in the system are restored reversibly. In the development of the equilibrium properties, we will assume that the reversible processes are linear and that thermodynamic equilibrium is established at each point in an infinitesimal change.

1.3 INTERACTION DIAGRAMS AND FIRST-ORDER EQUILIBRIUM PROPERTY NOMENCLATURE AND REPRESENTATION

It is appropriate that we now preview the spectrum of first-order equilibrium properties about which we shall later discuss in more detail. To do this, it is necessary to define the *conjugate parameters* from which the general first-order interaction diagram can be constructed. The four pairs of conjugate parameters are the following: (T,S), (E,P), (B,M), and (σ,ε), which give rise to $\sum_{n=1}^{8}(n-1) = 28$ first-order properties including 4 principal effects and 24 coupled effects. The conjugate parameter pairs are (temperature, entropy), (electric field strength, polarization), (magnetic flux density, magnetization), and (stress, strain), respectively. The conjugate pairs (E,P) and (B,M) are chosen in preference to others for the sake of consistency, with the thermodynamic developments yet to come.

Shown in Figure 1.1 is the generalized interaction diagram for the first-order equilibrium properties where the names, symbols, and tensor rank (in parentheses) are given for each of the eight parameters. The four *principal effects* are represented by horizontal lines (i.e., between conjugate parameters), whereas the *coupled effects* are given by the nonhorizontal lines. The vertical lines represent *dependent coupled properties* relating any two intensive parameters (or any two extensive parameters). The set of 16 "compliance" effects are shown by arrows that point to the dependent variables, which, in this case, are the extensive parameters. *Extensive parameters* are those that depend on the amount of material of the solid phase system. Parameters that are independent of the amount of material in the solid phase are called *intensive parameters* and are associated only with the external conditions (fields) imposed on the system. Thus, the arrows in Figure 1.1 are drawn from the intensive (independent) parameters to the extensive (dependent) parameters. Reversal of the arrows defines the set of 16 "rigidity" effects that will later be shown as the collective inverse of the "compliance" effects.

For the convenience of the reader, the 16 compliance equilibrium properties are presented in Table 1.2 in the order of increasing tensor rank, first for the principle effects and then for the

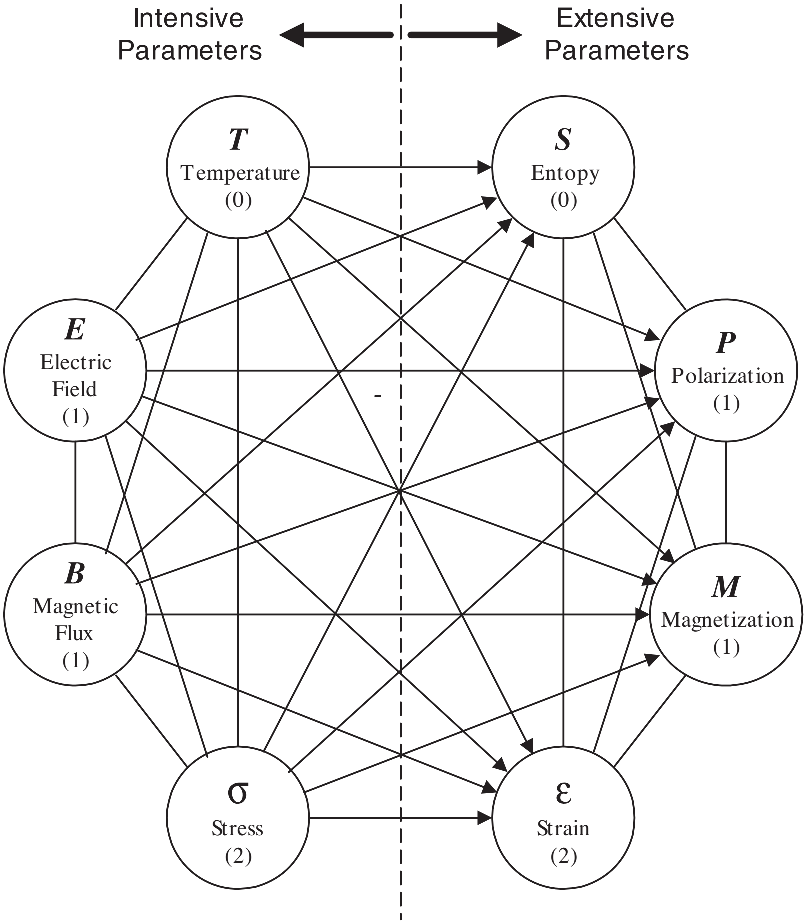


FIGURE 1.1: Generalized interaction diagram for the 28 first-order effects showing the names, symbols, and tensor rank (in parentheses) for each of the 8 parameters.

TABLE 1.2: The set of 16 compliance effects and their associated parameter pairs showing the 4 principal effects and 12 coupled effects as listed in the order of increasing tensor rank

PARAMETER PAIR	ASSOCIATED PROPERTY	TENSOR RANK
	Principal effects	
(S, T)	Heat capacity	0
(P, E)	Dielectric susceptibility	2
(M, B)	Magnetic susceptibility	2
(ε, σ)	Elasticity	4
	Interaction (coupled) effects	
(S, E)	Pyroelectric effect	1
(P, T)	Converse pyroelectric effect	1
(S, B)	Pyromagnetic effect (magnetocaloric effect)	1
(M, T)	Converse pyromagnetic effect	1
(S, σ)	Piezocaloric effect	2
(ε, T)	Thermal expansion (converse piezocaloric effect)	2
(P, B)	Magnetoelectric susceptibility	2
(M, E)	Converse magnetoelectric susceptibility	2
(P, σ)	Direct piezoelectric effect	3
(ε, E)	Converse piezoelectric effect (first-order electrostriction)	3
(M, σ)	Direct piezomagnetic effect	3
(ε, B)	Converse piezomagnetic effect (first-order magnetostriction)	3

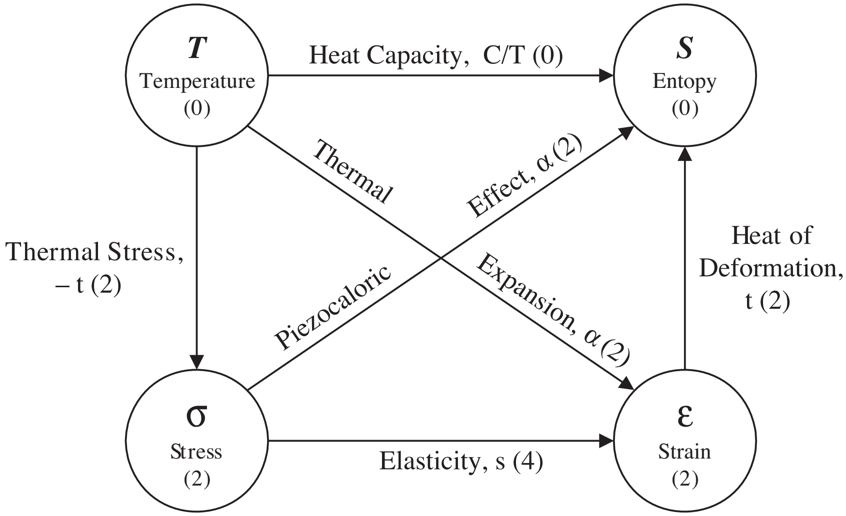


FIGURE 1.2: Interaction diagram representing the thermal, thermoelastic, and elastic effects. The arrows point to the dependent variable.

interaction (coupled) effects. Note that each parameter pair is given in (extensive, intensive) notation form.

Other equilibrium properties, not mentioned above, include those in Figure 1.1 for which no one-way arrows are shown. Some of these are of little or no interest to the developments in this text. Most of those equilibrium properties that remain are higher-order effects that can usually be defined in Taylor series expansions of the appropriate parameters. The higher-order effects are usually of high tensor rank and are, accordingly, more complicated. These include such effects as electrostriction, magnetostriction, and a variety of optical effects. Many of these effects will be considered in later chapters.

To provide a little more background detail, we will next consider an interaction diagram associated with the thermal and mechanical variables, that is, one that represents the thermal, thermoelastic, and elastic effects. This interaction diagram is shown in Figure 1.2 where the arrows again point toward the dependent variables.

Noting from Figure 1.2 that both the stress and temperature fields contribute to an elastic strain, we write in differential form,

$$d\varepsilon_{ij} = s^{T}_{ijkl}\, d\sigma_{kl} + \alpha^{\sigma}_{ij}\, dT \tag{1.2}$$

or in integrated form

$$\varepsilon_{ij} = s^{T}_{ijkl}\, \sigma_{kl} + \alpha^{\sigma}_{ij}\, \Delta T. \tag{1.3}$$

In these equations, $s^T_{ijkl} = (\partial\varepsilon_{ij} / \partial\sigma_{kl})_T$ is the isothermal (temperature independent) elastic compliance, and $\alpha^\sigma_{ij} = (\partial\varepsilon_{ij} / \partial T)_\sigma$ is the isopiestic (stress invariant) coefficient of thermal expansion. The fourth-rank tensor property s^T_{ijkl} represents a principal effect (elasticity) because it relates the conjugate parameters σ and ε. The second-rank tensor property α^σ_{ij}, on the other hand, represents a coupled effect (thermal expansion) because it relates the cross parameters T and ε at constant stress, σ.

By similar reasoning, one notes from Figure 1.2 that a positive increase in stress as well as an increase in temperature and strain produces an increase in the entropy of a crystal. In differential form, we write

$$\mathrm{d}S = \alpha^T_{ij}\,\mathrm{d}\sigma_{ij} + (C^\sigma / T)\mathrm{d}T \tag{1.4}$$

or in integrated form

$$\Delta S = \alpha^T_{ij}\,\sigma_{ij} + (C^\sigma / T)\Delta T. \tag{1.5}$$

Here, $\alpha^T_{ij} = (\partial S / \partial\sigma_{ij})_T$ is the isothermal piezocaloric coefficient, equal to the coefficient of thermal expansion measured under constant stress, and $C^\sigma = T(\partial S / \partial T)_\sigma$ is the isopiestic (constant stress) heat capacity. The fact that $(\partial S / \partial\sigma_{ij})_T = (\partial\varepsilon_{ij} / \partial T)_\sigma$ is a consequence of thermodynamic arguments to be discussed in detail later.

The properties just described have been defined in such a way that only the intensive parameters are held constant. Other coupled effects result from an association of the thermal and mechanical variables but which will have both intensive and extensive parameters held constant. Suppose it is desirable to equate the isothermal elastocaloric (heat of deformation) with the isometric thermal stress coefficient as depicted by the vertical arrows in Figure 1.2. When this is done, we write

$$(\partial S / \partial\varepsilon_{ij})_T = -(\partial\sigma_{ij} / \partial T)_\varepsilon = t_{ij}, \tag{1.6}$$

a result that follows from developments that will be presented later. Note that the isometric thermal stress coefficient describes the negative or compressive stress produced when a mechanically constrained crystal is heated. Equation (1.6) is one of many Maxwell relations to be discussed later in Chapters 4 and 5.

1.4 INTERACTION DIAGRAM FOR THE FIRST-ORDER NONEQUILIBRIUM TENSOR PROPERTIES

There is another important group of properties common to crystals that deal with thermodynamically irreversible phenomena. These are the transport properties that involve the flow of charge, heat, and mass. A complete understanding of these effects is possible only through the use of fluctuation theory, the principle of microscopic reversibility, and the Onsager reciprocal relations, that is, through the use of the thermodynamics of irreversible processes. In contrast, the interactions between equilibrium properties are easily deduced by using standard thermodynamic (thermostatic) arguments.

Although it is not commonly done, the first-order transport properties may also be represented by interaction diagrams. To do this, it must be stated clearly that the use of such diagrams in no way implies thermodynamic reversibility in the same sense as for the equilibrium properties, but rather implies microscopic reversibility as used in fluctuation theory. To construct a useful interaction diagram for first-order nonequilibrium properties, three pairs of conjugate parameters that are physically measurable are used. These pairs are the three current densities (fluxes) and their conjugate driving forces representing the flow of current (J^n, $\nabla\phi^E$), heat (J^q, $\nabla\phi^T$), and mass (J^m, $\nabla\phi^C$). Shown in Figure 1.3 is the interaction diagram for the first-order transport properties that positions the temperature gradient ($\nabla\phi^T$), electric potential gradient ($\nabla\phi^E$), and concentration gradient ($\nabla\phi^C$)

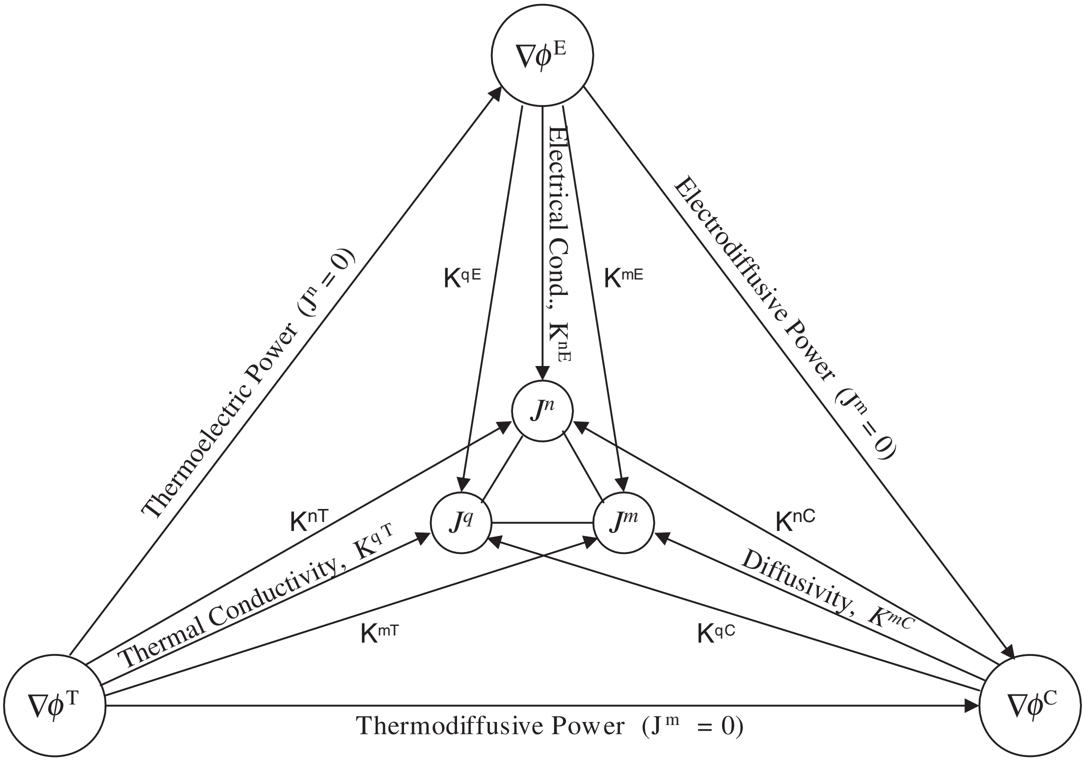


FIGURE 1.3: Interaction diagram for the first-order nonequilibrium (transport) properties showing the 9 conductivities and 3 power coefficients, all 12 of which are second-rank tensor properties.

in clockwise sequence on the outside of the interaction triangle. The heat current (J^q), electron (or ion) current (J^n), and mass current densities (J^m) are placed inside the gradient triangle nearest their respective conjugate parameters. All transport parameters, it will be noted, are tensors of rank 1, that is, vectors. This diagram represents $\sum_{n=1}^{6}(n-1) = 15$ relationships, which include nine conductivities each relating a flux to a gradient, three "power" coefficients each relating one gradient to another, and three relationships between the current densities. The 12 conductivities and power coefficients are each second-rank tensors. The relationships between fluxes are interpreted, for example, as the heat or entropy associated with the flow of charge for the (J^q, J^n) relationship and similarly for the two other pairs. These current density relationships have not been considered as tensor properties.

There exist other transport properties not included in the interaction diagram of Figure 1.3. These arise primarily from the application of magnetic and/or stress fields applied to crystals exhibiting one or more of the properties represented in the $J - \nabla\phi$ interaction diagram. This leads to important thermomagnetic and galvanomagnetic, piezoresistance, piezothermoelectric, and the piezogalvanomagnetic effects and to other higher-order transport properties.

The phenomenological developments of the transport properties in crystalline solids are the topics covered in Part II of this text. These properties will be discussed in some depth based on the basic principles of irreversible thermodynamics. The treatment is, by its nature, more difficult than that presented in Part I, dealing with the phenomenological developments of the equilibrium tensor properties—the basic principle of irreversible thermodynamics are statistical in nature, dealing mainly with fluctuation theory. Recognizing this, special care is taken to present the more complex developments in a manner that minimizes this difficulty.

• • • •

CHAPTER 2

Introduction to Tensor Notation, Tensor Transformations, Tensor Calculus, and Matrix Representation

2.1 INTRODUCTION TO TENSOR AND MATRIX NOTATION

To help understand the tensor notation used in Section 1.3 and in subsequent sections, we provide here an introduction to tensor analysis in the use of scalars, vectors, and tensors of second- and higher-order rank. To define explicitly the various tensor operations involved in a comprehensive treatment of the physical properties of solids, reference must be made to a coordinate system. This leads naturally to subscript notation and matrix forms, which will be used exclusively throughout this book.

Tensors are known to be abstract quantities that are used in the study of many physical laws of nature. There are different kinds of tensors (e.g., polar, axial, magnetic, axial–magnetic), and each kind is classified by its tensor rank, r. In general, a tensor is specified by $n^{(r)}$ components, where n is the number of dimensions of space being used. In three-dimensional Euclidean space, the number of components of a given tensor is $3^{(r)}$. We will be concerned only with orthogonal Euclidean coordinates (Cartesian coordinates) and with Cartesian tensors, thereby allowing the distinction between covariant and contravariant tensors laws to disappear, and hence of no concern to us.

A tensor of rank r that is specified by $3^{(r)}$ components in rectangular Cartesian coordinates is given in tensor subscript notation by T_{ijk}, that is, by r number of subscripts each taking on values 1, 2, 3 corresponding to three-dimensional Cartesian space. The components of these tensors can be represented by a matrix of symbols arranged in rows and columns. Consider, for example, a second-rank tensor T_{ij} relating two vectors p_i and q_j, with components p_1, p_2, and p_3, and q_1, q_2, and q_3, respectively. The tensor equation becomes

$$p_i = T_{ij} q_j \quad (i, j = 1,2,3), \tag{2.1}$$

where summation from 1 to 3 with respect to the repeating (dummy) suffix, j, is understood. This is called the *Einstein summation convention*, which allows the summation sign Σ to be dropped. Expanding Eq. (2.1), as required by summation, gives the following three equations for p_i:

$$\begin{aligned} p_1 &= T_{11}q_1 + T_{12}q_2 + T_{13}q_3 \\ p_2 &= T_{21}q_1 + T_{22}q_2 + T_{23}q_3 \\ p_3 &= T_{31}q_1 + T_{32}q_2 + T_{33}q_3 \end{aligned} \tag{2.2}$$

which can be represented in matrix form as

$$\begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix} \cdot \begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix} \tag{2.3}$$

or simply in matrix symbolic notation

$$p = Tq. \tag{2.4}$$

Vectors may be represented either by a (3 × 1 = rows × column) column matrix as in Eq. (2.3) or as a (1 × 3) row matrix

$$\begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} \qquad \text{or} \qquad \begin{bmatrix} p_1 & p_2 & p_3 \end{bmatrix},$$

depending on the type of matrix operation to be performed. The nine components of a second-rank tensor, T_{ij}, may be represented by a (3 × 3) matrix as in Eq. (2.3) or as either a (9 × 1) column matrix or (1 × 9) row matrix, as will be demonstrated later. In any case, it must be understood that a matrix is nothing more than an array of symbols or numbers arranged in rows and columns. The matrix array has no physical meaning in itself but may represent a tensor that does have physical significance.

2.2 TRANSFORMATION OF TENSORS

The tensor concept is intimately connected with the transformation laws for tensors. In fact, a tensor can be regarded as a mathematical entity having the transformation properties required by the physical quantities that it represents. The transformation of a tensor from one set of Cartesian coordinates to another set does not alter the tensor's physical significance but rather is simply another equivalent way of representing it.

A tensor may be classified as to its symmetry, that is, it may be symmetrical (or partially symmetrical), asymmetrical, or antisymmetrical. However, depending on its transformation law, the tensor may be further characterized as polar, axial, magnetic, or axial–magnetic. The components of an axial tensor change sign if the handedness of the coordinate axes is changed, whereas the components of a magnetic tensor change sign only if the atomic magnetic moments are reversed. Polar tensors, on the other hand, are unaffected by either change in handedness or reversal of magnetic moments. In this section, attention will be focused on the transformation laws of polar tensors.

2.2.1 Transformation of Scalars

Tensors of rank 0 are nondirectional physical quantities called *scalars* and are invariant under a coordinate transformation. Typical examples are mass, temperature, entropy, and heat capacity; thus, for example, $T' = T$ for the transformation of entropy.

2.2.2 Transformation of Vectors

Tensors of rank 1 are called *vectors*. Polar vectors (as distinguished from axial vectors) transform like the coordinates of a point. Let T_j be a polar vector with respect to axes $0x_1$, $0x_2$, $0x_3$ that is to be transformed to T'_i with respect to axes $0x'_1$, $0x'_2$, $0x'_3$ symbolized by $T \rightarrow T'$. Each T'_i is obtained by resolving the T_j along the axes $0x'_1$ as shown in Figure 2.1. The components for the three T'_i are given by

$$\begin{aligned} T'_1 &= a_{11}T_1 + a_{12}T_2 + a_{13}T_3 \\ T'_2 &= a_{21}T_1 + a_{22}T_2 + a_{23}T_3 \\ T'_3 &= a_{31}T_1 + a_{32}T_2 + a_{33}T_3 \end{aligned} \tag{2.5}$$

or

$$T'_i = a_{ij}T_j \qquad (i, j = 1,2,3 = 1 - 3) \tag{2.6}$$

in convenient tensor subscript notation. Here, the a_{ij} are called the *direction cosines*, for which examples are shown in Figure 2.1. Thus, nine direction cosines are required to specify the transformation of a polar vector where i and j represent the new and old axes, respectively.

Equations in (2.5) can also be conveniently represented in the matrix form

$$\begin{bmatrix} T'_1 \\ T'_2 \\ T'_3 \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \cdot \begin{bmatrix} T_1 \\ T_2 \\ T_3 \end{bmatrix} \tag{2.7}$$

or simply

$$T' = aT \tag{2.8}$$

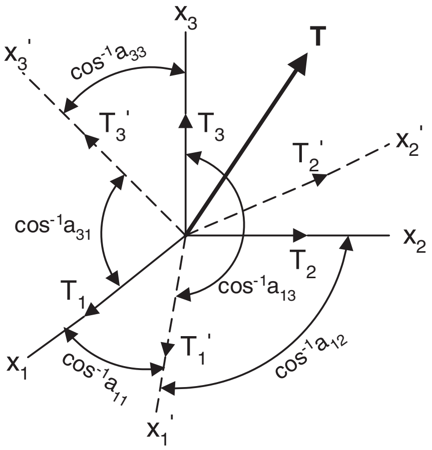


FIGURE 2.1: Transformation of the polar vector $T \rightarrow T'$ showing sample direction cosines.

in matrix symbolic notation. The reverse transformation symbolized by $T' \rightarrow T$ is given by

$$T = \tilde{a}T' = a^{-1}T', \tag{2.9}$$

where a is an orthogonal matrix and

$$\tilde{a} = \begin{bmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{bmatrix} \tag{2.10}$$

is the transpose of a always equal to its inverse, $\tilde{a} = a^{-1}$.

Examples of polar vectors are force, electric field, and polarization. Other vectors, such as mechanical moment, angular momentum, and the curl of a polar vector, are examples of axial vectors. Still other vectors, such as magnetic field strength, magnetic flux density, and magnetization, are both axial and magnetic in character and will be considered at a later time.

2.2.3 Transformation of Second-Rank Tensors

The transformation law for polar second-rank tensors can be developed from the transformation law for polar vectors. As in Eq. (2.4), consider a second-rank polar tensor that linearly relates two polar vectors p and q. With respect to two sets of axes $0x_i$ and $0x_i'$ and in matrix symbolic notation, Eq. (2.4) becomes

$$p = Tq \qquad \text{with respect to } 0x_i \tag{2.11}$$

$$p' = T'q' \qquad \text{with respect to } 0x'_i \tag{2.11a}$$

Transforming the components of p and q' separately, one obtains in matrix notation

$$p' = ap \tag{2.12}$$

$$q = \tilde{a}q', \tag{2.12a}$$

after which, by introducing Eqs. (2.11) and (2.12a) into Eq. (2.12), there results in matrix notation

$$p' = ap = aTq = aT\tilde{a}q' = T'q'.$$

It now follows that

$$T' = aT\tilde{a} \tag{2.13}$$

or

$$T'_{ij} = a_{ik}a_{jl}T_{kl} \qquad (i, j, k, l = 1, 2, 3 = 1-3) \tag{2.14}$$

in tensor subscript notation. Both Eqs. (2.13) and (2.14) represent the transformation law for polar second-rank tensors. In Eq. (2.14), the components of T'_{ij} are obtained by direct summation of the repeating (dummy) subscripts k and l, whereas in Eq. (2.13), the same components are given in the form

$$T' = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix} \begin{bmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{bmatrix}, \tag{2.15}$$

which are conformable for matrix multiplication.

2.2.4 Symmetrical and Antisymmetrical Second-Rank Tensors

Any second-rank tensor T_{ij} can be expressed as the sum of symmetrical S_{ij} and antisymmetrical A_{ij} tensors. In subscript notation and matrix symbolic notation, this is written as

$$T_{ij} = (T_{ij} + T_{ji})/2 + (T_{ij} - T_{ji})/2 = (T + \tilde{T})/2 + (T - \tilde{T})/2 = S_{ij} + A_{ij}, \tag{2.16}$$

where it follows that

$$S=\begin{bmatrix} T_{11} & ½(T_{12}+T_{21}) & ½(T_{13}+T_{31}) \\ ½(T_{21}+T_{12}) & T_{22} & ½(T_{23}+T_{32}) \\ ½(T_{13}+T_{31}) & ½(T_{32}+T_{23}) & T_{33} \end{bmatrix}=\begin{bmatrix} S_{11} & S_{12} & S_{31} \\ & S_{22} & S_{23} \\ \text{Sym.} & & S_{33} \end{bmatrix}=\tilde{S}, \tag{2.17}$$

$$A=\begin{bmatrix} 0 & ½(T_{12}-T_{21}) & ½(T_{13}-T_{31}) \\ ½(T_{21}-T_{12}) & 0 & ½(T_{23}-T_{32}) \\ ½(T_{31}-T_{13}) & ½(T_{32}-T_{23}) & 0 \end{bmatrix}=\begin{bmatrix} 0 & A_{12} & -A_{31} \\ -A_{12} & 0 & A_{23} \\ A_{31} & -A_{23} & 0 \end{bmatrix}=-\tilde{A}. \tag{2.18}$$

Clearly, S is specified generally by six independent components, whereas A is specified generally by three independent components. Thus, a symmetrical second-rank tensor is equal to its transpose, $S=\tilde{S}$, where S_{11}, S_{22}, and S_{33} are called the *principal components* that lie along the leading diagonal of the (S_{ij}) matrix. In the case of an antisymmetrical second-rank tensor, the principal components are zero. The stress tensor σ_{ij} is an example of a symmetrical second-rank tensor, such that $\sigma_{ij}=\sigma_{ji}$.

Equation (2.17) permits simplification of the matrix forms for symmetrical second-rank tensors. Writing the subscripts in a positive permutation of 123 gives the following results:

$$\begin{array}{lcccccc} \text{Tensor notation} & S_{11} & S_{22} & S_{33} & S_{23}(=S_{32}) & S_{31}(=S_{13}) & S_{12}(=S_{21}) \\ \text{Strain notation} & S_1 & S_2 & S_3 & 2S_{23} & 2S_{32} & 2S_{12} \\ \text{Matrix notation} & S_1 & S_2 & S_3 & S_4 & S_5 & S_6 \end{array} \tag{2.19}$$

The notation in (2.19) leads to three useful (6 × 1) column forms:

$$S=\begin{bmatrix} S_{11} \\ S_{22} \\ S_{33} \\ S_{23} \\ S_{31} \\ S_{12} \end{bmatrix} \text{ or } \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ 2S_4 \\ 2S_5 \\ 2S_6 \end{bmatrix} \text{ or } \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix} \tag{2.20}$$

or their (1 × 6) row transpositions. The single subscript form will be the form of choice for use in matrix symbolic equations. The third form in (2.20) is also the accepted matrix form for the strain tensor.

Examples of symmetrical second-rank tensors are stress, strain, thermal expansion, dielectric and magnetic susceptibilities, and others. From Eq. (2.18), it is clear that the principal components of an antisymmetrical second-rank tensor are null, leaving only three antisymmetrical components, A_{23}, A_{31}, and A_{12}. Examples of antisymmetrical second-rank tensors include the rotational component of a generalized elastic deformation leaving strain $\varepsilon_{ij} = \varepsilon_{ji}$ as a symmetrical second-rank tensor.

2.2.5 Quadratic Transformation Forms

The transformation of third- and fourth-rank tensor components is greatly facilitated by the use of quadratic transformation forms, which can be readily obtained from the transformation law for second-rank tensors. It is assumed that any second-rank tensor involved in the description of a third- or fourth-rank tensor is symmetrical such that use can be made of the linear transformation law

$$S' = aS\tilde{a} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \cdot \begin{bmatrix} S_{11} & S_{12} & S_{31} \\ S_{12} & S_{22} & S_{23} \\ S_{31} & S_{23} & S_{33} \end{bmatrix} \cdot \begin{bmatrix} a_{11} & a_{21} & a_{31} \\ a_{12} & a_{22} & a_{32} \\ a_{13} & a_{23} & a_{33} \end{bmatrix}. \tag{2.21}$$

Carrying out the indicated multiplication and arranging the components of S' and S into (6×1) column matrices permits Eq. (2.21) to be represented in the quadratic form

$$\begin{bmatrix} S'_1 \\ S'_2 \\ S'_3 \\ S'_4 \\ S'_5 \\ S'_6 \end{bmatrix} = \left[\begin{array}{ccc|ccc} a_{11}^2 & a_{12}^2 & a_{13}^2 & 2a_{12}a_{13} & 2a_{13}a_{11} & 2a_{11}a_{12} \\ a_{11}^2 & a_{22}^2 & a_{23}^2 & 2a_{22}a_{23} & 2a_{23}a_{21} & 2a_{21}a_{22} \\ a_{11}^2 & a_{32}^2 & a_{33}^2 & 2a_{32}a_{33} & 2a_{33}a_{31} & 2a_{31}a_{32} \\ \hline a_{21}a_{31} & a_{22}a_{32} & a_{23}a_{33} & a_{22}a_{33}+a_{23}a_{32} & a_{21}a_{33}+a_{23}a_{31} & a_{21}a_{32}+a_{22}a_{31} \\ a_{31}a_{11} & a_{32}a_{12} & a_{33}a_{13} & a_{12}a_{33}+a_{13}a_{32} & a_{11}a_{33}+a_{13}a_{31} & a_{11}a_{32}+a_{12}a_{31} \\ a_{11}a_{21} & a_{12}a_{22} & a_{13}a_{23} & a_{12}a_{23}+a_{13}a_{22} & a_{11}a_{23}+a_{13}a_{21} & a_{11}a_{22}+a_{12}a_{21} \end{array} \right] \cdot \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{bmatrix}$$

or simply in symbolic matrix notation

$$S' = \alpha S. \tag{2.22}$$

Here, α is a (6×6) matrix called the *quadratic transformation matrix* for a symmetrical second-rank tensor and where the third single subscript notation of (2.20) has been applied. With few exceptions, the property tensors of higher order, which are commonly encountered, are represented by third- and fourth-rank tensors having some inherent symmetry. Thus, where it is necessary to specify the transformation law for these matter tensors, rather extensive practical use will be made of the α transformation form—a method preferred over the more cumbersome method of direct summation of the repeating suffixes in the tensor subscript forms.

A mnemonic diagram for the quadratic transformation matrix α can be constructed by dividing it into four sections as follows:

$$\left[\begin{array}{l:c} \text{Square of element } a_{ij} & \text{Twice the product of row} \\ \text{of } [a_{ij}] \text{ matrix} & \text{omissions of } [a_{ij}] \text{ matrix} \\ \hdashline \text{Product of column} & \text{Cross product of} \\ \text{omissions of } [a_{ij}] \text{ matrix} & \text{minor of element } a_{ij} \end{array}\right].$$

The content of these four sections can be verified by an inspection of Eq. (2.22) in expanded form.

Not all property tensors exhibit inherent symmetry, and for this reason, a similar quadratic transformation law must be written for an asymmetrical second-rank tensor. In this case, the transformation matrix becomes a (9×9) quadratic form. The development of this more general form follows from Eq. (2.15) by carrying out the indicated multiplication and arranging the components of T' and T as (9×1) matrices similar to (2.20) but with no symmetry. The result is given by

$$T' = \beta T, \tag{2.23}$$

where β is called the (9×9) *general quadratic transformation matrix* for asymmetrical second-rank tensors presented in Eq. (9.31). The β transformation form is useful in describing the transformation laws for the less common piezothermoelectric and elastothermoelectric power properties as well as the piezomagnetoelectric and elastomagnetoelectric effects.

2.2.6 Transformation of Third-Rank Tensors

Consider a third-rank tensor, T, relating a polar vector, p, and a polar second-rank tensor, q, written with respect to two sets of coordinate exes, $0x_i$ and $0x'_i$:

$$p_i = T_{ijk}q_{jk} \qquad \text{or} \qquad p = Tq \qquad \text{for axes } 0x_i \tag{2.24}$$

and

$$p'_l = T'_{lmn}q'_{mn} \qquad \text{or} \qquad p' = T'q' \qquad \text{for axes } 0x'_i \tag{2.25}$$

For the case where q is a symmetrical second-rank tensor (hence, $q = \tilde{q}$), it follows that for the transformations $p' = ap$, $q' = \alpha q$, and $q = \alpha^{-1}q'$, there results

$$p' = ap = aTq = aT\alpha^{-1}q' = T'q',$$

giving for the transformation law for T

$$T' = aT\alpha^{-1}, \tag{2.26}$$

where α^{-1} is the inverse of α and where it is understood that $\alpha^{-1} \neq \tilde{\alpha}$ in general. In tensor subscript notation, Eq. (2.26) is written as

$$T'_{ijk} = a_{il}a_{jm}a_{kn}T_{lmn} \qquad (i - n = 1 - 3) \tag{2.27}$$

The partial symmetry of T in Eq. (2.24) is implied by the symmetry of q. This is easily shown by using tensor subscript notation giving

$$p_i = T_{ijk}q_{jk} = T_{ikj}q_{kj}, \tag{2.28}$$

which permits

$$T_{ijk} = T_{ikj}\,.$$

In matrix subscript notation, Eq. (2.28) becomes

$$p_i = T_{im}q_m \qquad (i = 1 - 3;\ m = 1 - 6), \tag{2.29}$$

where q is now a (6×1) column matrix and Eq. (2.29) becomes

$$p = \begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \\ T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \\ T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ q_3 \\ q_4 \\ q_5 \\ q_6 \end{bmatrix} = Tq, \tag{2.30}$$

with respect to axes $0x_i$. Note that subscript m in Eq. (2.29) is unfolded according to the matrix notation in (2.20). This permits a reduction in the T matrix from a (3×9) to a (3×6) matrix, as given in Eq. (2.30), both of which avoid the need for a three-dimensional representation.

The tensors T_{ijk} and T_{ikj} in Eq. (2.28) are called *tensor isomers* and represent a certain partial symmetry. The tensor T_{ijk} has a total of 3! = 6 isomers possible, which are obtained by the permutation of pairs of subscripts. In comparison, the transpose of a second-rank tensor T_{ij} is its only isomer. Examples of third-rank tensor properties that exhibit this partial symmetry are the piezoelectric effect, first-order electrostriction, piezomagnetic effect and first-order magnetostriction, the linear electro-optical effect, the thermal–electro-optical effect, and others.

The transformation of components for the partially symmetrical third-rank tensor $T_{ijk} = T_{ikj}$ is carried out in accordance with Eq. (2.26) for new and old sets of axes, $0x'_i$ and $0x_i$, respectively:

$$T' = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \cdot \begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \\ T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \\ T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} \end{bmatrix} \begin{bmatrix} \alpha_{11}^{-1} & \alpha_{12}^{-1} & \alpha_{13}^{-1} & \alpha_{14}^{-1} & \alpha_{15}^{-1} & \alpha_{16}^{-1} \\ \alpha_{21}^{-1} & \alpha_{22}^{-1} & \alpha_{23}^{-1} & \alpha_{24}^{-1} & \alpha_{25}^{-1} & \alpha_{26}^{-1} \\ \alpha_{31}^{-1} & \alpha_{32}^{-1} & \alpha_{33}^{-1} & \alpha_{34}^{-1} & \alpha_{35}^{-1} & \alpha_{36}^{-1} \\ \alpha_{41}^{-1} & \alpha_{42}^{-1} & \alpha_{43}^{-1} & \alpha_{44}^{-1} & \alpha_{45}^{-1} & \alpha_{46}^{-1} \\ \alpha_{51}^{-1} & \alpha_{52}^{-1} & \alpha_{53}^{-1} & \alpha_{54}^{-1} & \alpha_{54}^{-1} & \alpha_{56}^{-1} \\ \alpha_{61}^{-1} & \alpha_{62}^{-1} & \alpha_{63}^{-1} & \alpha_{64}^{-1} & \alpha_{65}^{-1} & \alpha_{66}^{-1} \end{bmatrix}$$

which represents the matrix equation

$$T' = aT\alpha^{-1} \tag{2.31}$$

It may be recalled that the inverse (or reciprocal) A_{ij}^{-1} of a matrix A is the transpose of the cofactor (A_{ij}) of the element A_{ij} divided by the non-zero determinant of A_{ij}. That is,

$$(A_{ij})^{-1} = \frac{(A_{ji})}{|A_{ij}|} \quad \text{or} \quad A^{-1} = \frac{(\tilde{A})}{|A|} \tag{2.32}$$

where $(A_{ij}) = (-1)^{(i+j)}|M_{ij}|$ is the cofactor of element A_{ij} and $|M_{ij}|$ is its minor (the determinant that remains after removing the ith row and jth column in $|A_{ij}|$).

Obviously, transformation of tensors of rank 3 can be quite laborious. Fortunately, the linear and quadratic transformation matrices representing the symmetry operation for crystals are relatively uncomplicated. As will be shown later in Section 3.5, these matrices often consist of components that are 0, 1, or -1, and in most cases, $\alpha^{-1} = \tilde{\alpha}$, a result that is not true generally.

2.2.7 Transformation of Fourth-Rank Tensors

In similar fashion, the transformation law for a fourth-rank tensor property can be deduced from the transformation laws of the tensor variables it relates. Consider the fourth-rank tensor property relating two polar second-rank tensor variables with reference to the two sets of axes, $0x_i$ and $0x'_i$

$$p_{ij} = T_{ijkl}q_{kl} \qquad \textit{or} \qquad p = Tq \qquad \textit{for axes } 0x_i \tag{2.33}$$

and

$$p'_{mn} = T'_{mnop} q'_{op} \qquad \text{or} \qquad p' = T'q' \qquad \text{for axes } 0x'_i. \tag{2.34}$$

If both p and q are symmetrical second-rank tensors, convenient use can again be made of the α quadratic transformation form. Because p and q' transform as $p' = \alpha p$ and $q = \alpha^{-1} q'$, then

$$p' = \alpha p = \alpha T q = \alpha T \alpha^{-1} q' = T'q'$$

or

$$T' = \alpha T \alpha^{-1} \tag{2.35}$$

as the transformation equation for T in matrix symbolic notation. In tensor subscript notation, Eq. (2.35) becomes

$$T'_{ijkl} = a_{im} a_{jn} a_{ko} a_{lp} T_{mnop} \qquad (i - p = 1 - 3) \tag{2.36}$$

The partial symmetry of T_{ijkl} is implied by the symmetry of $p_{ij} = p_{ji} = p_m$ and $q_{kl} = q_{lk} = q_n$ where it is now proper to write

$$p_m = T_{mn} q_n \qquad (m, n = 1 - 6) \tag{2.37}$$

The partial symmetry expressed by Eq. (2.37) permits a reduction in the number of independent coefficients needed to specify T from $3^{(4)} = 81$ to 36. Because both p and q are represented by (6×1) matrices, it follows that T must be a (6×6) matrix and that Eq. (2.37) can be presented as

$$\begin{bmatrix} p_1 \\ p_2 \\ p_3 \\ p_4 \\ p_5 \\ p_6 \end{bmatrix} = \begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \\ T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \\ T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} \\ T_{41} & T_{42} & T_{43} & T_{44} & T_{45} & T_{46} \\ T_{51} & T_{52} & T_{53} & T_{54} & T_{55} & T_{56} \\ T_{61} & T_{62} & T_{63} & T_{64} & T_{65} & T_{66} \end{bmatrix} \cdot \begin{bmatrix} q_1 \\ q_2 \\ q_3 \\ q_4 \\ q_5 \\ q_6 \end{bmatrix}. \tag{2.38}$$

Just as for the case of the partially symmetrical third-rank tensor, the transformation law for the partially symmetrical fourth-rank tensor in Eq. (2.37) is most conveniently represented in matrix form according to $T' = \alpha T \alpha^{-1}$ in Eq. (2.35), giving

$$T' = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} & \alpha_{14} & \alpha_{15} & \alpha_{16} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} & \alpha_{24} & \alpha_{25} & \alpha_{26} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} & \alpha_{34} & \alpha_{35} & \alpha_{36} \\ \alpha_{41} & \alpha_{42} & \alpha_{43} & \alpha_{44} & \alpha_{45} & \alpha_{46} \\ \alpha_{51} & \alpha_{52} & \alpha_{53} & \alpha_{54} & \alpha_{55} & \alpha_{56} \\ \alpha_{61} & \alpha_{62} & \alpha_{63} & \alpha_{64} & \alpha_{65} & \alpha_{66} \end{bmatrix} \begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \\ T_{21} & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \\ T_{31} & T_{32} & T_{33} & T_{34} & T_{35} & T_{36} \\ T_{41} & T_{42} & T_{43} & T_{44} & T_{45} & T_{46} \\ T_{51} & T_{52} & T_{53} & T_{54} & T_{55} & T_{56} \\ T_{61} & T_{62} & T_{63} & T_{64} & T_{65} & T_{66} \end{bmatrix} \begin{bmatrix} \alpha^{-1}_{11} & \alpha^{-1}_{12} & \alpha^{-1}_{13} & \alpha^{-1}_{14} & \alpha^{-1}_{15} & \alpha^{-1}_{16} \\ \alpha^{-1}_{21} & \alpha^{-1}_{22} & \alpha^{-1}_{23} & \alpha^{-1}_{24} & \alpha^{-1}_{25} & \alpha^{-1}_{26} \\ \alpha^{-1}_{31} & \alpha^{-1}_{32} & \alpha^{-1}_{33} & \alpha^{-1}_{34} & \alpha^{-1}_{35} & \alpha^{-1}_{36} \\ \alpha^{-1}_{41} & \alpha^{-1}_{42} & \alpha^{-1}_{43} & \alpha^{-1}_{44} & \alpha^{-1}_{45} & \alpha^{-1}_{46} \\ \alpha^{-1}_{51} & \alpha^{-1}_{52} & \alpha^{-1}_{53} & \alpha^{-1}_{54} & \alpha^{-1}_{54} & \alpha^{-1}_{56} \\ \alpha^{-1}_{61} & \alpha^{-1}_{62} & \alpha^{-1}_{63} & \alpha^{-1}_{64} & \alpha^{-1}_{65} & \alpha^{-1}_{66} \end{bmatrix} \qquad (2.39)$$

Here again, it is shown that numerical manipulation required to transform a higher-rank tensor is considerable, particular for an arbitrary rotation of axes. In such cases, use of the computer is recommended. However, as pointed out earlier, transformation matrices representing most crystal symmetry operations are strikingly simple, allowing tensor transformations in most cases to be carried out with little difficulty by using $\alpha^{-1} = \tilde{\alpha}$ in Eqs. (2.31) and (2.39) or even by the method of direct inspection discussed later.

The maximum inherent symmetry possible for fourth-rank tensors is given by

$$T_{mn} = T_{nm} \qquad (m, n = 1 - 6)\,. \qquad (2.40)$$

In this case, the leading diagonal of components becomes the $mn = nm$ symmetry line. This eliminates the 15 coefficients below the leading diagonal symmetry line as independent components. The remaining 21 coefficients are now represented by the symmetrical (6 × 6) matrix

$$[T_{mn}] = \begin{bmatrix} T_{11} & T_{12} & T_{13} & T_{14} & T_{15} & T_{16} \\ & T_{22} & T_{23} & T_{24} & T_{25} & T_{26} \\ & & T_{33} & T_{34} & T_{35} & T_{36} \\ & & & T_{44} & T_{45} & T_{46} \\ & \text{(Sym.)} & & & T_{55} & T_{56} \\ & & & & & T_{66} \end{bmatrix} = [T_{nm}] \qquad (2.41)$$

The symmetrical matrix of Eq. (2.41) is used to represent the elastic compliance and stiffness moduli as well as the many properties involving these moduli. The inherent symmetry expressed by $T_{mn} = T_{nm}$ results solely from thermodynamic arguments that are presented in Section 4.4.

Property tensors with tensor rank greater than four are not as common as some of those of lesser tensor rank. Nevertheless, a few fifth- and sixth-rank tensor properties have either been measured experimentally or have been predicted to exist on theoretical grounds. Examples are the fifth-rank piezoelectro-optical, piezomagneto-optical, and sixth-rank quadratic piezo-optical effects mentioned in Section 7.3.2 and the quadratic piezothermoelectric power and quadratic piezo-

TABLE 2.1: The transformation laws for polar tensors up through the rank 4 showing tensor rank, tensor subscript notation, matrix symbolic notation, and the referred matrix text equation.

	TRANSFORMATION LAW		
RANK	TENSOR SUBSCRIPT NOTATION	MATRIX SYMBOLIC NOTATION	REFERRED MATRIX EQUATION
0	$T' = T$	—	—
1	$T'_i = a_{ij} T_j$	$T' = at$	(2.8)
2	$T'_{ij} = a_{ik} a_{jl} T_{kl}$	$T' = aT\tilde{a}$	(2.13)
3	$T'_{ijk} = a_{il} a_{jm} a_{kn} T_{lmn}$	$T' = aT\alpha^{-1}$	(2.31)
4	$T'_{ijkl} = a_{im} a_{jn} a_{ko} a_{lp} T_{mnop}$	$T' = \alpha T\alpha^{-1}$	(2.35)

resistance effects represented in Eqs. (9.26) and (9.38), respectively, both of which are sixth-rank tensor properties.

2.2.8 Summary of Tensor Transformation Laws

For the convenience of the reader, Table 2.1 summarizes the transformation laws for polar tensors up through rank 4 that exhibit some inherent symmetry. The transformation equations are given in both tensor subscript form, where summation over the dummy (repeating) subscripts is understood, and in conformable matrix symbolic form, the latter being derived from equations of the form $p = Tq$. The transformation equations for the fifth- and sixth-rank tensor properties mentioned above will be left as additional exercises for the reader.

In the matrix equations, use is made of the quadratic transformation matrix α, which assumes a) some inherent symmetry for a given tensor T and b) that the first and third forms in the column matrices of Eqs. (2.20) are equated. If no inherent symmetry exists in T, the matrix forms of the transformation laws in Table 2.1 may still be used but with the α matrix replaced by the more general β transformation form given in Eq. (9.31) applicable to asymmetrical second-rank tensors.

2.3 INTRODUCTION TO TENSOR ALGEBRA

Up to this point, we have made some use of tensor algebra without specific mention of the laws involved. We will now review various standard operations involving tensor addition and multiplication with some exceptions. The subjects of axial tensors, tensor differentiation, tensor field subject matter, and the vector cross product will be reviewed later in Sections 2.4, 2.5, and 2.6, respectively.

2.3.1 Tensor Addition

The addition (or subtraction) of corresponding components of two or more tensors all having the same tensor rank yields a resultant tensor of the same rank. As an example, consider adding components of two symmetrical second-rank polar tensors A and B expressed in both tensor subscript and symbolic matrix notation:

$$R_{ij} = A_{ij} + B_{ij} \qquad \textit{or} \qquad R = A + B$$

This requires that $R_{11} = A_{11} + B_{11}$, $R_{22} = A_{22} + B_{22}$, … $R_{12} = A_{12} + B_{12}$ for all six independent components of the resultant matrix R. The sum rule may be generalized by the equation

$$R_{ijk\ldots} = A_{ijk\ldots} + B_{ijk\ldots} + \ldots, \tag{2.42}$$

which is restricted to components of tensors having the same rank and tensor character. The sum rule obeys the commutative, associative, and distributive laws of additions well-known in Cartesian algebra.

2.3.2 Tensor Multiplication

For the reader's convenience and by using the symbol ⊗ to represent the outer and inner product operations, we review the following tensor multiplication laws best illustrated by using conformable matrix forms:

$$\begin{array}{ll} \text{Cumulative law} & A \otimes B = B \otimes A \\ \text{Associative law} & A \otimes (B \otimes C) = (A \otimes B) \otimes C \\ \text{Distributive law} & A \otimes (B + C) = A \otimes B + A \otimes C \end{array} \tag{2.43}$$

These laws are written in the order of increasing extent to which they are obeyed by the tensor multiplication operations. Generally speaking, the distributive law is always obeyed if the sum rule is obeyed, the associative law is obeyed if the permutation tensor is not involved, and the commutative law is never obeyed except for scalar products. The tensor representation of the vector cross product and the properties of the Kronecker delta and permutation tensor will be reviewed later in Section 2.6.3.

2.3.3 Outer Product

The product of two tensors AB that yields a resultant tensor of tensor rank equal to the sum of the tensor ranks of A and B $(r_A + r_B)$ is called the *outer product* or *dyadic product* of A and B. For example, the outer product of a vector A_i and a symmetrical second-rank tensor B_{jk} yields a tensor of third-rank R_{ijk}. That is,

$$R_{ijk} = A_i B_{jk} \qquad (i, j, k = 1 - 3)$$

or

$$R_{im} = A_i B_m \qquad (i = 1 - 3;\ m = 1 - 6). \tag{2.44}$$

The expanded matrix form of Eq. (2.44) yields a (3×6) AB matrix given by

$$R = \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} \cdot \begin{bmatrix} B_1 & B_2 & B_3 & B_4 & B_5 & B_6 \end{bmatrix} = \begin{bmatrix} A_1B_1 & A_1B_2 & A_1B_3 & A_1B_4 & A_1B_5 & A_1B_6 \\ A_2B_1 & A_2B_2 & A_2B_3 & A_2B_4 & A_2B_5 & A_2B_6 \\ A_3B_1 & A_3B_2 & A_3B_3 & A_3B_4 & A_3B_5 & A_3B_6 \end{bmatrix}.$$

Note that if $B \neq \widetilde{B}$, then the product AB yields a (3×9) matrix.

The outer product rule can be generalized by the tensor subscript equation

$$R_{ijk\ldots opq\ldots} = A_{ijk\ldots} B_{opq\ldots}, \tag{2.45}$$

where R has a tensor rank equal to the sum of the ranks of A and B, that is, $r_R = r_A + r_B$, a fact that is lost in the use of symbolic matrix notation $R = AB$.

2.3.4 Tensor Contraction

When a single subscript in the product or two tensors of the same rank r are set equal, a single contraction results producing a tensor of rank $(r - 2)$. The product of two tensors of arbitrary rank results in tensor contraction called the *inner product* and is generalized in tensor subscript notation as

$$R_{\ldots ijlm} = A_{\ldots ijk} B_{klm\ldots} \tag{2.46}$$

or $R = A{\cdot}B$ in tensor symbolic notation. Here, R is a tensor of rank $r_R = (r_A + r_B) - 2$ having the same tensor character as that of A and B. As an example, consider the single contraction (inner) product of a polar vector and a partially symmetrical third-rank polar tensor $(B_{ijk} = B_{ikj})$ given by

$$R_{jk} = A_i B_{ijk} \qquad (i, j, k = 1 - 3)$$

or

$$R_m = A_i B_{im} \qquad (i = 1 - 3;\ m = 1 - 6)$$

In expanded matrix form, this becomes

$$R = [A_1 \quad A_2 \quad A_3] \cdot \begin{bmatrix} B_{11} & B_{12} & B_{13} & B_{14} & B_{15} & B_{16} \\ B_{21} & B_{22} & B_{23} & B_{24} & B_{25} & B_{26} \\ B_{31} & B_{32} & B_{33} & B_{34} & B_{35} & B_{36} \end{bmatrix} = [R_1 \quad R_2 \quad R_3 \quad R_4 \quad R_5 \quad R_6],$$

which yields the components of symmetrical polar second-rank tensor R in the form of a (1×6) matrix.

Double contraction results when two subscripts in the product of two tensors of the same rank r are set equal, producing a tensor of rank $r - 4$. The double contraction product of two tensors of arbitrary tensor rank is generalized in tensor subscript notation as

$$R_{\ldots hk\ldots} = A_{\ldots hij} B_{ijk\ldots} \tag{2.47}$$

or $R = A \cdot B$ in tensor symbolic notation. Here, R is a tensor of rank $r_R = (r_A + r_B) - 4$ having the same tensor character as that of the A and B combination. An example of double contraction is

$$R_{ij} = A_{ijkl} B_{kl} \qquad (i, j, k, l = 1 - 3), \tag{2.48}$$

which was used in Eq. (2.33) to represent a polar fourth-rank that relates two polar second-rank tensors.

Tensor contraction continues through triple, quadruple, etc. contractions and becomes complete when the product of two tensors of the same rank yields a scalar. This product is called the *scalar product*, which is generalized as

$$R = A_{ijk\ldots} B_{ijk\ldots} = \mathrm{tr}\,(AB) \tag{2.49}$$

called the *trace* of AB. An example is the scalar product of two symmetrical second-rank tensors,

$$R = A_{ij} B_{ij},$$

represented in matrix form as the scalar product

$$R = [A_1 \;\; A_2 \;\; A_3 \;\; A_4 \;\; A_5 \;\; A_6]\begin{bmatrix} B_1 \\ B_2 \\ B_3 \\ B_4 \\ B_5 \\ B_6 \end{bmatrix} = \mathrm{tr}(AB)$$

$$= A_1B_1 + A_2B_2 + A_3B_3 + A_4B_4 + A_5B_5 + A_6B_6 \qquad (2.50)$$

2.4 AXIAL TENSORS

The tensors discussed so far have been polar tensors that transform, such that the sign of their components is unaltered by a transformation that changes the handedness of the coordinate axes. Table 2.1 gives the transformation laws for polar tensors. Tensors having components that change sign when the handedness of the coordinate axes is changed by a transformation are called *axial tensors* or *pseudo tensors.*

To generalize, axial tensors transform according to

$$T'_{ijk\ldots} = |a| a_{im} a_{jn} a_{ko} \cdots T_{mno\ldots}\,. \qquad (2.51)$$

Here, for example, the "handedness" factor $|a|$ for a second-rank tensor is the determinant of the transformation matrix (a_{ij}) given symbolically by

$$|a| = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = a \cdot \begin{vmatrix} e & f \\ h & i \end{vmatrix} - b \cdot \begin{vmatrix} d & f \\ g & i \end{vmatrix} + c \cdot \begin{vmatrix} d & e \\ g & h \end{vmatrix}$$

where, for example, $\begin{vmatrix} e & f \\ h & i \end{vmatrix} = ei - fh$. Thus, $|a| = -1$ for a transformation that changes the handedness of the axes, and $|a| = 1$ if the handedness is left unchanged by the transformation. Table 2.1 for polar tensor transformations applies to axial tensors if the handedness factor $|a| = \pm 1$ is included on the right-hand side of each transformation law. For a scalar, the transformation law becomes $T' = |a|T$. An example of an axial (pseudo)-scalar is the optical rotatory power, ρ. Vectors, such as magnetic field strength, magnetic flux density, and magnetization, are both axial and magnetic in character. As a second example, the Hall tensor R_{ijk} is both antisymmetrical (in subscripts j,k or i,k)

and axial–magnetic but which can be represented as a polar–magnetic second-rank tensor as discussed in Section 10.3. The reader must be aware of the fact that axial tensors and antisymmetrical tensors are two entirely different tensor characteristics the distinction of which will be made evident in Section 2.6.3. Magnetic tensor character is discussed in Appendix A.

2.5 TAYLOR'S SERIES EXPANSION AND THE TENSOR DIFFERENTIATION LAWS

Taylor's series is a type of power series used to express a given function of one or more variables by means of a polynomial in the neighborhood where the function is regular (analytic). A valid Taylor's series expansion requires that the series be convergent within a finite interval and that all derivatives (or partial derivatives) of the function be continuous in that interval. For the general case of multivariable tensor functions, the Taylor's series expansion is given symbolically by

$$f(P_i, Q_j, R_{kl}\dots) = \sum_{n=0}^{\infty} \frac{1}{n!} \left\{ (P_i - P_i^0)\frac{\partial}{\partial P_i} + (Q_j - Q_j^0)\frac{\partial}{\partial Q_j} + (R_{kl} - R_{kl}^0)\frac{\partial}{\partial R_{kl}} + \dots \right\}^n f(P_i^0, Q_j^0, R_{kl}^0\dots), \quad (2.52)$$

where $n = 1, 2, 3, \dots$ is an integer and $f(P_i^0, Q_j^0, R_{kl}^0\dots)$ signifies that after the function is operated on, the resulting coefficients are evaluated at the reference values of $P_i = P_i^0$, $Q_j = Q_j^0$, $R_{kl} = R_{kl}^0$, and so forth. Because the function f may itself be a tensor quantity of arbitrary tensor rank, the resulting coefficients are tensors given in accordance with the tensor differentiation laws

$$T_{\dots ijkl\dots} = \left(\frac{\partial A_{\dots ij}}{\partial B_{kl\dots}}\right)_{C,D,\dots}, U\dots_{ijkl\dots rs\dots} = \left(\frac{\partial^2 A_{\dots ij}}{\partial B_{kl\dots}\, \partial C_{rs\dots}}\right)_{D,E,\dots} \ \dots,\ \text{et} \quad (2.53)$$

Here, the law expressed by $T_{\dots ijkl\dots}$ implies that all remaining components of B and all components of C, D, and so forth are held constant and that $T_{\dots ijkl\dots}$ has the tensor rank $r_A + r_B$ and the combined tensor character of A and B. The law expressed by $U\dots_{ijkl\dots rs\dots}$ for a second-order derivative implies that U has a tensor rank of $r_A + r_B + r_C$ with the combined tensor character of A, B, and C, where it is understood that the remaining components of B and C and all components of D, E, and so forth are held constant. Notice that our rule of subscript order is read from top-to-bottom–left-to-right. However, because other subscript order schemes can be found in literature, care must be taken to recognize which scheme is used.

As an example of the use of Eq. (2.53), let the electric polarization P_i be a function of electrical field strength E_j and stress σ_{kl} and let $P_i(E_j, \sigma_{kl})$ be expanded in a Maclaurin series (special case of a Taylor series) about the state of zero electric field and zero stress to give

$$P_j(E_j, \sigma_{kl}) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(E_j \frac{\partial}{E_j} + \sigma \frac{\partial}{\sigma} \right)^n P_i(0,0), \tag{2.54}$$

giving the result

$$P_j(E_j, \sigma_{kl}) = P_i(0,0) + \left(\frac{\partial P_i}{\partial E_j} \right)_{(0,0)} E_j + \left(\frac{\partial P_i}{\partial \sigma_{kl}} \right)_{(0,0)} \sigma_{kl} + \frac{1}{2!} \left[\left(\frac{\partial^2 P_i}{\partial E_j \partial E_m} \right)_{(0,0)} E_j E_m \right.$$
$$\left. + 2 \left(\frac{\partial^2 P_i}{\partial E_j \partial \sigma_{kl}} \right)_{(0,0)} E_j \sigma_{kl} + \left(\frac{\partial^2 P_i}{\partial \sigma_{kl} \partial \sigma_{no}} \right)_{(0,0)} \sigma_{kl} \sigma_{no} \right] + \cdots$$

As will be shown in later chapters, the various coefficients (in parentheses) define certain tensor properties. For example, $\kappa_0^{-1}(\partial P_i / \partial E_j) = \chi_{ij}$ is the dielectric susceptibility tensor for a crystal and κ_0 is the permittivity in a vacuum. The quantity $(\partial P_i / \partial \sigma_{kl}) = d_{ikl}$ is the piezoelectric tensor. Here, both χ_{ij} and d_{ikl} are first-order ($n = 1$) effects evaluated, in this case, at zero electric field and zero stress. The three properties given within the square brackets are second-order ($n = 2$) effects and are represented by third-, fourth-, and fifth-rank tensors also evaluated at zero electric field and zero stress. Note that had the expansion in Eq. (2.54) also been taken about the state of reference temperature T^0, it would be called a Taylor's series—hence, the basic distinction between a Maclaurin's series and a Taylor's series.

2.6 TENSOR FIELDS AND TENSOR OPERATORS

For purposes of this section, we will use the symbol ψ to represents a Cartesian tensor field of rank r in a region R and specified by $3^{(r)}$ continuous functions of position $\psi_{ijk\ldots}(x_1, x_2, x_3)$ or simply $\psi_{ijk\ldots}(x)$. We will cover only the tensor gradient and divergence, Kronecker delta, permutation tensor, vector cross product, and tensorial contraction because these will be used later in both Parts I and Part II of this text. Other related subjects such as Stoke's theorem and Green's theorem in a plane and their application to thermodynamics will be discussed in sufficient detail as they become needed in later developments. The curl of a tensor will be left to further reading (see Endnotes).

2.6.1 Gradient of a Tensor Field

The components of a field tensor of rank r can be differentiated with respect to the coordinates of a point, resulting in a tensor of rank $r + n$, where n is the order of the differential operator used. One can generalize the tensor gradient as the outer product of two tensors, a field tensor $\psi_{ijk\ldots}(x)$ of rank r and the nth-order operator $\partial_{pst\ldots}$ of rank n. That is,

$$T_{ijk\cdots pst} = \partial_{pst\cdots}\psi_{ijk\cdots} = \frac{\partial\psi_{ijk\cdots}}{\partial x_p \partial x_s \partial x_t \cdots} \tag{2.55}$$

written as $T = \text{grad}\,\psi = \nabla\psi$ in tensor symbolic notation. Here, T transforms as a tensor of rank $r + n$ and is represented by $3^{(r+n)}$ continuous functions of position $T(x)$ in Cartesian space. Note that Eq. (2.55) has been written by using the rule of subscript order given in Section 2.5.

The simplest application of Eq. (2.55), and one in which we are particularly interested, is the gradient of a scalar field. If the scalar field is represented by ϕ, then its gradient is a Cartesian vector having components given as

$$\partial_i\phi = \left[\frac{\partial\phi}{x_1}, \frac{\partial\phi}{x_2}, \frac{\partial\phi}{x_3}\right] \tag{2.56}$$

or written as $\text{grad}\,\phi = \nabla\phi$ in vector symbolic notation. See Eq. (8.1) in Chapter 8 as an example. The gradient of a scalar points in the direction of the maximum rate of change and that has a magnitude equal to that maximum rate of change. Examples of a scalar field are the electrostatic potential (or voltage), chemical potential, and temperature. Thus, the gradient of any scalar field is always from low to high potential as, for example, from low to high temperature. Thus, Fourier's law requires that the heat must flow from high to low temperature in a direction opposite to the temperature gradient, hence, the minus sign in Eq. (8.7) presented in Part II of this text.

Application of Eq. (2.55) to the field vector $\psi_i(x)$ results in the asymmetrical dyadic $\partial_j\psi_i = \partial\psi_i/\partial x_j$ called the *vector gradient* of the given field with components given by a 3 × 3 Jacobian matrix,

$$T_{ij} = \left[\frac{\partial\psi_i}{\partial x_j}\right] = \begin{bmatrix} \partial_1\psi_1/\partial x_1 & \partial_1\psi_1/\partial x_2 & \partial_1\psi_1/\partial x_3 \\ \partial_2\psi_2/\partial x_1 & \partial_2\psi_2/\partial x_2 & \partial_2\psi_2/\partial x_3 \\ \partial_3\psi_3/\partial x_1 & \partial_3\psi_3/\partial x_2 & \partial_3\psi_3/\partial x_3 \end{bmatrix} \tag{2.57}$$

We will have no further need to apply Eq. (2.55) to tensor fields of tensor rank greater than $r = 1$.

2.6.2 Divergence of a Tensor Field

The divergence of a tensor can be generalized by the single-contraction product of a field tensor $\psi_{ijk\ldots}(x)$ of rank r with the vector operator ∂_i yielding a tensor of rank $r-1$ given by

$$T_{jk\ldots} = \partial_i \psi_{ijk\ldots} = \frac{\partial \psi_{ijk\ldots}}{\partial x_i} \tag{2.58}$$

or as $T = \operatorname{div}\psi = \nabla \cdot \psi$ in tensor symbolic notation. Contraction can be carried out on any of the indices of $\psi_{ijk\ldots}(x)$, but the results will, in general, be different.

A physical interpretation of Eq. (2.58) is reasonably straightforward. The divergence of a tensor gives at each point the rate per unit volume at which the physical entity represented by ψ is issuing from that volume. The *divergence theorem* (also known as Gauss' theorem) is widely used and provides the integral definition of divergence of a tensor field given by

$$\operatorname{div}\psi \equiv \lim_{\Delta V \to 0} \left(\frac{\oint_s \mathrm{d}S \cdot \psi}{\Delta V} \right) \tag{2.59}$$

where $\oint_s \mathrm{d}S \cdot \psi$ is called the net flux of ψ out of S. Thus, Eq. (2.59) defines the divergence of a tensor field at a point P in V as the limiting value of the flux of ψ per unit volume out of S when $\Delta V \to 0$.

The simplest example is the divergence of a vector field $\psi_i(x)$ equal to a scalar $\partial_i \psi_i$ having magnitude

$$\partial_i \psi_i = \frac{\partial \psi_1}{\partial x_1} + \frac{\partial \psi_2}{\partial x_2} + \frac{\partial \psi_3}{\partial x_3} = \operatorname{tr}(\partial_j \psi_i), \tag{2.60}$$

which is equal to the trace of the vector gradient in Eq. (2.57). A well-known example of the application of Eq. (2.60) is the steady state in a thermoelectric system when the divergence of the energy flux vanishes, that is, $\nabla \cdot J^u = 0$. This means that the heat energy emitted to the surroundings, say, by Joule (I^2R-type) heating in a volume element must be exactly balanced by the heat energy absorbed by that volume element from the surroundings.

2.6.3 Kronecker Delta, Permutation Tensor, Vector Cross Product, and Tensorial Contraction

The Kronecker delta is defined by

$$\delta_{ij} = \begin{pmatrix} 1 & \text{if} & i = j \\ 0 & \text{if} & i \neq j \end{pmatrix} \quad \text{or} \quad [\delta_{ij}] = \begin{bmatrix} \delta_{11} & \delta_{12} & \delta_{13} \\ \delta_{21} & \delta_{22} & \delta_{23} \\ \delta_{31} & \delta_{32} & \delta_{33} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{2.61}$$

Now, if T_i is the ith component of a vector, then with the definitions of Eqs. (2.61), there results the expressions $\delta_{ij}T_i = T_j$ and $\delta_{ij}T_j = T_i$, or for a tensor T_{jk}, there results $\delta_{ij}T_{jk} = T_{ik}$ and $\delta_{ij}T_{ik} = T_{jk}$. All express the *substitution property of the Kronecker delta*, which will be used in Section 9.3 of this text.

The *permutation tensor* e_{ijk} (also called the Levi–Civita tensor, *alternating tensor*, or e-tensor) is an antisymmetrical, axial, third-rank tensor defined by

$$e_{ijk} \equiv \left\{ \begin{matrix} +1 \text{ if } ijk \text{ is an even permutation of } 123 \\ -1 \text{ if } ijk \text{ is an odd permutation of } 123 \\ 0 \text{ if any two subscripts are the same} \end{matrix} \right\} \tag{2.62}$$

A common application of e_{ijk} is the vector cross product or $\vec{R} = \vec{B} \times \vec{C}$ described by the equation given in tensor notation

$$R_i = e_{ijk}B_jC_k \qquad (i, j, k, = 1, 2, 3) \tag{2.63}$$

The three components of R_i are readily found by expansion of Eq. (2.63) or by using the matrix form

$$\begin{bmatrix} R_1 \\ R_2 \\ R_3 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} B_1C_1 \\ B_2C_2 \\ B_3C_3 \\ B_2C_3 \\ B_2C_1 \\ B_1C_2 \\ B_3C_2 \\ B_1C_3 \\ B_2C_1 \end{bmatrix} = \begin{bmatrix} B_2C_3 - B_3C_2 \\ B_3C_1 - B_1C_3 \\ B_1C_2 - B_2C_1 \end{bmatrix} \tag{2.64}$$

Equations in (2.64) can be represented simply by $R = e(BC)$ in matrix symbolic notation, where the *dyadic product* (BC) has been unfolded as the 9×1 form of T_{ij} in Eq. (2.3). The top row of the $[3 \times 9]$ matrix is unfolded as 111, 122, 133, 123, 131, 112, 132, 113, 121, then 211, 222, 233, 223, 231, 212, 232, 213, 221 for the second row, and 311, 322, 333, 323, 331, 312, 332, 313, 321 for the third row.

The difference between the antisymmetrical and axial character of a tensor is nicely described in terms of the e-tensor. The permutation tensor has been described as antisymmetrical. This is true by virtue of the fact that if any two subscripts of the component e_{ijk} are set equal, the component becomes zero—the antisymmetrical property. The e-tensor is also axial due to the fact that if any two subscripts are interchanged, which is equivalent to reversing the handedness of the axes, the value of the e-tensor changes sign, 1 to −1, or vice versa. These special features of the e-tensor will be useful in dealing with the magneto-optical and galvanomagnetic effects discussed in Sections 7.3.4 and 10.2.

A generalization of the single contraction product involving e_{ijk} without restriction on tensor rank and character is given by

$$A_{jklm\cdots} = e_{ijk} T_{ilm\cdots} \tag{2.65}$$

or simply by $A = e \cdot T$ in tensor symbolic notation. This equation states that a tensor T of rank r can be represented by its *dual* A of rank $r + 1$. Here, A has the combined tensor character of e and T but retains the physical properties of T. Thus, if T represents an axial second-rank tensor (e.g., the magnetoelectric susceptibility discussed in Section 4.5, then A must be an antisymmetrical (nonaxial) tensor with the physical properties of T. A common application of Eq. (2.65) is the case where an axial vector is converted to an antisymmetrical second-rank tensor given by

$$A_{jk} = e_{ijk} R_i \tag{2.66}$$

A generalization of double contraction product involving e_{ijk} can be represented, with certain restrictions to tensors of arbitrary tensor rank and character, by the equation

$$A_{ilm\cdots} = e_{ijk} T_{jklm\cdots} \tag{2.67}$$

or simply by $A = e : T$ in tensor symbolic notation. Here, the tensor rank of A is $r - 1$ when the tensor rank of T is r. The restrictions imposed on Eq. (2.67) are simply that tensor T must be of second-rank or higher and that it must be antisymmetrical in j and k if it is necessary that all components of T be retained by A in the conversion. Thus, as an example, $e_{ijk} S_{jk} = 0$ if $S = \tilde{S}$. As a second example, the reverse conversion to Eq. (2.66) permits an antisymmetrical second-rank tensor to be converted to an axial vector expressed as

$$R_i = e_{ijk} A_{jk} \tag{2.68}$$

Or, as a third example, if T is an antisymmetrical third-rank tensor in j,k only but is also axial, then A must be a polar (true) second-rank tensor as expressed by

$$A_{il} = e_{ijk} T_{jkl} \tag{2.69}$$

Here, A is said to be the dual of T. Equation (2.69) will find use in Section 10.3 when dealing with the Hall tensor.

Further tensorial contraction using the permutation tensor is possible by highly restricted. A common example is the triple scalar product $V = \vec{a} \times \vec{b} \cdot \vec{c}$, which represents the volume of a general parallelepiped of sides $\vec{a}, \vec{b}, \vec{c}$ In tensor notation, this scalar product is simply written as

$$V = e_{ijk} a_i b_j c_k \tag{2.70}$$

Thus, V does not transform as a simple scalar but rather as a pseudo (axial) scalar according to $V' = |a| V$.

The generalized Kronecker delta denoted by $\delta_{ijk}^{\alpha\beta\gamma} = e_{\alpha\beta\gamma} e_{ijk} = \Delta^K$ is given by the matrix

$$\Delta^K = \begin{bmatrix} \delta_{\alpha i} & \delta_{\alpha j} & \delta_{\alpha k} \\ \delta_{\beta i} & \delta_{\beta j} & \delta_{\beta k} \\ \delta_{\gamma i} & \delta_{\gamma j} & \delta_{\gamma k} \end{bmatrix} \tag{2.71}$$

such that the contraction products follow Section 2.3.4, leading to the matrix for triple contraction given by $e\tilde{e} = 2\mathrm{tr}(e\tilde{e}) = 6$ as used in Section 7.3.4.

• • • •

CHAPTER 3

Crystal Systems, Symmetry Elements, and Symmetry Transformations

3.1 INTRODUCTION

In the previous chapter, it was shown that the possession of inherent symmetry by a tensor of rank r had the effect of reducing the number of independent components representing it from $3^{(r)}$ to some number that was determined by the number of indices that could be interchanged. In this section, we will discuss certain additional limitations placed on the relationships between the components of a tensor property by the structural symmetry of the crystal within which the property is manifest. Remember, however, that not all tensors are affected by crystal symmetry. Second-rank field tensors such as stress and strain possess certain intrinsic symmetry, but their components are unaffected by the symmetry of the crystal. On the other hand, property tensors, which may relate two or more field tensors and hence possess their intrinsic symmetry, will also acquire the symmetry of the crystal within which the property is evinced. Thus, property tensors may possess a higher symmetry than that possessed by the crystal.

When the components representing a given property tensor vary with crystallographic direction, the crystal is said to be *anisotropic* with respect to that property. Conversely, if the components of a given property tensor are invariant with crystallographic direction, the crystal is said to be *isotropic* with respect to that particular property. A crystal may possess partial isotropy with respect to a given property if, for example, the components of the property are invariant with direction in a particular crystallographic plane but vary with direction out of that plane.

The term *crystal symmetry*, as used above, refers not to the atomic structure but to the morphology or macroscopic symmetry of the crystal. During the natural growth of some crystals, the planes of highest atomic density have a propensity to form the external faces of the crystal. A naturally occurring quartz crystal is a good example. The special relationship between these faces produces a symmetry that forms the basis of classification of crystals into 32 conventional symmetry classes called *point groups*. Thus, each of the 32 point groups defines a symmetry class. It is the point group symmetry (i.e., macroscopic symmetry) of a crystal that imposes certain limitations on the relationships between different components of a macroscopic tensor property. For magnetic crystals, the atomic magnetic spin moments, viewed collectively over the crystal, become important in symmetry considerations. This leads to the formation of the 90 magnetic point groups. There are, however, certain microscopic symmetry elements that take place at the atomic level and that are not possible in a point group, conventional or magnetic. Several symmetry operations at the atomic level are used to classify the microscopic symmetry elements in a three-dimensional space lattice, and these are called a *space group*. There are 230 conventional space groups and 1651 magnetocrystalline space groups, and every crystal must belong to one or more of these groups. We will not further consider space groups, conventional or magnetic, since they fall outside the scope of this text.

3.2 MACROSCOPIC CRYSTAL SYMMETRY AND SYMMETRY TRANSFORMATIONS

There are two fundamental macroscopic symmetry operations that can be performed at a point to generate all 32 point groups representing the 32 crystal classes. These two operations are rotation and center of symmetry. We will consider these in some detail along with the appropriate symmetry transforms and then develop the symbology used to designate the 32 point groups.

3.2.1 Permissible Rotations

When a perfect crystal can be brought into congruence with itself by a rotation about an axis, it is said to possess a *proper rotation axis* of symmetry. One-, two-, three-, four-, and sixfold rotation axes are permissible as expressed by $\phi = 2\pi / n$, where $n = 1, 2, 3, 4$, or 6. These permissible rotations are presented in Table 3.1 and are often referred to as monad, diad, triad, tetrad, and hexad axes of rotation, respectively. Rotations for $n = 5, 7, \ldots$ are not permissible.

3.2.2 Center of Symmetry

Taking the origin of coordinates as the center of symmetry, this operation consists of moving each point (x, y, z) to a position $(-x, -y, -z)$ as shown in Figure 3.1. This represents an inversion of axes through the origin of coordinates and is expressed by the transformation matrix $(a_{ij}) = -(\delta_{ij})$, where (δ_{ij}) is the *unitary matrix*. Note that in tensor subscript notation, δ_{ij} is called the Kronecker delta previously discussed in Section 2.6.3.

TABLE 3.1: Permissible rotations to bring a perfect crystal into self-congruence

n	1	2	3	4	6
Rotation, $\phi = 2\pi / n$	$\phi = 360°$	$\phi = 180°$	$\phi = 120°$	$\phi = 90°$	$\phi = 60°$

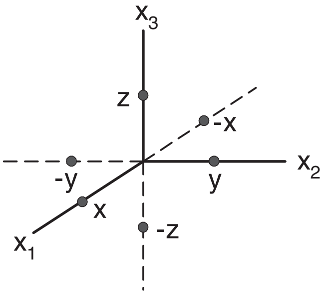


FIGURE 3.1: Coordinate axes showing a center of symmetry.

The two operations, an *n*-fold proper rotation and a center of symmetry, may be combined to produce *rotoinversion* axes designated by $\bar{x} = \bar{1}, \bar{2}, \bar{3}, \bar{4}$, or $\bar{6}$. The rotoinversion operation is one of *n*-fold rotation followed by inversion through a center of coordinates. If the transformation matrices for these two operations are a_1 and a_2 $(= -\delta_{ij})$, respectively, then the resultant transformation matrix is $a = a_2 a_1 = (-\delta_{ij})a_1 = -a_1$. A twofold rotoinversion axis of symmetry, $\bar{2}$, is identical to a reflection across a mirror plane (sometimes called a *plane of symmetry*) lying perpendicular to the $\bar{2}$ axis. This is illustrated in Figure 3.2, where the symbol commonly used to designate a plane of symmetry is m $(=\bar{2})$.

As an example, the rotoinversion transformation matrix representing a reflection across the mirror plane x_1, x_2 is

$$a = -(\delta_{ij})\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \qquad (3.1)$$

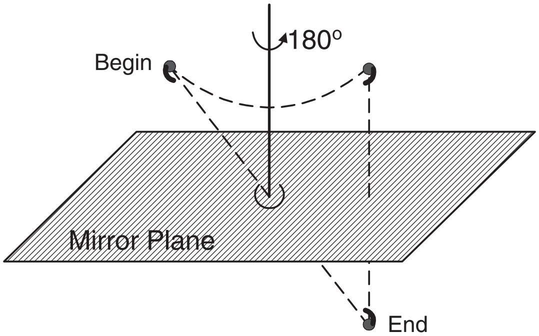


FIGURE 3.2: Graphical illustration of a twofold rotoinversion axis of symmetry.

which is obvious from an inspection of Figure 3.2. Here, the first and second matrices represent a center of symmetry and a 180° rotation about the $0x_3$ axis, respectively—the order is immaterial. Remember that the entries (1's, −1's, and 0's in this case) in a transformation matrix represent the direction cosines as illustrated in Figure 2.1.

Other combinations of the two fundamental symmetry elements are possible and are designated by certain symbology. An n-fold rotoinversion axis lying in a plane of symmetry is designated as $\bar{X}m = \bar{n}m$. An n-fold rotation axis of symmetry perpendicular to a plane of symmetry is designated as $X/m = n/m$. As an example, consider a fourfold rotation axis of symmetry about $0x_3$ lying normal to the x_1, x_2 plane of symmetry. This symmetry operation designated as $4/m (= 4\bar{2})$, has a transformation matrix

$$a = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \tag{3.2}$$

TABLE 3.2: Symmetry transformation symbology used to identify the 32 point groups

X	An n-fold rotation axis of symmetry
$\bar{X}$	An n-fold rotoinversion axis of symmetry
m	Plane of symmetry or mirror plane
X/m	Rotation axis with one mirror plane normal to it
$X2$	Rotation axis with a diad normal to it
$\bar{X}2$	Rotoinversion axis with a diad normal to it
Xm	Rotation axis with one mirror plane parallel to it
$\bar{X}m$	Rotoinversion axis with one mirror plane parallel to it
Xmm	Rotation axis with one mirror plane parallel to it*
X/mmm	Rotation axis with one mirror plane normal to it and one mirror plane parallel to it*

*The last element in three- and four-element forms such as Xmm and X/mmm is usually unnecessary to generate the group (see Table 3.6 for examples).

and the 4/*m* point group would be generated by repeated operations represented by the above transformation matrix product. The symbology used to identify the 32 point groups is presented in Table 3.2, where *X* and *n* are interchangeable, and all rotations are taken to be CCW (positive rotations).

3.3 SPACE LATTICES, UNIT CELLS, CRYSTALLOGRAPHIC PLANES, AND DIRECTIONS—MILLER INDICES

A crystal is defined as a special arrangement of atoms that repeats itself periodically in three dimensions. If this periodicity is precise and if it is continuous ad infinitum, the crystal is said to be perfect. Of course, real crystals cannot be perfect because they have finite bounds (free surfaces) and contain internal imperfections such as impurities, vacancies, dislocations, and usually subboundaries. We will treat crystals as being of finite dimensions but without internal defects.

The atomic arrangement in a crystal is conveniently represented as a three-dimensional network of straight lines called a *space lattice*. The intersections of lines are points of the space lattice that may represent the residence of a single atom or a group of atoms distributed in some fashion about the point. There are 14 space lattices called *Bravais lattices* into which all crystal structures must fall. Each space lattice has some convenient set of axes that is conventionally used with it. Six different systems of axes are commonly used in crystallography. Each set of lattice axes 0x, 0y, 0z represents the directions along which the primitive translation vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ lie as illustrated in Figure 3.3.

The six different systems of axes define the six crystal systems into which fall the 14 Bravais lattices and hence all the crystal structures possible. These are presented in Table 3.3 together with the unit cell axes and angles, the lattice symbols, and the minimum symmetry elements required for

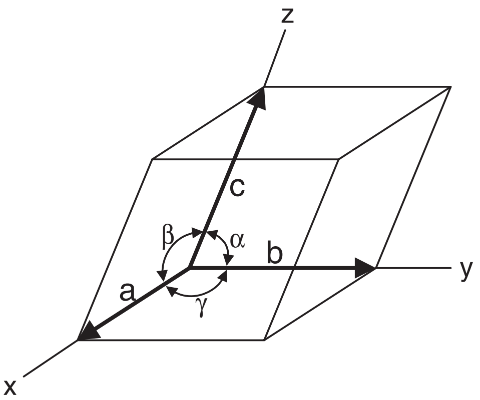


FIGURE 3.3: General space lattice showing the primitive translation vectors and angles.

membership in each system. The lattice symbols P, F, I, C, and R are the Hermann–Mauguin notation for primitive (P), face-centered (F), body-centered (I), base-centered (C), and rhombohedral (R) unit cells. Thus, a given crystal system may exist as more than one Bravais lattice. For example, the orthorhombic crystal system exists in primitive, face-centered, body-centered, and base-centered crystal structures.

The space lattice is then generated by the translation vector

$$\vec{T} = m\vec{a} + p\vec{b} + q\vec{c}, \tag{3.3}$$

where m, p, and q are integers. The totality of all such translation operations for all values of m, p, and q is called the translation group of the crystal. The magnitudes (a, b, and c) of primitive translation vectors $\vec{a}, \vec{b}, \vec{c}$ are called the *lattice parameters*, which, together with the lattice angles (α, β, γ), define the unit cell of a crystal.

Before continuing with the subject of macroscopic crystal symmetry elements and symmetry transformations, it will be instructive to review the notation for describing crystallographic planes and directions. Shown in Figure 3.4 are the generalized Miller and Miller–Bravais indices for planes and directions for the six crystal systems in Table 3.3 where the hexagonal and trigonal systems are treated together.

Here, referring to Figure 3.4(a), the Miller indices for the plane (hkl) are the reciprocals of the intercepts ($1 / i_x$, $1 / i_y$, $1 / i_z$). For example, if the intercepts are ($i_x = 1$, $i_y = 1$, $i_z = 1$), then

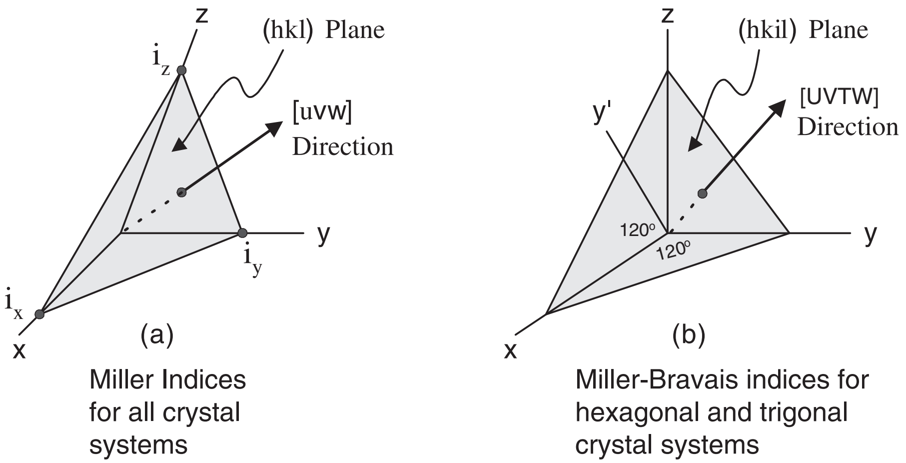


FIGURE 3.4: Notation for description of planes and directions showing Miller indices for all crystal systems and the Miller–Bravais indices for the hexagonal and trigonal crystal systems.

TABLE 3.3: The 14 Bravais lattices showing the conventional unit cell axes and angles together with their lattice symbols and minimum symmetry elements

CRYSTAL SYSTEM	UNIT CELL AXES AND ANGLES	LATTICE SYMBOLS	MINIMUM SYMMETRY ELEMENTS
Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	P	1 (or $\bar{1}$)
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90° \neq \beta$	P, C	2 (or $\bar{2}$)
Orthorhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	P, F, I, C	222 (or $\bar{2}\bar{2}\bar{2}$)
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	P, I	4 (or $\bar{4}$)
Trigonal and hexagonal	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	R, P	3 (or $\bar{3}$); 6 (or $\bar{6}$)
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90°$	P, F, I	4 triads along <111>

taking the reciprocals of the intercepts gives (111) for the plane. As a second example, if the intercepts are ($i_x = 1$, $i_y = 1/2$, $i_z = 1/3$) along axes 0*x*, 0*y*, and 0*z*, respectively, then the Miller indices for the plane would be (1, 2, 3). For the hexagonal and trigonal crystal systems represented in Figure 3.4(b), the *i* index in (*hkil*) is determined by $i = -(h + k)$ but is sometimes replaced by a dot as ($hk \cdot l$).

The Miller indices for direction [*uvw*] are found by "walking" along all axes, *x*, *y*, and *z* in turn, from origin to the end of the lattice vector. Referring to Figure 3.3, one would measure distances along *x*, *y*, and *z* axes in units of *a*, *b*, and *c*, respectively, or their fractions. As an example, and again referring to Figure 3.3, a lattice vector represented by *a*, *b*, *c* would be designated by [111], or a lattice vector (1/2)*a*, –*b*, 0 in the *x*–*y* plane would be designated as $[1/2, \bar{1}, 0]$ or clearing fractions $[1, \bar{2}, 0]$. Referring to Figure 3.4(b), the same direction in the hexagonal and trigonal systems would be designated as $[UVTW] = [1, \bar{2}, 1, 0]$, where $T = -(U + V)$. In the cubic system, for which $a = b = c$, any direction [*uvw*] is perpendicular to the plane (*hkl*) of the same indices. Planes of the form are designated as {*hkl*} and {*hkil*}, whereas the directions of the form are indicated as ⟨*uvw*⟩ and ⟨*UVTW*⟩. The four index forms apply specifically to the hexagonal and trigonal systems. The number of non-parallel planes of the form {*hkl*} is found by multiplying [permutation term] × [sign term]/2. For example {123} has $[3!][2^3]/2 = 24$ non-parallel planes of this form. Directions of the form ⟨123⟩ also have 24 nonparallel directions of that form.

TABLE 3.4: The 32 conventional point groups showing crystal system, group number, and the international short symmetry notation

CRYSTAL SYSTEM	GROUP NUMBER	INTERNATIONAL (SHORT) NOTATION
Triclinic	1	1
	2	$\Vert\bar{1}\Vert$
Monoclinic	3	2
	4	m
	5	$\Vert 2/m \Vert$
Orthorhombic	6	222
	7	$mm2$
	8	$\Vert mmm \Vert$
Tetragonal	9	4
	10	$\bar{4}$
	11	$\Vert 4/m \Vert$
	12	422
	13	$4mm$
	14	$\bar{4}2m$
	15	$\Vert 4/mmm \Vert$

TABLE 3.4: (continued)

CRYSTAL SYSTEM	GROUP NUMBER	INTERNATIONAL (SHORT) NOTATION
Trigonal (rhombohedral)	16	3
	17	$\|\bar{3}\|$
	18	32
	19	$3m$
	20	$\|\bar{3}m\|$
Hexagonal	21	6
	22	$\bar{6}$
	23	$\|6/m\|$
	24	622
	25	$6mm$
	26	$\bar{6}m2$
	27	$\|6/mmm\|$
Cubic (isometric)	28	23
	29	$\|m3\|$
	30	432
	31	$\bar{4}3m$
	32	$\|m3m\|$

3.4 THE MACROSCOPIC SYMMETRY OF CRYSTALS AND THE 32 CONVENTIONAL POINT GROUPS

The 32 conventional point groups are listed in Table 3.4 in the order of increasing symmetry. The symbols used to represent the symmetry elements characteristic of each crystal class belong to the Hermann–Mauguin international short system. There are two other systems used for this purpose. They are the full symbol notation and Schoenflies symbols; neither of which will be used in this text.

The 11 point groups, designated by the symbol $\|X\|$ in the seven crystal systems, each possess a center of symmetry and meet the requirements for complete (maximum) symmetry allowable for classification in that system. These 11 point groups are called the *holohedral groups*. Finally, it should be noted that a given point group is generated by the repeated symmetry operations required by the elements of that group. This fact will be important in later developments.

A point group that contains a center of symmetry is called *centrosymmetrical*. A group contains a center of symmetry if the product of the transformation matrices, representing the symmetry elements of the group, becomes $-(\delta_{ij})$, where (δ_{ij}) is the unitary matrix. As an example, the group $2/m$ has the following transformation matrix

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \cos(p\pi) & 0 & 0 \\ 0 & \cos(p\pi) & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{3.4}$$

where p is an integer representing the repeated twofold rotation operation and $\pi = 180°$. Clearly, $\cos(p\pi) = -1$ for $p = \pm1, \pm3, \pm5\ldots$, and the transformation for $2/m$ above becomes $-(\delta_{ij})$, proving that $2/m$ contains a center of symmetry and is represented by $\|2/m\|$ in Table 3.4.

3.5 NEUMANN'S PRINCIPLE AND ITS APPLICATION TO TENSOR PROPERTIES

Basic and most important to a discussion of the effect of crystal symmetry on the tensor properties of crystals is *Neumann's principle*, which states,

> *The symmetry elements of any physical property of a crystal must include all the symmetry elements of the point group of the crystal.*

This means that the component of a tensor representing a property must remain invariant under a transformation of coordinates governed by a symmetry operation valid for the point group of the crystal. Mathematically, this is represented as

$$T_{ijk\ldots} = T_{ijk\ldots}. \tag{3.5}$$

TABLE 3.5: The 10 possible generating matrices are shown for both the s and σ forms

Center of symmetry, $s^{(1)} = (\bar{1}) = \begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{bmatrix}$ Direct inspection method: 1→−1, 2→−2, 3→−3	$\sigma^{(1)} = \begin{bmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 0 & 1\end{bmatrix} = I$	$\sigma^{-1} = \tilde{\sigma} = I$ I is the identity (unit) matrix
Twofold CCW rotation about y, $s^{(2)} = (2y) = \begin{bmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{bmatrix}$ Direct inspection method: 1→−1, 2→2, 3→−3	$\sigma^{(2)} = \begin{bmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & -1 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 0 & -1\end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$
Twofold CCW rotation about z, $s^{(3)} = (2z) = \begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}$ Direct inspection method: 1→−1, 2→−2, 3→3	$\sigma^{(3)} = \begin{bmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & -1 & 0 & 0\\ 0 & 0 & 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 0 & 0 & 1\end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$
Reflection plane ⊥ to x, $s^{(4)} = (m \perp x) = \begin{bmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}$ Direct inspection method: 1→−1, 2→2, 3→3	$\sigma^{(4)} = \begin{bmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1 & 0 & 0\\ 0 & 0 & 0 & 0 & -1 & 0\\ 0 & 0 & 0 & 0 & 0 & -1\end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$
Reflection plane ⊥ to y, $s^{(5)} = (m \perp y) = \begin{bmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix}$ Direct inspection method: 1→1, 2→−2, 3→3	$\sigma^{(5)} = \begin{bmatrix}1 & 0 & 0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0 & 0 & 0\\ 0 & 0 & 0 & -1 & 0 & 0\\ 0 & 0 & 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0 & 0 & -1\end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$

TABLE 3.5: (continued)

Reflection plane ⊥ to z, $s^{(6)} = (m \perp z) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$ Direct inspection method: 1→1, 2→2, 3→−3	$\sigma^{(6)} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$
Threefold CCW rotation about z, $s^{(7)} = (3z) = \begin{bmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ Direct inspection method: not applicable	$\sigma^{(7)} = \begin{bmatrix} 1/4 & 3/4 & 0 & 0 & 0 & -\sqrt{3}/2 \\ 3/4 & 1/4 & 0 & 0 & 0 & \sqrt{3}/2 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 & \sqrt{3}/2 & -1/2 & 0 \\ \sqrt{3}/4 & -\sqrt{3}/4 & 0 & 0 & 0 & -1/2 \end{bmatrix}$	To form σ^{-1}. interchange $-\sqrt{3}$ and $\sqrt{3}$
Fourfold CCW rotation about x, $s^{(8)} = (4x) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}$ Direct inspection method: 1→1, 2→3, 3→−2	$\sigma^{(8)} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$
Fourfold CCW rotation about z, $s^{(9)} = (4z) = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ Direct inspection method: 1→2, 2→−1, 3→3	$\sigma^{(9)} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$
Cyclic interchange of x_i, $s^{(10)} = (3_{[111]}) = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}$ Direct inspection method: 1→2, 2→3, 3→1	$\sigma^{(10)} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix}$	$\sigma^{-1} = \tilde{\sigma}$

If, on the other hand, a particular component of a tensor changes sign after such a transformation of coordinates, the component must vanish for that crystal in accordance with Neumann's principle. Mathematically, this is expressed as

$$T_{ijk\ldots} = -T_{ijk\ldots} = 0 \tag{3.6}$$

Application of Neumann's principle to property tensors requires the use of transformation laws for tensors. The transformation laws for both polar and axial property tensors must be valid for any symmetry operation permissible by a given point group. If s represents a *symmetry operator*, that is, the transformation matrix of a symmetry operation valid for a particular point group, then the generalized transformation laws become

$$T_{ijk\ldots} = s_{im} s_{jn} s_{ko} \ldots T_{mno} \tag{3.7}$$

for polar property tensors and

$$T_{ijk\ldots} = |s|\, s_{im} s_{jn} s_{ko} \ldots T_{mno} \tag{3.8}$$

for axial tensors, where $|s|$ is the determinant of the symmetry operator (see Section 2.4).

For a given crystal class, there will be as many sets of equations for each property tensor as there are symmetry operations valid for the point group of that class. However, the number of operators derived from these symmetry operations can be reduced considerably to some minimum number required to generate the point group. These are called *generation operators*, which result from the 10 (s) generating matrices given in Table 3.5. The σ generating matrices are the quadratic forms of the s matrices and are applicable only to symmetrical property tensors as represented by Eq. (2.22) in Section 2.2.5. We note here that $s^{(0)} = (1) = (\delta_{ij})$, $\sigma^{(0)} = I$, and $[\sigma^{(0)}]^{-1} = \tilde{\sigma}^{(0)} = I$ are identity (unit) matrices.

The minimum number of generating matrices (derived from the 10 generating matrices in Table 3.5) required for each of the 32 point groups are given in Table 3.6. The point groups are designated by using the international short-form symbology as used in Table 3.4. The generating matrices will be used to determine the nonzero components of a given property tensor as required for a particular point group and in accordance with the appropriate transformation law. The symbol $\|X\|$ appearing in Table 3.6 is used to designate the holohedral group defined earlier. The minimum generating matrices can also be used to generate the stereograms for the 32 point groups (see Endnotes).

The work required for simplifying the components of a given tensor can be greatly reduced by recognizing that a tensor of rank r transforms like the products of r coordinates of a point. For example, the center-of-symmetry operator $s^{(1)} = (-\delta_{ij})$ requires that

TABLE 3.6: Minimum generating matrices for the 32 point groups showing the 11 centrosymmetrical crystal classes designated by $\|X\|$

CRYSTAL SYSTEM	INTERNATIONAL SYMBOL (SHORT FORM)	MINIMUM GENERATING MATRICES
Triclinic	1	$s^{(0)}$
	$\|\bar{1}\|$	$s^{(1)}$
Monoclinic	2	$s^{(2)}$
	m	$s^{(5)}$
	$\|2/m\|$	$s^{(2)}, s^{(5)}$
Orthorhombic	222	$s^{(2)}, s^{(3)}$
	$mm2$	$s^{(3)}, s^{(5)}$
	$\|mmm\|$	$s^{(4)}, s^{(5)}, s^{(6)}$
Tetragonal	4	$s^{(9)}$
	$\bar{4}$	$s^{(11)}$
	$\|4/m\|$	$s^{(6)}, s^{(9)}$
	422	$s^{(12)}, s^{(9)}$
	$4mm$	$s^{(4)}, s^{(9)}$
	$\bar{4}2m$	$s^{(12)}, s^{(11)}$
	$\|4/mmm\|$	$s^{(4)}, s^{(6)}, s^{(9)}$

$(\bar{4}z) = s^{(1)} \cdot s^{(9)} = s^{(11)}$, $(2x) = s^{(1)} \cdot s^{(4)} = s^{(12)}$

TABLE 3.6: (continued)

CRYSTAL SYSTEM	INTERNATIONAL SYMBOL (SHORT FORM)	MINIMUM GENERATING MATRICES
Trigonal	3	$s^{(7)}$
	$\|\bar{3}\|$	$s^{(13)}$
	32	$s^{(12)}, s^{(7)}$
	$3m$	$s^{(4)}, s^{(7)}$
	$\|\bar{3}m\|$	$s^{(4)}, s^{(13)}$
Hexagonal	6	$s^{(14)}$
	$\bar{6}$	$s^{(15)}$
	$\|6/m\|$	$s^{(6)}, s^{(14)}$
	622	$s^{(12)}, s^{(14)}$
	$6mm$	$s^{(4)}, s^{(14)}$
	$\bar{6}2m$	$s^{(4)}, s^{(15)}$
	$\|6/mmm\|$	$s^{(4)}, s^{(6)}, s^{(14)}$
Cubic	23	$s^{(12)}, s^{(10)}$
	$\|m3\|$	$s^{(4)}, s^{(10)}$
	432	$s^{(8)}, s^{(10)}$
	$\bar{4}3m$	$s^{(16)}, s^{(10)}$
	$\|m3m\|$	$s^{(4)}, s^{(10)}, s^{(17)}$

$$(\bar{3}\,z) = s^{(1)} \cdot s^{(7)} = s^{(13)},\ (6z) = s^{(3)} \cdot s^{(7)} = s^{(14)}$$

$$(\bar{6}\,z) = s^{(1)} \cdot s^{(14)} = s^{(15)},\ (\bar{4}x) = s^{(1)} \cdot s^{(8)} = s^{(16)}$$

$$m \perp (110) = s^{(4)} \cdot s^{(9)} = s^{17}$$

$$\begin{Bmatrix} x_1 & \rightarrow & -x_1 \\ x_2 & \rightarrow & -x_2 \\ x_3 & \rightarrow & -x_3 \end{Bmatrix} \text{ or } \begin{Bmatrix} 1 & \rightarrow & -1 \\ 2 & \rightarrow & -2 \\ 3 & \rightarrow & -3 \end{Bmatrix} \tag{3.9}$$

This means that for a polar property tensor of odd rank, any combination of subscripts will result in $T' = -T = 0$ in accordance with Neumann's principle. Similarly, for an axial property tensor of even rank, any combination of subscripts will result in $T' = -T = 0$ also in accordance with Neumann's principle. This process of simplification is called the *method of direct inspection* and is applicable to all point groups except those in the trigonal and hexagonal crystal systems. For a particular crystal class in these two systems, it is necessary to operate on a property tensor with each generating matrix in turn. The use of the quadratic generation operators is then recommended, especially for property tensors of rank greater than two. Note that throughout this text, the notation for crystallographic axes will adhere to the accepted convention $x_1 = x$, $x_2 = y$, and $x_3 = z$ in accordance with Figure 3.1.

3.6 APPLICATION OF NEUMANN'S PRINCIPLE TO SYMMETRICAL SECOND-RANK PROPERTY TENSORS

The macroscopic symmetry of a given crystal can dramatically affect the number of nonzero components of a property tensor that are permitted to exist in that crystal. This is easily demonstrated by applying Neumann's principle to a symmetrical second-rank property tensor S_{ij}, which may represent any of several properties to be studied in subsequent chapters. Typical examples are the dielectric susceptibility and thermal expansion coefficient. We begin with the triclinic crystal system and continue in the direction of increasing symmetry to the cubic system. For this purpose, use will be made of the generation matrices for the 11 holohedral point groups in Table 3.6—those possessing a center of symmetry and the necessary generating matrices for complete symmetry. As we progress from the triclinic to cubic system, use will be made of the method of direct inspection except for the trigonal and hexagonal systems as indicated earlier.

1. Triclinic system: Because all symmetrical second-rank property tensors are centrosymmetrical, they cannot be made null by the center-of symmetry operation. The symmetry transformation becomes

$$S' = s^{(1)} S \tilde{s}^{(1)} = S = \begin{bmatrix} S_{11} & S_{12} & S_{31} \\ S_{12} & S_{22} & S_{23} \\ S_{31} & S_{23} & S_{33} \end{bmatrix} \tag{3.10}$$

leaving the property S_{ij} unchanged, with all six independent components needed to represent it.

2. Monoclinic system: The monoclinic system requires use of the generation operators $s^{(2)}$ and $s^{(5)}$ via holohedral group $\|2/m\|$. Beginning with $s^{(2)}$, S' transforms as

$$S' = s^{(2)} S \,\tilde{s}^{(2)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} S_{11} & S_{12} & S_{31} \\ S_{12} & S_{22} & S_{23} \\ S_{31} & S_{23} & S_{33} \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$
$$= \begin{bmatrix} S_{11} & -S_{12} & S_{31} \\ & S_{22} & -S_{23} \\ \text{Sym.} & & S_{33} \end{bmatrix}. \tag{3.11}$$

Applying Neumann's principle requires that $S_{12} = S_{23} = 0$, giving the result

$$S = \begin{bmatrix} S_{11} & 0 & S_{31} \\ & S_2 & 0 \\ \text{Sym.} & & S_{33} \end{bmatrix}, \tag{3.12}$$

where $S_{22} = S_2$ is a principal component along $0x_2 = 0y$. Application of operator $s^{(5)}$ leaves the result of Eq. (3.12) unchanged. The same result could have been obtained with greater ease by using the direct inspection method. For example, the use of generating matrix $s^{(2)}$ in Table 3.5 gives

$$s^{(2)} \to \begin{Bmatrix} x_1 & \to & -x_1' \\ x_2 & \to & x_2' \\ x_3 & \to & -x_3' \end{Bmatrix} \text{ or } \begin{Bmatrix} 1 & \to & -1 \\ 2 & \to & 2 \\ 3 & \to & -3 \end{Bmatrix} \tag{3.13}$$

It now follows that components having a single 1 or single 3 subscript (but not both) must be zero in accordance with Neumann's principle, that is, $S_{23} = S_{12} = 0$ (all others must remain nonzero), which is applicable to the three classes of the monoclinic crystal system.

3. Orthorhombic system: The holohedral group $\|mmm\|$ has the generation matrices $s^{(4)}$, $s^{(5)}$, and $s^{(6)}$, which cover all classes of the orthorhombic system. From Table 3.5, these three operators are given by

$$s^{(4)} \to \begin{Bmatrix} 1 & \to & -1 \\ 2 & \to & 2 \\ 3 & \to & 3 \end{Bmatrix} s^{(5)} \to \begin{Bmatrix} 1 & \to & 1 \\ 2 & \to & -2 \\ 3 & \to & 3 \end{Bmatrix} s^{(6)} \to \begin{Bmatrix} 1 & \to & 1 \\ 2 & \to & 2 \\ 3 & \to & -3 \end{Bmatrix}. \tag{3.14}$$

Taken separately and using the direct inspection method together with Neumann's principle, the generation matrices $s^{(4)}$, $s^{(5)}$, and $s^{(6)}$ require all components having a single 1, a single

2, or a single 3 be zero. Thus, $S_{23} = S_{31} = S_{12} = 0$, with all others being nonzero. Therefore, S is now represented by

$$S = \begin{bmatrix} S_{11} & 0 & 0 \\ 0 & S_{22} & 0 \\ 0 & 0 & S_{33} \end{bmatrix} = \begin{bmatrix} S_1 & 0 & 0 \\ & S_2 & 0 \\ \text{Sym.} & & S_3 \end{bmatrix}. \tag{3.15}$$

The arrays in Eq. (3.15) apply to all crystal classes of the orthorhombic system. The second-rank property components S_1, S_2, and S_3 are the principal components along the crystallographic axes $0x = [100]$, $0y = [010]$, and $0z = [001]$, respectively.

4. Tetragonal system: The holohedral group $\|4/mmm\|$ has the generating matrices $s^{(4)}$, $s^{(6)}$, and $s^{(9)}$, of which $s^{(4)}$ and $s^{(6)}$ have previously been used for the orthorhombic crystal system, and operator $s^{(5)}$ leaves these results unchanged. Then, applying the operator $s^{(9)}$ from Table 3.5 to the results of the orthorhombic system requires, by the direct inspection method, that

$$s^{(9)} \rightarrow \begin{Bmatrix} x_1 & \rightarrow & x_2' \\ x_2 & \rightarrow & -x_1' \\ x_3 & \rightarrow & x_3' \end{Bmatrix} \text{ or } \begin{Bmatrix} 1 & \rightarrow & 2 \\ 2 & \rightarrow & -1 \\ 3 & \rightarrow & 3 \end{Bmatrix}. \tag{3.16}$$

The results are $S_{31} = S_{32} = -S_{31} = 0$ and $S_{11} = S_{22} = S_1$ in accord with Neumann's principle. This means that the property tensor S_{ij} is everywhere isotropic in the x,y (001) plane. Thus, the components of S_{ij} for all point groups of the tetragonal crystal system are represented by the array

$$S = \begin{bmatrix} S_1 & 0 & 0 \\ & S_1 & 0 \\ \text{Sym.} & & S_3 \end{bmatrix}. \tag{3.17}$$

5. Trigonal and hexagonal systems: The holohedral groups $\|\bar{3}m\|$ and $\|6/mmm\|$ contain generating operators $s^{(1)}$, $s^{(3)}$, $s^{(4)}$, $s^{(6)}$, and $s^{(7)}$. The application of the operators $s^{(1)}$, $s^{(3)}$, $s^{(4)}$, and $s^{(6)}$ to the tensor S_{ij} will leave unchanged the results obtained for the tetragonal systems. Therefore, there remains only the application of the operator $s^{(7)}$. Because the method of direct inspection is not applicable here, we must perform the transformation given by

$$S' = s^{(7)} S \tilde{s}^{(7)} = \sigma^{(7)} S. \tag{3.18}$$

But this transformation can be given more conveniently by using the quadratic transformation

$$S' = \sigma^{(7)} S = \begin{bmatrix} 1/4 & 3/4 & 0 & 0 & 0 & -\sqrt{3}/2 \\ 3/4 & 1/4 & 0 & 0 & 0 & \sqrt{3}/2 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1/2 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 & \sqrt{3}/2 & -1/2 & 0 \\ \sqrt{3}/4 & -\sqrt{3}/4 & 0 & 0 & 0 & -1/2 \end{bmatrix} \begin{bmatrix} S_1 \\ S_2 \\ S_3 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} S_1 \\ S_1 \\ S_3 \\ 0 \\ 0 \\ 0 \end{bmatrix}. \qquad (3.19)$$

This indicates that the components of S_{ij} for all point groups of the trigonal and hexagonal crystal systems are the same as those for the tetragonal system. Consequently, these three systems may be treated as a single group with respect to symmetrical second-rank tensor properties. They are often called the *optically uniaxial crystal systems*.

6. Cubic system: The holohedral group $\|m3m\|$ contains generation operators $s^{(4)}$, $s^{(9)}$, and $s^{(10)}$, all but $s^{(10)}$, of which have been applied to the previous, less symmetrical systems. So there now remains the application of the generation operator $s^{(10)}$, to the results obtained for the tetragonal, trigonal, and hexagonal systems. The method of direct inspection, which is again applicable, requires that

$$s^{(10)} \rightarrow \begin{Bmatrix} x_1 & \rightarrow & x_2' \\ x_2 & \rightarrow & x_3' \\ x_3 & \rightarrow & x_1' \end{Bmatrix} \text{ or } \begin{Bmatrix} 1 & \rightarrow & 2 \\ 2 & \rightarrow & 3 \\ 3 & \rightarrow & 1 \end{Bmatrix}. \qquad (3.20)$$

Then by application of Neumann's principle there results

$$S_1 = S_2 = S_3 = S, \qquad (3.21)$$

meaning that any cubic crystal system is isotropic with respect to any symmetrical second-rank property tensor.

To summarize, the effect of crystal symmetry on properties that are represented by symmetrical second-rank tensors is given in Table 3.7. The effect of crystal symmetry on other tensor properties will be given at the time the individual properties are considered. This is especially desirable for the property tensors of higher rank because they often possess unique inherent symmetry. This is particularly true for the axial and axial–magnetic property tensors for which both axial and magnetic symmetry must be considered.

TABLE 3.7: Effect of crystal symmetry on symmetrical second-rank tensor properties

SYSTEM	HOLOHEDRAL GENERATING MATRICES	INDEPENDENT COMPONENTS OF THE PROPERTY MATRIX
Triclinic	$s^{(1)}$	$\begin{bmatrix} S_{11} & S_{12} & S_{31} \\ & S_{22} & S_{23} \\ \text{Sym.} & & S_{33} \end{bmatrix}$
Monoclinic	$s^{(2)}, s^{(5)}$	$\begin{bmatrix} S_{11} & 0 & S_{31} \\ & S_{2} & 0 \\ \text{Sym.} & & S_{33} \end{bmatrix}$
Orthorhombic	$s^{(4)}, s^{(5)}, s^{(6)}$	$\begin{bmatrix} S_{1} & 0 & 0 \\ & S_{2} & 0 \\ \text{Sym.} & & S_{3} \end{bmatrix}$
Tetragonal, trigonal, and hexagonal	$s^{(1)}, s^{(3)}, s^{(4)}, s^{(6)}, s^{(7)}, s^{(9)}$	$\begin{bmatrix} S_{1} & 0 & 0 \\ & S_{1} & 0 \\ \text{Sym.} & & S_{3} \end{bmatrix}$
Cubic	$s^{(4)}, s^{(9)}, s^{(10)}$	$\begin{bmatrix} S & 0 & 0 \\ & S & 0 \\ \text{Sym.} & & S \end{bmatrix}$

3.7 EFFECT OF NEUMANN'S PRINCIPLE ON THE 11 CENTROSYMMETRICAL CRYSTAL CLASSES

With reference to Table 3.6, it is clear that each of the 11 holohedral groups, those designated by $\|X\|$, contain the center-of-symmetry operator $s^{(1)} = (-\delta_{ij})$, which requires that the symmetry transformations of (3.9) be applied to any crystal system that contains a center of symmetry. As a result, Neumann's principle requires that for all centrosymmetrical crystal classes

$$T' = -T = 0 \Rightarrow \begin{Bmatrix} \text{for polar tensors of odd rank} \\ \text{for axial tensors of even rank} \end{Bmatrix}. \tag{3.22}$$

Thus, all 11 of the centrosymmetrical crystal classes, those that contain a center-of-symmetry, will be lacking in odd-rank polar tensor properties and even-rank axial tensor properties. For example, the piezoelectric tensor d_{ikl}, included in Eq. (2.54), is a polar third-rank tensor property whose property components vanish for any of the 11 centrosymmetrical (holohedral) classes designated by $\|X\|$ in Tables 3.4 and 3.6. Another example is the pyroelectric coefficient defined by $\Delta P_i = P_i \Delta T$, where the three components of p_i are null for any of the 11 centrosymmetrical crystal classes. All axial and axial–magnetic tensor properties of even rank will be lacking property components for any of the centrosymmetrical crystal classes. The 90 magnetic point groups come into play only for magnetic and axial–magnetic tensor properties of odd rank, further reducing the number of existing components over those required strictly by conventional symmetry arguments.

3.8 LONGITUDINAL AND TRANSVERSE EFFECTS FOR SYMMETRICAL SECOND-RANK PROPERTY TENSORS

Use of either the longitudinal or transverse effects, or both, offers a convenient and practical means of measuring the components of symmetrical second-rank property tensors. To demonstrate these effects, it will be helpful to consider the symmetrical second-rank tensor as being a property relating a cause parameter q to an effect parameter p according to

$$S_{ij} = \frac{p_i}{q_j} = \frac{p_j}{q_i} = S_{ji}. \tag{3.23}$$

Referring to Figure 2.1, with the transformation matrix represented as

$$a = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} = \begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{bmatrix} \tag{3.24}$$

for convenience, the generalized transformation law for longitudinal and transverse effects becomes

$$S' = aS\tilde{a} = \begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{bmatrix} \begin{bmatrix} S_{11} & S_{12} & S_{31} \\ & S_{22} & S_{23} \\ \text{Sym.} & & S_{33} \end{bmatrix} \begin{bmatrix} l_1 & m_1 & n_1 \\ l_2 & m_2 & n_2 \\ l_3 & m_3 & n_3 \end{bmatrix}. \tag{3.25}$$

Equation (3.25) is valid for any crystal system in which the property S_{ij} is manifest. We will now explore the effect of crystal symmetry on the longitudinal and transverse effects.

1. Triclinic system: For the triclinic system, no restrictions are placed on the orientation of the reference axes. If the effect parameter p is sensed along the $0x_1'$ when the cause parameter q is applied in that same direction, the longitudinal effect for the triclinic system is given by

$$S'_{11} = \frac{p'_1}{q'_1} = \begin{bmatrix} l_1 & l_2 & l_3 \end{bmatrix} \cdot \begin{bmatrix} S_{11} & S_{12} & S_{31} \\ & S_{22} & S_{23} \\ \text{Sym.} & & S_{33} \end{bmatrix} \cdot \begin{bmatrix} l_1 \\ l_2 \\ l_3 \end{bmatrix}$$
$$= l_1^2 S_{11} + l_2^2 S_{22} + l_3^2 S_{33} + 2l_2 l_3 S_{23} + 2l_3 l_1 S_{31} + 2l_1 l_2 S_{12}. \tag{3.26}$$

Here, the longitudinal effect is simply the magnitude of S measured along some arbitrary direction $0x'_1$.

Similarly, if p is sensed along $0x'_1$ when q is applied along $0x'_2$, or vice versa, the transverse effect given by

$$S'_{12} = \frac{p'_1}{q'_2} = \frac{p'_2}{q'_1} = \begin{bmatrix} l_1 & l_2 & l_3 \end{bmatrix} \cdot \begin{bmatrix} S_{11} & S_{12} & S_{31} \\ & S_{22} & S_{23} \\ \text{Sym.} & & S_{33} \end{bmatrix} \cdot \begin{bmatrix} m_1 \\ m_2 \\ m_3 \end{bmatrix}$$
$$= l_1 m_1 S_{11} + l_2 m_2 S_{22} + l_3 m_3 S_{33} + (l_2 m_3 + l_3 m_2) S_{23} +$$
$$(l_3 m_1 + l_1 m_3) S_{31} + (l_1 m_2 + l_2 m_1) S_{12} \tag{3.27}$$

is also applicable to the triclinic crystal system. Thus, to measure all six independent components of S_{ij}, six independent measurements must be made using either the longitudinal effect or transverse effect or some suitable combination thereof. The six resulting equations must then be solved simultaneously to obtain the six components.

2. Monoclinic system: Applied to the monoclinic crystal system, Eqs. (3.26) and (3.27) for the triclinic system can be simplified to the extent that $S_{23} = S_{12} = 0$, as indicated in Table 3.7. All other terms in thee expressions remain the same, with $S_{22} = S_2 = S_{[010]}$ being the principal component along $0x_2 = 0y = [010]$. Four independent measurements, using either the longitudinal or transverse effects or some combination of them, will yield four independent equations from which the four independent components of S_{ij} can be obtained. Note that the magnitude of the property S'_{11} measured along the axis of symmetry $0x_2 = 0y$ is the principal component S_2.
3. Orthorhombic system: The longitudinal and transverse effects can be put into special forms for the orthorhombic crystal system when we note that $S_{23} = S_{31} = S_{12} = 0$ and that the principal axes lie along the crystallographic axes. The longitudinal effect now becomes

$$S'_{11} = p'_1 / q'_1 = l_1^2 S_1 + l_2^2 S_2 + l_3^2 S_3$$
$$= l_{[100]}^2 S_{[100]} + l_{[010]}^2 S_{[010]} + l_{[001]}^2 S_{[001]}, \tag{3.28}$$

where $l_{\langle 100\rangle}$ are the direction cosines between any direction $0x'_1 = [uvw]$ and the crystallographic (principal) axes, [100], [010], and [001], and $S_{\langle 100\rangle}$ represent the three principal components along these axes. Similarly, if the direction $0x_2' = [m_1, m_2, m_3]$ is also taken with respect to the crystallographic axes, the transverse effect for the orthorhombic crystal system is given by

$$\begin{aligned} S_{12}' = p_1' / q_2' = p_2' / q_1' &= l_1 m_1 S_{11} + l_2 m_2 S_{22} + l_3 m_3 S_{33} \\ &= l_{[100]} m_{[100]} S_{[100]} + l_{[010]} m_{[010]} S_{[010]} + l_{[001]} m_{[001]} S_{[001]} \end{aligned} \tag{3.29}$$

Thus, knowing the orientation of the principal axes, three independent measurements using either the longitudinal effect or transverse effect or both, will yield the principal values S_1, S_2, and S_3.

4. Tetragonal, trigonal, and hexagonal systems: For the optically uniaxial crystal systems (tetragonal, trigonal, and hexagonal) the longitudinal effect requires measurement of the two independent components, S_1 and S_3, along any two arbitrary, but different, directions (one direction must be out of the (001) or (0001) plane). Accordingly, the longitudinal effect is established from Eq. (3.28) as

$$\begin{aligned} S_{11}' = p_1' / q_1' &= (l_{[100]}^2 + l_{[010]}^2) S_{[100]} + l_{[001]}^2 S_{[001]} \\ &= (1 - l_{[001]}^2) S_{[100]} + l_{[001]}^2 S_{[001]} \end{aligned} \tag{3.30}$$

since now $S_{[100]} = S_{[010]}$ due to the isotrophy of property S in the (001) or (0001) plane for the optically uniazial crystal systems.

Defining the Eulerian angles θ and ϕ, as shown in Figure 3.5, the longitudinal effect takes the form

$$S_{11}' = S_{\perp} \sin^2\phi + S_{\parallel} \cos^2\phi \tag{3.31}$$

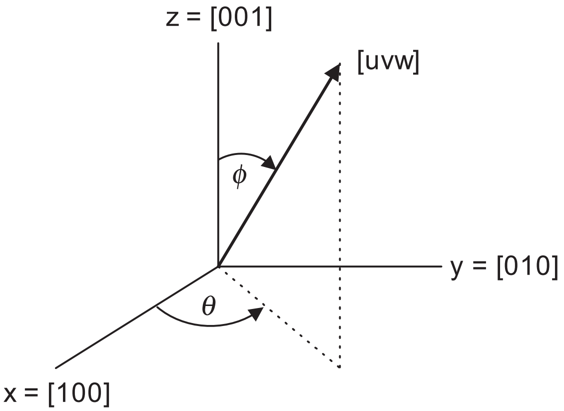


FIGURE 3.5: Arbitrary direction $[uvw]$ expressed in terms of the Eulerian angles ϕ and θ.

independent of θ. Here $S_{\perp} = S_{\langle uv0 \rangle}$ is the magnitude of the property along any direction $\langle uv0 \rangle$ perpendicular to the [001], and $S_{\parallel} = S_{[001]}$ is the magnitude of the property parallel to the [001] direction. Consequently, the magnitude of the property in any direction $[uvw] = 0x_1'$ depends only on the angle ϕ and the values $S_{\perp}$ and $S_{\parallel}$. For the trigonal and hexagonal crystal systems, the longitudinal effect may be represented alternatively as

$$S_{11}' = S_{\langle UVT0 \rangle} \sin^2 \phi + S_{[0001]} \cos^2 \phi \tag{3.32}$$

for measurement in any direction $0x_1' = [UVTW]$.

The transverse effect for the optically uniaxial crystal systems is established from Eq (3.29) noting again that $S_{[100]} = S_{[010]} = S_{\perp}$ and $S_{[001]} = S_{\parallel}$. Therefore, by knowing the direction cosines for directions $0x_1' = [l_1, l_2, l_3]$ and $0x_2' = [m_1, m_2, m_3]$ with respect to the crystallographic axes, the transverse effect can be measured. As always, the transverse effect is more difficult to measure than the longitudinal effect.

5. Cubic system: For the cubic system, the magnitude of the property S is the same in all directions, that is, it is isotropic relative to the property S and requires only one measurement of its magnitude in any direction.

• • • •

CHAPTER 4

Generalized Thermostatics and the Systematic Correlation of Physical Properties

4.1 ENERGY REPRESENTATIONS AND THE CRITERIA FOR THERMODYNAMIC EQUILIBRIUM

In classical thermodynamics, the *first law* is expressed as the change in internal energy of a closed system given by

$$\mathrm{d}U = đQ + đW,$$

where $đQ$ is the thermal energy (heat) transferred to the system and $đW$ is the external work done on the system. Here, $đQ$ and $đW$ are *inexact differentials* called *Pfaffians*—they are path-dependent. For a closed solid-phase system, the infinitesimal change in internal energy is given by the first and second laws of thermodynamics as

$$\mathrm{d}U = đQ + \sum_i đW_i = T\mathrm{d}S + đW_{\text{Elect.}} + đW_{\text{Mag.}} + đW_{\text{Mech.}} + đW_{\text{Chem.}} \tag{4.1}$$

in which $đQ = T\mathrm{d}S$ is the infinitesimal reversible heat absorbed by the solid-phase system at an absolute temperature T, and $\mathrm{d}S$ is the infinitesimal entropy change associated with the absorbed heat $đQ$. $\sum_i đW_i$ is the sum of all infinitesimal reversible work (electrical, magnetic, mechanical and chemical) done on the solid-phase system by the surroundings.

Each work term in Eq. (4.1) is represented by the product of a particular intensive parameter and an infinitesimal change in its conjugate extensive parameter. In crystalline materials, the atoms are essentially immobile compared to the gaseous (or liquid) state. This complicates the energy representation. For example, in classical PVT thermodynamics, pressure P is an adequate intensive parameter for gases, but it is not adequate to describe the effect of applying surface forces to a solid. Similarly, volume V, used as the extensive parameter for gases, must be replaced by reference volume times strain $V_0\varepsilon$ for solids. Thus, $-P\mathrm{d}V$ work in the classical sense (for gases) must be replaced by

TABLE 4.1: Intensive and extensive parameters for a solid-state system and their SI units

INTENSIVE PARAMETERS	EXTENSIVE PARAMETERS
T — Temperature (°K)	S — Entropy (J/°K)
E — Electric field intensity (V/m)	$\hat{P}$ — Total electric dipole moment (Cm)
B — Magnetic flux density (N / A · m = tesla, T)	I — Total magnetic dipole moment (Am^2)
σ — Stress (N/m^2)	$V_0\varepsilon$ — Strain times reference state volume (m^3)
μ —Chemical potential (J/mol)	N — Mole number

elastic strain energy $\sigma d\,(V_0\varepsilon)$ for the case of solids. Furthermore, the fact that solids can develop a net polarization or magnetization adds additional complications to the energy representation—electrical and magnetic work terms must be added.

The intensive and extensive parameters that best describe the equilibrium tensor properties of crystals are presented in Table 4.1 along with their SI units. Note that the magnetic intensive parameter is the magnetic flux density $B = \mu_0 H$ measured in the absence of the crystal system (μ_0 is the permeability in a vacuum and H is the magnetic field strength). Using these parameters, the total infinitesimal change in internal energy for a solid-phase system is given by

$$\mathrm{d}U = T\mathrm{d}S + E\,\mathrm{d}\hat{P} + B\mathrm{d}I + \sigma\,\mathrm{d}(\varepsilon V_0) + \mu\,\mathrm{d}N \tag{4.2}$$

in agreement with the respective work terms given in Eq. (4.1). From Euler's theorem on homogeneous first-order forms, the corresponding *Euler relation* is given by

$$U = TS + E\hat{P} + BI + \sigma(\varepsilon V_0) + \mu N. \tag{4.3}$$

The Euler relation is a *thermodynamic potential* seen to combined first and second laws of thermodynamics in terms of the product of conjugate parameters (in energy units of Joules, *J*) given in Table 4.1. The Euler relation will later be used in the generation of other useful thermodynamic potentials for a closed solid-phase system of one component (dN = 0).

Differentiating Eq. (4.3) gives the result

$$\mathrm{d}U = T\mathrm{d}S + S\mathrm{d}T + E\mathrm{d}\hat{P} + \hat{P}\mathrm{d}E + B\mathrm{d}I + I\mathrm{d}B + \sigma\,\mathrm{d}(\varepsilon V_0) + (\varepsilon V_0)\mathrm{d}\sigma + \mu\,\mathrm{d}N + N\mathrm{d}\mu,$$

which compared to Eq. (4.2) requires that

$$S\,\mathrm{d}T + \hat{P}\mathrm{d}E + I\mathrm{d}B + (\varepsilon V_0)\mathrm{d}\sigma + N\mathrm{d}\mu = 0 \tag{4.4}$$

Equation (4.4) is the general form of *Gibbs-Duhem equation* for a solid-phase system of a single component ($\mathrm{d}\,N = 0$).

The concepts of equilibrium and spontaneous (irreversible) processes are best understood in terms of the thermodynamic potentials G and F called the Gibbs and Helmholtz free energies, respectively. The extended *Gibbs free energy* for a single component solid-phase system is defined as

$$G \equiv \mu N = U - TS - E\hat{P} - BI - \sigma\,(\varepsilon V_0), \tag{4.5}$$

which follows from the Euler relation. This potential is the *Legendre transform* of U that simultaneously replaces S by T, $\hat{P}$ by E, I by B and εV_0 by σ as the independent variables. Differentiating Eq. (4.5) for a closed solid-phase system of one component and introducing Eq. (4.2) gives the infinitesimal change in Gibbs free energy

$$\mathrm{d}G = -S\,\mathrm{d}T - \hat{P}\mathrm{d}E - I\mathrm{d}B - (\varepsilon V_0)\mathrm{d}\sigma \tag{4.6}$$

In actual experimental situations, it is often a simple matter to hold the intensive parameters constant. When this is done, that is, when T, E, B, and σ are held fixed, the solid-phase system is said to be thermally, electrically, magnetically and mechanically free resulting in

$$\mathrm{d}G = 0 \tag{4.7}$$

as the criterion for thermodynamic equilibrium. When one or more of the intensive parameters are varied, then

$$\mathrm{d}G < 0\,, \tag{4.8}$$

and the process is said to be spontaneous or irreversible. Clearly, the condition $\mathrm{d}G > 0$ applies to a process that will not take place without changing the thermodynamic parameters of the system.

The *Helmholtz free energy* is a thermodynamic potential defined as

$$F \equiv U - TS\,. \tag{4.9}$$

Thus, the Helmholtz free energy is the Legendre transform that replaces the entropy S by temperature T as the independent variable. Differentiating Eq. (4.9) for a closed solid-phase system of one component and introducing Eq. (4.2) gives the infinitesimal change in the Helmholtz free energy as

$$\mathrm{d}\,F = -S\mathrm{d}\,T + E\mathrm{d}\,\hat{P} + B\mathrm{d}\,I + \sigma\,\mathrm{d}(\varepsilon V_0) \tag{4.10}$$

which eliminates the difficult task of holding entropy constant to establish equilibrium but retains the extensive parameters $\hat{P}$, I, and εV_0 as the independent variables. Thus, in experimental situations when T, $\hat{P}$, I, and εV_0 are held constant, the system is said to be thermally free but electrically, magnetically, and mechanically, clamped. Under these conditions,

$$\mathrm{d}F = 0 \tag{4.11}$$

as the criterion for thermodynamic equilibrium. It also follows that $\mathrm{d}\,F < 0$ corresponds to an irreversible or spontaneous thermally free process at constant $\hat{P}$, I, and ε, whereas $\mathrm{d}\,F > 0$ corresponds, to a spontaneous isothermal but electrical, magnetic and mechanical clamped process. Other thermodynamic potentials may also serve usefully as criteria for thermodynamic equilibrium under the appropriate clamped and/or free conditions.

4.1.1 Energy Density Representation

In applying thermodynamic arguments to solid-state systems in which the various tensor components must be manipulated, it becomes burdensome to carry the reference volume V_0 along with strain to establish the true extensive mechanical parameter. Because the strains are infinitesimal in magnitude, all equations can be divided by the volume of the fiducial or reference state, which is equal to the instantaneous volume V_0 of the solid phase. When this is done, the internal energy density and Gibbs free energy density for a closed system of one component ($\mathrm{d}N = 0$) become

$$\mathrm{d}u = \mathrm{d}U/V_0 = T\mathrm{d}s + E\,\mathrm{d}P + B\,\mathrm{d}M + \sigma\,\mathrm{d}\varepsilon \tag{4.12}$$

and

$$\mathrm{d}g = \mathrm{d}G/V_0 = -s\,\mathrm{d}T - P\mathrm{d}E - M\,\mathrm{d}B - \varepsilon\mathrm{d}\sigma, \tag{4.13}$$

respectively. The extensive parameters are now defined as follows:

$s = S/V_0 =$ *entropy density* (J/°K/m^3),
$P = \hat{P}/V_0 =$ total electric dipole moment/unit volume = *polarization* (C/m^2),
$M = I/V_0 =$ total magnetic dipole moment/unit volume = *magnetization* (A/m), and
$\varepsilon = \varepsilon V_0/V_0 =$ *elastic strain* (dimensionless).

The criteria for equilibrium still apply but in energy density form, and the Euler relation $u = U/V_0$ and Helmholtz free energy density $f \equiv u - Ts$ follow from the above definitions.

By using the energy density representation for simplicity, other thermodynamic potentials, in addition to g and f, can be generated by Legendre transformations of u. Listed in Table 4.2 are the 16 thermodynamic potentials and their differentials for a closed solid-phase system of one component. Some of these will prove to be useful. For example the *generalized enthalpy density h,* which is given by thermodynamic potential ϕ_5, is used to define the heat capacity of a solid at constant E, B,

TABLE 4.2: The 16 thermodynamic potential densities and their differentials for a closed solid state system of one component

THERMODYNAMIC POTENTIALS		THERMODYNAMIC POTENTIAL DIFFERENTIALS
$\phi_1 = u - Ts - EP - BM - \sigma\varepsilon$	$= g$	$\mathrm{d}g = -s\,\mathrm{d}T - P\,\mathrm{d}E - M\,\mathrm{d}B - \varepsilon\,\mathrm{d}\sigma$
$\phi_2 = u - Ts - EP - BM$		$\mathrm{d}\phi_2 = -s\,\mathrm{d}T - P\,\mathrm{d}E - M\,\mathrm{d}B + \sigma\,\mathrm{d}\varepsilon$
$\phi_3 = u - Ts - EP - \sigma\varepsilon$		$\mathrm{d}\phi_3 = -s\,\mathrm{d}T - P\,\mathrm{d}E + B\,\mathrm{d}M - \varepsilon\,\mathrm{d}\sigma$
$\phi_4 = u - Ts - BM - \sigma\varepsilon$		$\mathrm{d}\phi_4 = -s\,\mathrm{d}T + E\,\mathrm{d}P - M\,\mathrm{d}B - \varepsilon\,\mathrm{d}\sigma$
$\phi_5 = u - EP - BM - \sigma\varepsilon$	$= h$	$\mathrm{d}h = T\,\mathrm{d}s - P\,\mathrm{d}E - M\,\mathrm{d}B - \varepsilon\,\mathrm{d}\sigma$
$\phi_6 = u - Ts - EP$		$\mathrm{d}\phi_6 = -s\,\mathrm{d}T - P\,\mathrm{d}E + B\,\mathrm{d}M + \sigma\,\mathrm{d}\varepsilon$
$\phi_7 = u - Ts - BM$		$\mathrm{d}\phi_7 = -s\,\mathrm{d}T + E\,\mathrm{d}P - M\,\mathrm{d}B + \sigma\,\mathrm{d}\varepsilon$
$\phi_8 = u - Ts - \sigma\varepsilon$		$\mathrm{d}\phi_8 = -s\,\mathrm{d}T + E\,\mathrm{d}P + B\,\mathrm{d}M - \varepsilon\,\mathrm{d}\sigma$
$\phi_9 = u - EP - BM$		$\mathrm{d}\phi_9 = T\,\mathrm{d}s - P\,\mathrm{d}E - M\,\mathrm{d}B + \sigma\,\mathrm{d}\varepsilon$
$\phi_{10} = u - EP - \sigma\varepsilon$		$\mathrm{d}\phi_{10} = T\,\mathrm{d}s - P\,\mathrm{d}E + B\,\mathrm{d}M - \varepsilon\,\mathrm{d}\sigma$
$\phi_{11} = u - BM - \sigma\varepsilon$		$\mathrm{d}\phi_{11} = T\,\mathrm{d}s + E\,\mathrm{d}P - M\,\mathrm{d}B - \varepsilon\,\mathrm{d}\sigma$
$\phi_{12} = u - Ts$	$= f$	$\mathrm{d}f = -s\,\mathrm{d}T + P\,\mathrm{d}E + M\,\mathrm{d}B + \varepsilon\,\mathrm{d}\sigma$
$\phi_{13} = u - EP$		$\mathrm{d}\phi_{13} = T\,\mathrm{d}s - P\,\mathrm{d}E + B\,\mathrm{d}M + \sigma\,\mathrm{d}\varepsilon$
$\phi_{14} = u - BM$		$\mathrm{d}\phi_{14} = T\,\mathrm{d}s + E\,\mathrm{d}P - M\,\mathrm{d}B + \sigma\,\mathrm{d}\varepsilon$
$\phi_{15} = u - \sigma\varepsilon$		$\mathrm{d}\phi_{15} = T\,\mathrm{d}s + E\,\mathrm{d}P + B\,\mathrm{d}M - \varepsilon\,\mathrm{d}\sigma$
$\phi_{16} = u$	$= u$	$\mathrm{d}u = T\,\mathrm{d}s + E\,\mathrm{d}P + B\,\mathrm{d}M + \sigma\,\mathrm{d}\varepsilon$

and σ, which is analogous to C_P in the classical sense. Still other potentials, such as ϕ_2, ϕ_3, ϕ_4, and including ϕ_5 are useful in developing Maxwell's relations for the dependent coupled effects holding certain intensive parameters constant. The reader will note that the differential forms $d\phi_i$ result by differentiating ϕ_i followed by introduction of Eq. (4.12), $\mathrm{d}u = T\,\mathrm{d}s + E\,\mathrm{d}P + B\,\mathrm{d}M + \sigma\,\mathrm{d}\varepsilon$ to complete the Legendre transform of u. For example, differentiating $\phi_{13} = u - EP$ gives

$$\begin{aligned} d\phi_{13} &= \mathrm{d}u - E\,\mathrm{d}P - P\,\mathrm{d}E = T\,\mathrm{d}s + E\,\mathrm{d}P + B\,\mathrm{d}M + \sigma\,\mathrm{d}\varepsilon - E\,\mathrm{d}P - P\,\mathrm{d}E \\ &= T\,\mathrm{d}s - P\,\mathrm{d}E + B\,\mathrm{d}M + \sigma\,\mathrm{d}\varepsilon \end{aligned}$$

4.2 THERMODYNAMIC DEFINITION OF PARAMETERS

Taking any closed solid-state system of one component ($\mathrm{d}N = 0$) in which reversible processes are occurring, the *fundamental equation of state* becomes $u = u\,(s, P_i, M_i, \varepsilon_{ij})$, where the tensor rank of the extensive parameters is indicated by the number of subscripts. Expanding an infinitesimal change in u in a Taylor series and neglecting the second, and higher-order differential terms, we write the first-order terms of du as

$$\mathrm{d}u = \left(\frac{\partial u}{\partial s}\right)_{P,M,\varepsilon} \mathrm{d}s + \left(\frac{\partial u}{\partial P_i}\right)_{s,M,\varepsilon} \mathrm{d}P_i + \left(\frac{\partial u}{\partial M_i}\right)_{s,P,\varepsilon} \mathrm{d}M_i + \left(\frac{\partial u}{\partial \varepsilon_{ij}}\right)_{s,P,\mathrm{M}} \mathrm{d}\varepsilon_{ij}$$

$$= T\mathrm{d}s + E_i \mathrm{d}P_i + B_i \mathrm{d}M_i + \sigma_{ij}\,\mathrm{d}\varepsilon_{ij} \quad (i, j = 1\text{–}3). \tag{4.14}$$

By comparing coefficients, we find the following thermodynamic definitions for the intensive parameters by holding certain extensive parameters constant as indicated by the symbols subscripted to the curved brackets:

$$\left(\frac{\partial u}{\partial s}\right)_{P,M,\varepsilon} \equiv T \qquad \text{The } \textit{absolute temperature} \tag{4.15}$$

$$\left(\frac{\partial u}{\partial P_i}\right)_{s,M,\varepsilon} \equiv E_i \qquad \text{The } \textit{external electric field strength} \text{ vector} \tag{4.16}$$

$$\left(\frac{\partial u}{\partial M_i}\right)_{s,P,\varepsilon} \equiv B_i \qquad \text{The } \textit{external magnetic flux density} \text{ vector} \tag{4.17}$$

$$\left(\frac{\partial u}{\partial \varepsilon_{ij}}\right)_{s,P,M} \equiv \sigma_{ij} \qquad \text{The } \textit{stress} \text{ tensor.} \tag{4.18}$$

In these definitions, T is a scalar and is specified by one component, E_i and B_i are vectors each specified by three components (B_i is axial magnetic in character), and σ_{ij} is usually a symmetrical second-rank polar tensor ($\sigma_{ij} = \sigma_{ji}$) specified by six components as in Eqs. (2.17) and (2.20).

Now, let the letter I represent the intensive parameters (T, E_i, B_i, σ_{ij}) and the letter e represent the extensive parameters (s, P_i, M_i, ε_{ij}) so that an infinitesimal change in the internal energy density is given in the compact form

$$\mathrm{d}u = I_m\,\mathrm{d}e_m \quad (m = 1\text{–}13). \tag{4.19}$$

Here, the sequence

$$(T\,\mathrm{d}\,s + E_1\mathrm{d}\,P_1 + E_2\,\mathrm{d}\,P_2 + E_3\,\mathrm{d}\,P_3 + B_1\,\mathrm{d}\,M_1 + B_2\,\mathrm{d}\,M_2 + B_3\,\mathrm{d}\,M_3 + \sigma_1\,\mathrm{d}\,\varepsilon_1 + \sigma_2\,\mathrm{d}\varepsilon_2 + \cdots \sigma_6\,\mathrm{d}\varepsilon_6)$$

has been written in the form ($I_1 \mathrm{d}\, e_1 + I_2 \mathrm{d}\, e_2 + \cdots + I_{13} \mathrm{d}\, e_{13}$), where the stress and strain components have been unfolded according to the matrix scheme of Eq. (2.20) for symmetric second-rank tensors.

In a similar manner, the extensive tensor parameters can be defined by using the generalized Gibbs free energy density. For any closed solid-phase system of one component, the fundamental equation of state becomes $g = g\,(T, E_i, B_i, \sigma_{ij})$, and we write for the first differential of g

$$\mathrm{d}g = \left(\frac{\partial g}{\partial T}\right)_{E,B,\sigma} \mathrm{d}T + \left(\frac{\partial g}{\partial E_i}\right)_{T,B,\sigma} \mathrm{d}E_i + \left(\frac{\partial g}{\partial B_i}\right)_{T,E,\sigma} \mathrm{d}B_i + \left(\frac{\partial g}{\partial \sigma_{ij}}\right)_{T,E,B} \mathrm{d}\sigma_{ij}$$

$$= -s\,\mathrm{d}T - P_i \mathrm{d}E_i - M_i \mathrm{d}B_i - \varepsilon_{ij}\,\mathrm{d}\sigma_{ij}. \tag{4.20}$$

Again, by comparing coefficients there results the following definitions for the extensive parameters of a closed system holding certain intensive parameters constant:

$$-\left(\frac{\partial g}{\partial T}\right)_{E,B,\sigma} \equiv s \qquad \text{The } \textit{entropy density} \tag{4.21}$$

$$-\left(\frac{\partial g}{\partial E_i}\right)_{T,B,\sigma} \equiv P_i \qquad \text{The total electric dipole moment per unit volume or } (\textit{polarization}) \tag{4.22}$$

$$-\left(\frac{\partial g}{\partial B_i}\right)_{T,E,\sigma} \equiv \mathrm{M}_i \qquad \text{The total magnetic dipole moment per unit volume or } (\textit{magnetization}) \tag{4.23}$$

$$-\left(\frac{\partial g}{\partial \sigma_{ij}}\right)_{T,E,B} \equiv \varepsilon_{ij} \qquad \text{The } \textit{strain} \text{ tensor.} \tag{4.24}$$

As with their conjugate intensive parameters, s is a scalar, P_i and M_i are vectors of three components each (M_i is axial magnetic in character), and ε_{ij} is usually represented as a symmetrical second-rank tensor ($\varepsilon_{ij} = \varepsilon_{ji}$) specified by six components as in Eq. (2.20).

An infinitesimal change in the Gibbs free energy density may also be represented in the compact form

$$dg = -e_m \, dI_m \qquad (m = 1-13), \tag{4.25}$$

where ($e_1\, dI_1 + e_2\, dI_2 + \ldots + e_{13}\, dI_{13}$) represents the sequence ($s\, d\, T + P_1\, d\, E_1 + P_2\, d\, E_2 + P_3\, d\, E_3 + M_1\, d\, B_1 + M_2\, d\, B_2 + M_3\, d\, B_3 + \varepsilon_1 d\, \sigma_1 + \varepsilon_2 d\, \sigma_2 + \cdots \varepsilon_6\, d\, \sigma_6$). Here again, the stress and strain components have been unfolded according to the scheme given by Eq. (2.20).

4.3 GENERALIZED COMPLIANCE AND RIGIDITY MATRICES

We now wish to know how the reversible variation of all intensive parameter components affect a given extensive parameter component and vice versa. Consider, as an example, the equation of state for the polarization of a solid-state system of one component as a function of the four intensive parameters given by $P_i = P_i(T, E_j, B_j, \sigma_{kl})$. In this case, an infinitesimal change in polarization is given by the Taylor series

$$dP_i = \sum_{n=1}^{\infty} \frac{1}{n!}\left(dT \frac{\partial}{\partial T} + dE_k \frac{\partial}{\partial E_k} + dB_k \frac{\partial}{\partial B_k} + d\sigma_{kl} \frac{\partial}{\partial \sigma_{kl}} \right)^n P_i(T, E, B, \sigma). \tag{4.26}$$

Similar Taylor series expansions can also be given for the remaining three equations of state

$$\begin{aligned} s &= s(T, E_k, B_k, \sigma_{kl}); \\ M_i &= M_i(T, E_k, B_k, \sigma_{kl}) \\ \varepsilon_{ij} &= \varepsilon_{ij}(T, E_k, B_k, \sigma_{kl}). \end{aligned} \tag{4.27}$$

Carrying out these Taylor series expansions and accepting only the first-order terms ($n = 1$), thus neglecting the second- and higher-order differential terms, the infinitesimal changes in the extensive parameters are given by the linear first-order equations:

$$\begin{aligned} ds &= \left(\frac{\partial s}{\partial T}\right)_{E,B,\sigma} dT + \left(\frac{\partial s}{\partial E_k}\right)_{T,B,\sigma} dE_k + \left(\frac{\partial s}{\partial B_k}\right)_{T,E,\sigma} dB_k + \left(\frac{\partial s}{\partial \sigma_{kl}}\right)_{T,E,B} d\sigma_{kl} \\ dP_i &= \left(\frac{\partial P_i}{\partial T}\right)_{E,B,\sigma} dT + \left(\frac{\partial P_i}{\partial E_k}\right)_{T,B,\sigma} dE_k + \left(\frac{\partial P_i}{\partial B_k}\right)_{T,E,\sigma} dB_k + \left(\frac{\partial P_i}{\partial \sigma_{kl}}\right)_{T,E,B} d\sigma_{kl} \\ dM_i &= \left(\frac{\partial M_i}{\partial T}\right)_{E,B,\sigma} dT + \left(\frac{\partial M_i}{\partial E_k}\right)_{T,B,\sigma} dE_k + \left(\frac{\partial M_i}{\partial B_k}\right)_{T,E,\sigma} dB_k + \left(\frac{\partial M_i}{\partial \sigma_{kl}}\right)_{T,E,B} d\sigma_{kl} \\ d\varepsilon_{ij} &= \left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)_{E,B,\sigma} dT + \left(\frac{\partial \varepsilon_{ij}}{\partial E_k}\right)_{T,B,\sigma} dE_k + \left(\frac{\partial \varepsilon_{ij}}{\partial B_k}\right)_{T,E,\sigma} dB_k + \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\right)_{T,E,B} d\sigma_{kl}. \end{aligned} \tag{4.28}$$

The partial derivatives are called the *property compliances*, where the subscripts indicate those intensive parameters that are held constant. Now, we designate the property compliances by the letter C with the appropriate subscripts and superscripts, such that $(\partial s / \partial T)_{E,B,\sigma} = C^{s,T}$, $(\partial s / \partial E_k)_{T,B,\sigma} = C_k^{s,E}$, etc., thereby permitting us to set Eqs. (4.28) in the matrix form given by Eq. (4.29). This matrix equation is called the *general property compliance matrix* for first-order equilibrium properties. The tensor rank of any compliance is indicated by the number of subscripts it has. Thus, it is seen that the tensor rank varies from zero for $C^{s,T}$ to rank 4 for the compliance $C_{ijkl}^{\varepsilon,\sigma}$.

$$\begin{bmatrix} \mathrm{d}s \\ \mathrm{d}P_i \\ \mathrm{d}M_i \\ \mathrm{d}\varepsilon_{ij} \end{bmatrix} = \begin{bmatrix} C^{s,T} & C_k^{s,E} & C_k^{s,B} & C_{kl}^{s,\sigma} \\ C_i^{P,T} & C_{ik}^{P,E} & C_{ik}^{P,B} & C_{ikl}^{P,\sigma} \\ C_i^{M,T} & C_{ik}^{M,E} & C_{ik}^{M,B} & C_{ikl}^{M,\sigma} \\ C_{ij}^{\varepsilon,T} & C_{ijk}^{\varepsilon,E} & C_{ijk}^{\varepsilon,B} & C_{ijkl}^{\varepsilon,\sigma} \end{bmatrix} \cdot \begin{bmatrix} \mathrm{d}T \\ \mathrm{d}E_k \\ \mathrm{d}B_k \\ \mathrm{d}\sigma_{kl} \end{bmatrix} \quad (i, j, k, l = 1-3) \tag{4.29}$$

A close inspection of the compliance matrix (4.29) reveals that it is, in reality, a (13 x 13) matrix of tensor components if stress and strain are taken as symmetrical second-rank tensors. This is illustrated in Table 4.3 where the individual property matrices are designated by ($r \times c$), meaning rows by columns. The four *principal effects* of the property compliance matrix lie along its leading diagonal and are shaded. The off-diagonal compliances represent the *coupled (interaction) effects*.

If we let e represent the extensive parameter components and I represent the intensive parameter components, then the set of linear first-order equations for the compliances in Table 4.3 are expressed in contracted subscript form as

$$\mathrm{d}e_m = C_{mn}\,\mathrm{d}I_n \quad (m, n = 1-13), \tag{4.30}$$

where it follows that

$$\begin{aligned} &C_{11} = C^{s,T} = (\partial s / \partial T)_{E,B,\sigma} \\ &C_{12} = C^{s,E_1} = (\partial s / \partial E_1)_{T,E_2,E_3,B,\sigma} \\ &\vdots \\ &C_{29} = C^{P_1,\sigma_2} = (\partial P_1 / \partial \sigma_2)_{T,E,B,\sigma_1,\sigma_3,\cdots\sigma_6} \\ &\vdots \\ &C_{46} = C^{P_3,B_2} = (\partial P_3 / \partial B_2)_{T,E,B_1,B_2,\sigma} \\ &\vdots \\ &C_{13,13} = C^{\varepsilon_6,\sigma_6} = (\partial \varepsilon_6 / \partial \sigma_6)_{\mathrm{T,E,B},\sigma_1,\sigma_2,\ldots\sigma_5} \end{aligned} \tag{4.31}$$

TABLE 4.3: Component arrangement of the general compliance matrix emphasizing the principal effects along the leading diagonal (shaded regions), all other being the coupled effects

	$n \rightarrow$	1	2	3	4	5	6	7	8	9	10	11	12	13
m ↓		T	E_1	E_2	E_3	B_1	B_2	B_3	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
1	s	$C^{s,T}$ (0)	$C^{s,E}$ (1×3)			$C^{s,B}$ (1×3)			$C^{s,\sigma}$ (1×6)					
2	P_1	$C^{P,T}$ (3×1)	$C^{P,E}$ (3×3)			$C^{P,B}$ (3×3)			$C^{P,\sigma}$ (3×6)					
3	P_2													
4	P_3													
5	M_1	$C^{M,T}$ (3×1)	$C^{M,E}$ (3×3)			$C^{M,B}$ (3×3)			$C^{M,\sigma}$ (3×6)					
6	M_2													
7	M_3													
8	ε_1	$C^{\varepsilon,T}$ (6×1)	$C^{\varepsilon,E}$ (6×3)			$C^{\varepsilon,B}$ (6×3)			$C^{\varepsilon,\sigma}$ (6×6)					
9	ε_2													
10	ε_3													
11	ε_4													
12	ε_5													
13	ε_6													

Thus, a given compliance is a quantity that expresses the rate of change of one particular extensive property component with respect to an intensive property component holding *all* other intensive parameter components constant.

Following the same procedure, the intensive parametric equations of state are

$$T = T(s, P, M, \varepsilon)$$

$$E = E(s, P, M, \varepsilon)$$

$$B = B(s, P, M, \varepsilon)$$

$$\sigma = \sigma(s, P, M, \varepsilon) \qquad (4.32)$$

From these, there results the following linear first-order equations expressing the infinitesimal changes in intensive parameters as functions of infinitesimal changes in the extensive parameters:

$$\begin{bmatrix} \mathrm{d}T \\ \mathrm{d}E_i \\ \mathrm{d}B_i \\ \mathrm{d}\sigma_{ij} \end{bmatrix} = \begin{bmatrix} R^{T,s} & R_k^{T,P} & R_k^{T,M} & R_k^{T,\varepsilon} \\ R_i^{E,s} & R_{ik}^{E,P} & R_{ik}^{E,M} & R_{ikl}^{E,\varepsilon} \\ R_i^{B,s} & R_{ik}^{E,P} & R_{ik}^{B,M} & R_{ikl}^{B,\varepsilon} \\ R_{ij}^{\sigma,s} & R_{ijk}^{\sigma,P} & R_{ijk}^{\sigma,\mathrm{M}} & R_{ijkl}^{\sigma,\varepsilon} \end{bmatrix} \cdot \begin{bmatrix} \mathrm{d}s \\ \mathrm{d}P_k \\ \mathrm{d}M_k \\ \mathrm{d}\varepsilon_{kl} \end{bmatrix} \qquad (i,j,k,l=1-3) \tag{4.33}$$

Here, the R matrix is called the *general property rigidity matrix* for the first-order equilibrium tensor properties. Equations (4.33) can be represented in contracted tensor subscript form as

$$\mathrm{d}I_m = R_{mn}\mathrm{d}e_n \qquad (m,n=1\text{–}13), \tag{4.34}$$

where it follows that the rigidity and compliance matrices have an inverse relationship given by

$$R = C^{-1}. \tag{4.35}$$

The rigidities have the meaning that

$$\begin{aligned} &R_{11} = R^{T,s} = (\partial T/\partial s)_{P,M,\varepsilon} \\ &\vdots \\ &R_{46} = R^{E_3,M_2} = (\partial E_3/\partial M_2)_{s,P,M_1,M_2,\varepsilon} \\ &\vdots \\ &R_{13,13} = R^{\sigma_6,\varepsilon_6} = (\partial\sigma_6/\partial\varepsilon_6)_{s,\,P,\,M,\,\varepsilon_1,\,\varepsilon_2,\,\ldots\,\varepsilon_5}. \end{aligned} \tag{4.36}$$

In the above developments, only infinitesimal reversible changes in the intensive and extensive parameters were considered, and all solid-phase systems were assumed closed on their boundaries. Furthermore, we have suppressed the names of the various property compliances and rigidities until symmetry considerations have been discussed in the next section. Let it suffice for now to say that the properties along the leading diagonals of the general compliance and rigidity matrices each represent four *principal effects*, whereas the off-diagonal symbols represent the 12 interaction effects often called *coupled effects*.

4.4 SYMMETRY OF THE GENERAL COMPLIANCE AND RIGIDITY MATRICES

The thermodynamic potentials listed in Table 4.2 are functions of thermodynamic properties of a given solid, and each of the thermodynamic properties has only one definite value for any given state of the solid. A thermodynamic property is, therefore, any quantity that depends on the state of the solid and that is independent of the path taken to reach that state. Such quantities are called *state functions* and form exact differentials. For the intensive and extensive parameters that are field tensors of rank 1 or 2 (T and s are scalars), the term thermodynamic property refers to an individual component of the tensor. For example, $\phi = g$ in Table 4.2 represents the Gibbs free energy density $g(\mathrm{T}, \mathrm{E}, \mathrm{B}, \sigma) = g(T, E_1, E_2, E_3, B_1, B_2, B_3,\ \sigma_1, \sigma_2, \ldots\ \sigma_3)$ in which g is given as function of 13 thermodynamic properties (intensive parameter components). Thus, it follows that although g is intensive in nature, internal energy density u is extensive in nature and all other ϕ_i in Table 4.2 are of mixed character.

Consider any thermodynamic property $\zeta(p,q)$ of a solid that is a function of any other two thermodynamic properties, p and q. Now suppose that the substance is taken from its initial thermodynamic state through a series of states allowing p and q to vary independently in some arbitrary manner and that the process may be either reversible or irreversible. Finally, if the substance is returned to its initial state, we would notice that $\Delta\,\zeta = 0$ since ζ depends only on the initial and final states, which, in this case, are the same. The independence of path of a given thermodynamic property ζ is expressed mathematically by Green's theorem in a plane (special case of Stoke's theorem) given by

$$\oint_C \varsigma(p,q) = \oint_C \left[\left(\frac{\partial \varsigma}{\partial p} \right) \mathrm{d}\,p + \left(\frac{\partial \varsigma}{\partial q} \right) \mathrm{d}\,q \right]$$

$$= \oint_C (M\,\mathrm{d}\,p + N\,\mathrm{d}\,q) = -\int_S \left[\left(\frac{\partial M}{\partial q} \right)_p - \left(\frac{\partial N}{\partial p} \right)_q \right] \mathrm{d}\,p\,\mathrm{d}\,q = 0 \qquad (4.37)$$

for any simple closed path C in a given region R'. It follows, therefore, that

$$\frac{\partial N}{\partial p} = \frac{\partial^2 \varsigma}{\partial p \partial q} = \frac{\partial^2 \varsigma}{\partial q \partial p} = \frac{\partial M}{\partial q} \qquad (4.38)$$

if $M(p,q)$ and $N(p,q)$ have continuous derivatives in region R'. Simply stated, the order of differentiation of any thermodynamic property ζ is immaterial. This result is essential in describing the symmetry of the generalized compliance and rigidity matrices from which come the Maxwell relations. It will also be most useful when discussing the symmetry of second- and higher-order tensor properties in subsequent chapters.

We now apply Eq. (4.38) to the extended Gibbs free energy density. From Eq. (4.25) for any component, e_m of an extensive parameter is defined by

$$e_m = -\frac{\partial g}{\partial I_m}. \qquad (4.39)$$

Also, its infinitesimal change is related to an infinitesimal change in a component of an intensive parameter given by d $e_m = C_{mn}$ d I_n, where the compliance is defined by

$$C_{mn} = \frac{\partial e_m}{\partial I_n}. \tag{4.40}$$

Because the order of differentiation is immaterial, we have the important result that

$$\frac{\partial e_m}{\partial I_n} = -\frac{\partial^2 g}{\partial I_n\, \partial I_m} = -\frac{\partial^2 g}{\partial I_m\, \partial I_n} = \frac{\partial e_n}{\partial I_n} \tag{4.41}$$

or

$$C_{mn} = C_{nm}. \tag{4.41a}$$

The meaning of Eq. (4.41) is straightforward. With reference to Table 4.3, only the principle effects (those along the diagonal and shaded) possesses *self-symmetry* expressed by

$$C^{P,E} = \tilde{C}^{P,E},\ \ C^{M,B} = \tilde{C}^{M,B},\ \ C^{\varepsilon,\sigma} = \tilde{C}^{\varepsilon,\sigma},$$

meaning that the principle property compliance matrices (of components) taken separately are equal to their transpose. All other (coupled) property compliance matrices are related to the corresponding ones across the leading diagonal according to the Maxwell relations given later in Section 4.5.2. For example, while $C^{P,B} = \tilde{C}^{M,E}$, it also follows that $C^{P,B} \neq \tilde{C}^{P,B}$ and $C^{M,E} \neq \tilde{C}^{M,E}$; or while $C^{P,\sigma} = \tilde{C}^{\varepsilon,E}$, it is clear that $C^{P,\sigma} \neq \tilde{C}^{P,\sigma}$ or $C^{\varepsilon,E} \neq \tilde{C}^{\varepsilon,E}$. Consequently, the 13 × 13 compliance component matrix shown in Table 4.3 is symmetric, about the leading diagonal (within the shaded regions), which reduces the number of independent compliance components from 169 to 91. This type of inherent symmetry is called *thermodynamic tensor symmetry* since it arises from thermodynamic arguments. It must be remembered that the symmetry expressed by $C_{mn} = C_{nm}$ applies only to the tensor components on the leading diagonal of the generalized compliance matrix.

By similar reasoning, it follows from Eq. (4.19) that

$$I_m = \frac{\partial u}{\partial e_n}, \tag{4.42}$$

where an infinitesimal change in any intensive parameter is given by d$I_m = R_m e_n$. Again applying Green's theorem in a plane yields the result

$$\frac{\partial I_m}{\partial e_n} = -\frac{\partial^2 u}{\partial e_n\, \partial e_m} = \frac{\partial^2 u}{\partial e_m\, \partial e_n} = \frac{\partial I_n}{\partial e_m} \tag{4.43}$$

or

$$R_{mn} = R_{nm}. \tag{4.43a}$$

We note that this result could have been deduced from Eq. (4.35). Consequently, the 13 × 13 rigidity component matrix is also symmetric about its leading diagonal thereby reducing the number of independent rigidity components from 169 to 91.

It must be understood that the so-called thermodynamic tensor symmetry is in no way associated with the symmetry of the crystal in which the tensor properties may or may not be manifest. Thus, the symmetry expressed by $C_{mn} = C_{nm}$ and $R_{mn} = R_{nm}$ applies generally to all crystal systems. Operation of the minimum generating matrices given in Table 3.6 and the application of Neumann's principle given in Section 3.6 for symmetric second-rank tensors may result in a reduction of independent components required to specify the property for that point group. This will be done separately and selectively for the tensor properties as they are discussed in later developments.

4.5 SYSTEMATIC ENUMERATION AND CORRELATION OF FIRST-ORDER TENSOR PROPERTIES—GENERALIZED MAXWELL RELATIONS

It is desirable at this point to enumerate and correlate the various properties represented by the general compliance and rigidity matrices given by Eqs. (4.29) and (4.33). To do this, we will begin with the principle effects that lie along the leading diagonal of the general compliance matrix and then proceed to the interaction (coupled) effects that are represented by the off-diagonal compliances. Again, we will assume a single solid-phase system that is closed on its boundaries and that all fields applied to it are infinitesimally small so as to avoid second- and higher-order effects.

4.5.1 Principal Effects

The principal properties are those that relate conjugate parameters and are defined as follows:

$$TC^{s,T} = T\left(\frac{\partial s}{\partial T}\right)_{E,\,B,\,\sigma} \equiv (C)_{E,\,B,\,\sigma},\ \textit{specific heat}\ \text{(Heat capacity per unit volume)} \tag{4.44}$$

$$\kappa_0^{-1}\, C_{ik}^{P,\,E} = \kappa_0^{-1}\left(\frac{\partial P_i}{\partial E_k}\right)_{T,\,B,\,\sigma} \equiv (\chi_{ik})_{T,\,B,\,\sigma},\ \textit{dielectric susceptibility}\ \text{tensor} \tag{4.45}$$

where κ_0 is the permittivity of a vacuum.

$$\mu_0 C_{ik}^{M,B} = \mu_0 \left(\frac{\partial M_i}{\partial B_k} \right)_{T,\,E,\sigma} \equiv (\psi_{ik})_{T,\,E,\sigma},\ \textit{magnetic susceptibility}\ \text{tensor} \tag{4.46}$$

where μ_0 is the permeability of a vacuum.

$$C_{ijkl}^{\varepsilon,\,\sigma} = \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right)_{T,\,E,\,B} \equiv (s_{ijkl})_{T,\,E,\,B},\ \textit{elastic compliance}\ \text{tensor} \tag{4.47}$$

By application of the results of the previous section, we find these principal effects have the following thermodynamic tensor symmetry:

$$\chi_{ik} = \chi_{ki} \quad (i, k = 1,2,3) \quad or \quad \chi = \tilde{\chi} \tag{4.48}$$

$$\psi_{ik} = \psi_{ki} \quad (i, k = 1,2,3) \quad or \quad \psi = \tilde{\psi} \tag{4.49}$$

$$s_{ijkl} = s_{klij} \quad (i, j, k, l = 1,2,3) \quad or \quad s_{mn} = s_{nm} \tag{4.50}$$

It follows, therefore, that the two susceptibilities are symmetrical second-rank tensors, whereas the fourth-rank elastic compliance tensor s_{ijkl} is symmetric with respect to the interchange of pairs (ij) and (kl). It will later be shown that σ_{ij} and ε_{ij} are nearly always symmetrical second-rank tensors.

4.5.2 Independent Coupled Effects

These coupled effects are represented by the off-diagonal compliances of the general compliance matrix and do *not* relate conjugate parameters. Consequently, they possess no thermodynamic tensor symmetry in themselves (self symmetry) as did the principal effects. However, since the general compliance component matrix is symmetric about its leading diagonal, there results the following six sets of *Maxwell relations* (57 in all) describing the six independent coupled effects all of which derive from the thermodynamic potential $\phi_1 = g$ in Table 4.2.

1. Pyroelectric Effect

$$\begin{aligned}
\left(\frac{\partial s}{\partial E_1} \right)_{T,E_2,E_3,B,\sigma} &= \left(\frac{\partial P_1}{\partial T} \right)_{E,B,\sigma} = (p_1)_{B,\sigma} \\
\vdots \qquad & \qquad\qquad \vdots \\
\left(\frac{\partial s}{\partial E_3} \right)_{T,E_1,E_2,B,\,\sigma} &= \left(\frac{\partial P_3}{\partial T} \right)_{E,B,\,\sigma} = (p_3)_{B,\,\sigma}
\end{aligned} \tag{4.51}$$

or, collectively, in matrix notation

$$C^{sE}\big)_{T,B,\sigma} = \tilde{C}^{PT}\big)_{E,B,\sigma} = \big(p\big)_{B,\sigma} \tag{4.52}$$

These equations state that the *electrocaloric coefficients* are numerically equal to the corresponding *pyroelectric coefficients*, and both are represented by the first-rank polar tensor p_k $(k=1,2,3)$. Thus, Eqs.(4.51) derive from $dg = -sdt - PdE - MdB - \varepsilon d\sigma$, to which we apply Stoke's theorem to give

$$\left[(\partial^2 g/\partial E\partial T) = (\partial^2 g/\partial T\partial E)\right]_{B,\sigma} \quad or \quad \left[(\partial/\partial E)(\partial g/\partial T) = (\partial/\partial T)(\partial g/\partial E)\right]_{B,\sigma}$$

where $\partial g/\partial T = -s$ and $\partial g/\partial E = -P$, thereby yielding Eqs. (4.51) at constant B and σ.

2. Pyromagnetic Effect

$$\begin{array}{lll}
\left(\dfrac{\partial s}{\partial B_1}\right)_{T,E,B_2,B_3,\sigma} = \left(\dfrac{\partial M_1}{\partial T}\right)_{E,B,\sigma} = (q_1)_{E,\sigma} \\
\qquad\vdots \qquad\qquad\qquad\qquad \vdots \\
\left(\dfrac{\partial s}{\partial B_3}\right)_{T,E,B_1,B_2,\sigma} = \left(\dfrac{\partial M_3}{\partial T}\right)_{E,B,\sigma} = (q_3)_{E,\sigma}
\end{array} \tag{4.53}$$

or, collectively, in matrix notation

$$C^{sB}\big)_{T,E,\sigma} = \tilde{C}^{M,T}\big)_{E,B,\sigma} = \big(q\big)_{E,\sigma}. \tag{4.54}$$

These equations state that the *magnetocaloric coefficients* are numerically equal to the corresponding *pyromagnetic coefficients*, and both are represented by the first-rank tensor q_k $(k=1,2,3)$, which is both axial and magnetic in tensor character.

3. Thermal Expansion

$$\begin{array}{lll}
\left(\dfrac{\partial s}{\partial \sigma_{11}}\right)_{T,E,B,\sigma_{22}\cdots\sigma_{12}} = \left(\dfrac{\partial \varepsilon_{11}}{\partial T}\right)_{E,B,\sigma} = (\alpha_{11})_{E,B} \\
\qquad\vdots \qquad\qquad\qquad\qquad \vdots \\
\left(\dfrac{\partial s}{\partial \sigma_{12}}\right)_{T,E,B,\sigma_{11}\cdots\sigma_{31}} = \left(\dfrac{\partial \varepsilon_{12}}{\partial T}\right)_{E,B,\sigma} = (\alpha_{12})_{E,B}
\end{array} \tag{4.55}$$

or, collectively, in matrix notation

$$C^{s\sigma}\big)_{T,E,B} = \tilde{C}^{\varepsilon,T}\big)_{E,B,\sigma} = (\alpha)_{E,B} \tag{4.56}$$

which states that the *piezocaloric coefficients* are numerically equal to the corresponding *thermal expansion coefficients* and that both are represented by the second-rank polar tensor $\alpha_{ik}(i,k = 1,2,3)$. It is assumed that stress, strain and thermal expansion are all symmetric second-rank tensors that are unfolded according to the schemes of Eqs. (2.19) or (2.20).

4. Magnetoelectric susceptibility

$$\begin{aligned}
\left(\frac{\partial P_1}{\partial B_1}\right)_{T,E,B_2,B_3,\sigma} &= \left(\frac{\partial M_1}{\partial E_1}\right)_{T,E,B_2,B_3,\sigma} = (\lambda_{11})_{T,\sigma} \\
&\vdots \qquad\qquad\qquad \vdots \\
\left(\frac{\partial P_2}{\partial B_1}\right)_{T,E,B_2,B_3,\sigma} &= \left(\frac{\partial M_1}{\partial E_2}\right)_{T,E_1,E_3,B,\sigma} = (\lambda_{21})_{T,\sigma}
\end{aligned} \tag{4.57}$$

or, collectively, in matrix notation

$$C^{PB})_{T,E,\sigma} = \tilde{C}^{ME})_{T,B,\sigma} = (\lambda)_{T,\sigma}. \tag{4.58}$$

Here, the corresponding coefficients of the *direct* and *converse magnetoelectric susceptibility* effects are numerically equal and are represented by the asymmetrical second-rank tensor λ_{ik} which is axial and magnetic in character. Note that the components have been unfolded according to the following schemes:

Tensor notation:	S_{11}	S_{22}	S_{33}	S_{23}	S_{31}	S_{12}	S_{32}	S_{13}	S_{21}	(4.59)
Matrix notation:	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	(4.60)

5. Piezoelectric Effect

$$\begin{aligned}
\left(\frac{\partial P_1}{\partial \sigma_{11}}\right)_{T,E,B,\sigma_{22}\cdots\sigma_{12}} &= \left(\frac{\partial \varepsilon_{11}}{\partial E_1}\right)_{T,E_2,E_3,B,\sigma} = (d_{111})_{T,B} \\
&\vdots \qquad\qquad\qquad \vdots \\
\left(\frac{\partial P_3}{\partial \sigma_{12}}\right)_{T,E,B,\sigma_{11}\cdots\sigma_{31}} &= \left(\frac{\partial \varepsilon_{12}}{\partial E_3}\right)_{T,E_1,E_2,B,\sigma} = (d_{312})_{T,B}
\end{aligned} \tag{4.61}$$

or, collectively, in matrix notation

$$C^{P\sigma})_{T,E,B} = \tilde{C}^{\varepsilon,E})_{T,B,\sigma} = (d)_{T,B}. \tag{4.62}$$

These equations state that the corresponding 18 components of the *direct* and *converse piezoelectric effects* are numerically equal and are represented by the third-rank polar tensor d_{ijkl} in the form of T_{im} given by Eq. (2.30) where the partial inherent symmetry is expressed by $d_{ikl} = d_{ilk} = d_{im}$.

6. Piezomagnetic Effect

$$\left(\frac{\partial M_1}{\partial \sigma_{11}}\right)_{T,E,B,\sigma_{22}\cdots\sigma_{12}} = \left(\frac{\partial \varepsilon_{11}}{\partial B_1}\right)_{T,E,B_2,B_3,\sigma} = (Q_{111})_{T,E}$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$\left(\frac{\partial M_3}{\partial \sigma_{12}}\right)_{T,E,B,\sigma_{11}\cdots\sigma_{31}} = \left(\frac{\partial \varepsilon_{12}}{\partial B_3}\right)_{T,E,B_1,B_2,\sigma} = (Q_{312})_{T,E} \tag{4.63}$$

or, collectively, in matrix notation

$$C^{M\sigma}\big)_{T,E,B} = \tilde{C}^{\varepsilon,B}\big)_{T,E,\sigma} = (Q)_{T,E}. \tag{4.64}$$

Similar to the piezoelectric effects, the corresponding 18 components of the direct and converse piezomagnetic effects are numerically equal. They are represented by the axial-magnetic third-rank tensor with the partial inherent symmetry $Q_{ikl} = Q_{ilk} = Q_{im}$, assuming that stress and strain are symmetric second-rank tensors and are expressed by a tensor of the form given by Eq. (2.30).

Thus, of the 16 properties represented by the general compliance matrix, only 10 are independent, 4 principal and 6 coupled effects. The same is true for the general rigidity matrix. It will be left as and exercise for the reader to repeat the above correlation procedure for the rigidities.

4.6 EFFECT OF MEASUREMENT CONDITIONS ON THE FIRST-ORDER TENSOR PROPERTIES

Frequently, it is desirable to convert property coefficients measured under one set of conditions to those measured under another set of conditions. As an example, ultrasonic wave velocity measurements provide isentropic (thermally clamped) elastic coefficients. However, it may be the isothermal (thermally free) elastic coefficients that are desired. A second, and perhaps most common example is the conversion of heat capacity at constant stress (mechanically free) to heat capacity at constant strain (mechanically clamped) or vice versa. There are many other such examples. The problem of converting property coefficients in the clamped state to those in the free state or vice versa is one, which we shall now consider.

Let a clamped compliance be that compliance that is measured holding any one of the extensive parameters (s, P, M, or ε) constant. Also, let a *free* compliance be one that is measured holding any one of the intensive parameters (T, E, B, or σ) constant. Now, consider any two extensive parameters $a = a(\alpha, \beta)$ and $b = b(\alpha, \beta)$ that are functions of any two intensive parameters α and β. From the equations $\mathrm{d}e_m = C_{mn}\mathrm{d}I_n$, we write

$$\mathrm{d}a = \left(\frac{\partial a}{\partial \alpha}\right)_\beta \mathrm{d}\alpha + \left(\frac{\partial a}{\partial \beta}\right)_\alpha \mathrm{d}\beta \tag{4.65}$$

and

$$\mathrm{d}b = \left(\frac{\partial b}{\partial \alpha}\right)_\beta \mathrm{d}\alpha + \left(\frac{\partial b}{\partial \beta}\right)_\alpha \mathrm{d}\beta. \tag{4.66}$$

Holding b constant and multiplying Eq. (4.66) by $(\partial\beta / \partial b)_\alpha$, we obtain

$$0 = \left\{\left(\frac{\partial \beta}{\partial b}\right)_\alpha \left(\frac{\partial b}{\partial \alpha}\right)_\beta \mathrm{d}\alpha + \left(\frac{\partial \beta}{\partial b}\right)_\alpha \left(\frac{\partial b}{\partial \beta}\right)_\alpha \mathrm{d}\beta\right\}_b ,$$

giving the result

$$\mathrm{d}\beta = -\left(\frac{\partial \beta}{\partial b}\right)_\alpha \left(\frac{\partial b}{\partial \alpha}\right)_\beta \mathrm{d}\alpha. \tag{4.67}$$

Introducing Eq. (4.67) into Eq. (4.65) gives

$$\mathrm{d}a = \left(\frac{\partial a}{\partial \alpha}\right)_\beta \mathrm{d}\alpha - \left(\frac{\partial a}{\partial \beta}\right)_\alpha \left(\frac{\partial \beta}{\partial b}\right)_\alpha \left(\frac{\partial b}{\partial \alpha}\right)_\beta \mathrm{d}\alpha. \tag{4.68}$$

Now, dividing Eq. (4.68) by $\mathrm{d}\alpha$ at constant b leads to the final result

$$\left(\frac{\partial a}{\partial \alpha}\right)_b - \left(\frac{\partial a}{\partial \alpha}\right)_\beta = -\left(\frac{\partial a}{\partial \beta}\right)_\alpha \left(\frac{\partial \beta}{\partial b}\right)_\alpha \left(\frac{\partial b}{\partial \alpha}\right)_\beta$$

or

$$(C^{a,\alpha})_b - (C^{a,\alpha})_\beta = -(C^{a,\beta})_\alpha (R^{\beta,b})_\alpha (C^{b,\alpha})_\beta \tag{4.69}$$

in symbolic notation. Equation (4.69) gives the difference between the clamped $(C^{a,\alpha})_b$ and free $(C^{a,\alpha})_\beta$ compliances and requires that all other intensive parameters γ, δ, and so forth be held constant and that b and β be conjugate parameters.

Application of Eq. (4.69) is simply accomplished by selecting the desired compliance through choice of a and α, and the clamped and free conditions through choice of the conjugate parameters b and β. For example, the difference between the mechanically clamped and free heat capacities is obtained by the following choice of parameters

$$\begin{Bmatrix} a = s & \alpha = T \\ b = \varepsilon & \beta = \sigma \end{Bmatrix} \qquad \textit{(E, B constant)}$$

Introducing these parameters into Eq. (4.69) results in

$$\left(\frac{\partial s}{\partial T}\right)_{\varepsilon} - \left(\frac{\partial s}{\partial T}\right)_{\sigma} = -\left(\frac{\partial s}{\partial \sigma_{ij}}\right)_{T}\left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}\right)_{T}\left(\frac{\partial \varepsilon_{kl}}{\partial T}\right)_{\sigma}, \qquad (4.70)$$

where E and B are assumed to be held constant. But $(\partial s / \partial\sigma_{ij})_T = (\partial\varepsilon_{ij} / \partial T)_\sigma = \alpha_j$ by Maxwell's relation and $(\partial\sigma_{ij} / \partial\varepsilon_{kl})_T = (c_{ijkl})_T$ where $(c_{ijkl})_T$ is the isothermal elastic stiffness coefficient. From this, we find the difference between the mechanically clamped and free heat capacities to be

$$C_\varepsilon - C_\sigma = -T\alpha_{ij}(c_{ijkl})\ \alpha_{kl} \qquad (i, j, k, l = 1-3)$$

in tensor subscript notation or, alternatively,

$$C_\varepsilon - C_\sigma = -T\alpha_i (c_{ij})_T\ \alpha_j = -T\tilde{\alpha}\,(c)_T\ \alpha \qquad (i, j = 1-6) \qquad (4.71)$$

in contracted tensor subscript and conformable matrix notation, respectively.

Now suppose we wish to know the difference between the isentropic (constant entropy) and isothermal dielectric susceptibilities. For this purpose the choice of parameters becomes

$$\begin{Bmatrix} a = P & \alpha = E \\ b = s & \beta = T \end{Bmatrix} \qquad \textit{(B constant)},$$

resulting in the equation

$$\left(\frac{\partial P_i}{\partial E_j}\right)_{s} - \left(\frac{\partial P_i}{\partial E_j}\right)_{T} = -\left(\frac{\partial P_i}{\partial T}\right)_{E}\left(\frac{\partial T}{\partial s}\right)_{E}\left(\frac{\partial s}{\partial E_j}\right)_{T}, \qquad (4.72)$$

where B and σ are held constant. However, because $(\partial P_i / \partial T)_E = (\partial s / E_i)_T = p_i$ from Maxwell's relations, there results

$$(\chi_{ij})_s - (\chi_{ij})_T = -\frac{T}{\kappa_0 C_E} p_i p_j \qquad (i, j = 1-3), \qquad (4.73)$$

where $T(\partial s / T)_E = C_E$ with B and σ held constant, and $p_i p_j$ is the dyadic or outer product of the pyroelectric coefficients.

The above two examples demonstrate how one could obtain the difference between clamped and free principal effects. However, the difference between clamped and free coupled effects can be obtained with equal ease. As a third example, suppose it is desired to know the difference between the electrically clamped and electrically free coefficients of thermal expansion. For this purpose, the choice of parameters must be

$$\begin{Bmatrix} a = \varepsilon & \alpha = T \\ b = P & \beta = E \end{Bmatrix} \qquad (B\ constant),$$

resulting in the equation

$$\left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)_P - \left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)_E = -\left(\frac{\partial \varepsilon_{ij}}{\partial E_k}\right)_T \left(\frac{\partial E_k}{\partial P_m}\right)_T \left(\frac{\partial P_m}{\partial T}\right)_E . \qquad (4.74)$$

But according to Maxwell's relations, $(\partial \varepsilon_{ij} / \partial E_k)_T = (\partial P_k / \partial \sigma_{ij})_E = d_{kij}$, with the result that

$$(\alpha_{ij})_P - (\alpha_{ij})_E = -\kappa_0^{-1} (d_{kij})_T (\chi_{km})^{-1}_{T,\sigma} (p_m)_\sigma \qquad (i, j, k, m = 1-3)$$

in tensor subscript notation or, alternatively,

$$(\alpha_i)_P - (\alpha_i)_E = -\kappa_0^{-1} (d_{ki})_T (\chi_{km})^{-1}_{T,\sigma} (p_m)_\sigma \qquad (i = 1-6;\ k, m = 1-3) \qquad (4.75)$$

or

$$\alpha_P - \alpha_E = -\kappa_0^{-1} \tilde{d}_T (\chi^{-1})_{T,\sigma} p_\sigma$$

in conformable matrix notation.

Because there are four principal effects each with three ways to vary the clamped and free compliances and six independent coupled effects each with two ways to vary the clamped and free compliances, there are a total of 24 equations of the type illustrated above. These are presented in

TABLE 4.4: Differences between clamped and free first-order property compliances given in conformable matrix order for the principal and coupled effects.

PRINCIPAL EFFECTS		COUPLED EFFECTS	
(1)	$C_P - C_E = -\kappa_0 T \tilde{p} (\chi_T)^{-1} p \}_{B,\sigma}$	(13)	$Q_s - Q_T = -(T / C_{B,\sigma}) q_\sigma \tilde{\alpha}_B \}_E$
(2)	$C_M - C_B = -\mu_0^{-1} T \tilde{q} (\psi_T)^{-1} q \}_{E,\sigma}$	(14)	$Q_P - Q_E = -\kappa_0^{-1} \lambda_\sigma (\chi_{B,\sigma})^{-1} d_B \}_T$
(3)	$C_\varepsilon - C_\sigma = -T \tilde{\alpha} c_T \alpha \}_{E,B}$	(15)	$d_s - d_T = -(T / C_{E,\sigma}) p_\sigma \tilde{p}_E \}_B$
(4)	$\chi_s - \chi_T = -(T / \kappa_0) C_E p \tilde{p} \}_{B,\sigma}$	(16)	$d_M - d_B = -\mu_0 \lambda_\sigma (\chi_{E,\sigma})^{-1} Q_E \}_T$
(5)	$\chi_M - \chi_E = -(\mu_0 / \kappa_0) \lambda (\psi_E)^{-1} \tilde{\lambda} \}_{T,\sigma}$	(17)	$\alpha_P - \alpha_E = -\kappa_0^{-1} \tilde{d}_T (\chi_{T,\sigma})^{-1} p_\sigma \}_B$
(6)	$\chi_\varepsilon - \chi_\sigma = -\kappa_o^{-1} d c_E \tilde{d} \}_{T,B}$	(18)	$\alpha_M - \alpha_B = -\mu_0 \tilde{Q}_T (\psi_{T,\sigma})^{-1} q_\sigma \}_E$
(7)	$\psi_s - \psi_T = -(\mu_0 T / C_B) q \tilde{q} \}_{E,\sigma}$	(19)	$q_P - q_E = -\kappa_0^{-1} \tilde{\lambda}_T (\chi_{T,B})^{-1} p_B \}_\sigma$
(8)	$\psi_P - \psi_E = -(\mu_0 / \kappa_0) \tilde{\lambda} (\chi_B)^{-1} \lambda \}_{T,\sigma}$	(20)	$q_\varepsilon - q_\sigma = -Q_T c_{T,B} \alpha_B \}_E$
(9)	$\psi_\varepsilon - \psi_\sigma = -\mu_0 Q c_B \tilde{Q} \}_{T,E}$	(21)	$p_M - p_B = -\mu_0 \lambda_T (\psi_{T,E})^{-1} q_E \}_\sigma$
(10)	$s_s - s_T = -(T / C_\sigma) \alpha \tilde{\alpha} \}_{E,B}$[*]	(22)	$p_\varepsilon - p_\sigma = -d_T c_{T,E} \alpha_E \}_B$
(11)	$s_P - s_E = -\kappa_0^{-1} \tilde{d} (\chi_\sigma)^{-1} d \}_{T,B}$	(23)	$\lambda_s - \lambda_T = -(T / C_{E,B}) p_B \tilde{q}_E \}_\sigma$
(12)	$s_M - s_B = -\mu_0 \tilde{Q} (\psi_\sigma)^{-1} Q \}_{T,E}$	(24)	$\lambda_\varepsilon - \lambda_\sigma = -d_B c_{E,B} \tilde{Q}_E \}_T$

[*] Difference between the isentropic (constant entropy density) and isothermal elastic compliances.

Table 4.4 in conformable matrix order. To use the table, one only needs to replace the symbols by their respective matrices and carry out the multiplication as indicated. The tilde appearing above some of the symbols indicates the transpose of the normal matrix form. This may be illustrated by expanding Eq. (4.75), which is Eq. (17) in Table 4.4 (all at constant B), as follows:

$$\begin{bmatrix}\alpha_1\\\alpha_2\\\alpha_3\\\alpha_4\\\alpha_5\\\alpha_6\end{bmatrix}_P-\begin{bmatrix}\alpha_1\\\alpha_2\\\alpha_3\\\alpha_4\\\alpha_5\\\alpha_6\end{bmatrix}_E=-\frac{1}{\kappa_0}\begin{bmatrix}d_{11}&d_{21}&d_{31}\\d_{12}&d_{22}&d_{32}\\d_{13}&d_{23}&d_{33}\\d_{14}&d_{24}&d_{34}\\d_{15}&d_{25}&d_{35}\\d_{16}&d_{26}&d_{36}\end{bmatrix}_T\begin{bmatrix}\chi^{-1}_{11}&\chi^{-1}_{12}&\chi^{-1}_{31}\\\chi^{-1}_{12}&\chi^{-1}_{22}&\chi^{-1}_{23}\\\chi^{-1}_{31}&\chi^{-1}_{23}&\chi^{-1}_{33}\end{bmatrix}_{T,\sigma}\begin{bmatrix}p_1\\p_2\\p_3\end{bmatrix}_\sigma. \tag{4.76}$$

Keep in mind that crystal symmetry considerations can greatly reduce the number of property components needed for use in equations of the type just given and, as a consequence, greatly reduce the matrix calculation time and effort to obtain a result.

The matrix equations in Table 4.4 may be used to obtain order-of-magnitude values for the differences between clamped and free compliances. However, in using any one equation, great care must be exercised in choosing representative magnitudes of the properties. Remember that the values of the components usually differ somewhat within each tensor and that these magnitudes my vary dramatically from crystal to crystal if, in fact, they exist at all by reason of normal crystal and magnetic symmetry.

It can be easily verified that the inverse of Eq. (4.69) is

$$R^{\alpha,a})_\beta-(R^{\alpha,a})_b=-(R^{\alpha,b})_b(C^{\alpha,b})_b(R^{\beta,\alpha})_b \tag{4.77}$$

giving the difference between free and clamped rigidity coefficients. In the case of rigidities, it is required that all other extensive parameters c, d, …, and so forth. be held constant and that b and β be conjugate parameters. This also leads to 24 equations of the type shown in Table 4.4.

• • • •

CHAPTER 5

The Dependent Coupled Effects and the Interrelationships Between First-Order Tensor Properties—Use of Interaction Diagrams

The independent principal and coupled first-order effects are featured in Table 4.3, which gives the component arrangement of the general compliance matrix. The four principal effects are those relating the conjugate parameters along the leading diagonal (the shaded regions) and possess thermodynamic self-symmetry. The six coupled effects are the off-diagonal regions in Table 4.3 and relate intensive parameters to nonconjugate extensive parameters—the opposite being true for the general rigidity matrix. Consequently, off-diagonal effects exhibit no self-symmetry. However, they do possess thermodynamic tensor symmetry expressed by the six Maxwell relations in Section 4.5.2 and by Eqs. (4.41a) and (4.43a). For this reason, they are labeled independent coupled effects.

5.1 THE DEPENDENT COUPLED EFFECTS

Additional coupled effects relating any two intensive parameters (or two extensive parameters) can be defined by suitable choice of the thermodynamic potentials given in Table 4.2 followed by application of Stoke's theorem (actually Green's theorem in a plane) discussed in Section 4.4. As an example, suppose it is desired to equate the isothermal elastocaloric coefficient $(\partial s / \partial \varepsilon)_T$ to the isometric thermal stress coefficient $(\partial \sigma / \partial T)_\varepsilon$ at constant P and B. For this purpose, ϕ_7 in Table 4.2 must be used together with Stoke's theorem. Thus, for $d\phi_7 = -s\,d\,T + E\,d\,P - M\,d\,B + \sigma\,d\,\varepsilon$, we have

$$\left[\frac{\partial^2 \phi_7}{\partial \varepsilon \partial T} = \frac{\partial^2 \phi_7}{\partial T \partial \varepsilon}\right]_{P,B} \quad \text{or} \quad \left[\frac{\partial}{\partial \varepsilon}\left(\frac{\partial \phi_7}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial \phi_7}{\partial \varepsilon}\right)\right]_{P,B},$$

with the result that

$$\left(\frac{\partial s}{\partial \varepsilon_{ij}}\right)_{T,P,B} = -\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{P,B,\varepsilon} = \left(t_{ij}\right)_{P,B}$$

There are many other examples of dependent coupled effects. In fact, an examination of Table 4.2 will indicate that there are four sets of clamped and/or free conditions for each of the six dependent coupled effects and their inverse, leading to a total of 48 equations of the type exemplified above. Thus, the choice of the thermodynamic potential used to obtain a given Maxwell relation will depend not only on the particular coupled effect involved but on what parameters are desired to be held constant.

For the sake of illustration here, let us require that all effects be defined in such a way that only the intensive parameters are held constant. By using just four thermodynamic potentials ϕ_2, ϕ_3, ϕ_4, and ϕ_5, the following six Maxwell relations, representing the six additional coupled effects, are given in the order of increasing tensor rank.

$$\left(\frac{\partial P_i}{\partial s}\right)_{E,B,\sigma} = -\left(\frac{\partial T}{\partial E_i}\right)_{s,B,\sigma} = \left(h_i\right)_{B,\sigma} \qquad \text{(from } \phi 5\text{)} \tag{5.1}$$

$$\left(\frac{\partial s}{\partial M_i}\right)_{T,E,\sigma} = -\left(\frac{\partial B_i}{\partial T}\right)_{E,M,\sigma} = \left(\eta_i\right)_{E,\sigma} \qquad \text{(from } \phi 3\text{)} \tag{5.2}$$

$$\left(\frac{\partial s}{\partial \varepsilon_{ij}}\right)_{T,E,B} = -\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{E,B,\varepsilon} = \left(t_{ij}\right)_{E,B} \qquad \text{(from } \phi 2\text{)} \tag{5.3}$$

$$\left(\frac{\partial M_j}{\partial P_i}\right)_{T,B,\sigma} = -\left(\frac{\partial E_i}{\partial B_j}\right)_{T,P,\sigma} = \left(\upsilon_{ij}\right)_{T,\sigma} \qquad \text{(from } \phi 4\text{)} \tag{5.4}$$

$$\left(\frac{\partial \varepsilon_{jk}}{\partial P_i}\right)_{T,B,\sigma} = -\left(\frac{\partial E_i}{\partial \sigma_{jk}}\right)_{T,P,B} = \left(\varepsilon_{ijk}\right)_{T,B} \qquad \text{(from } \phi 4\text{)} \tag{5.5}$$

$$\left(\frac{\partial \varepsilon_{jk}}{\partial M_i}\right)_{T,E,\sigma} = -\left(\frac{\partial B_i}{\partial \sigma_{jk}}\right)_{T,E,M} = \left(m_{ijk}\right)_{T,E} \qquad \text{(from } \phi 3\text{)} \tag{5.6}$$

The inverse of each of the above relations is readily obtained from a different thermodynamic potential chosen from the same group ϕ_2, ϕ_3, ϕ_4, and ϕ_5. For example, $(h_i^{-1})_{B,\sigma}$ results from ϕ_4.

5.2 INTERRELATIONSHIP BETWEEN FIRST-ORDER PROPERTIES—USE OF INTERACTION DIAGRAMS

An inspection of the general interaction diagram in Figure 1.1 reveals the important fact that the six interaction effects in Eqs. (5.1)–(5.6) are not independent effects because each can be expressed in terms of the first-order properties defined in Section 4.5. To illustrate, consider the interaction diagram in Figure 5.1 representing $(h_i)_{B,\sigma}$ in Eq. (5.1) for which the arrows point toward the dependent variable.

From Figure 5.1, there results the equation

$$\left[\left(\frac{\partial T}{\partial E_i}\right)=\left(\frac{\partial T}{\partial s}\right)\left(\frac{\partial s}{\partial E_i}\right)\right]_{B,\sigma} \quad \text{or} \quad -\left(h_i\right)_{B,\sigma}=\left[\left(\frac{T}{C^{\sigma}}\right)p_i\right]_{B,\sigma} \tag{5.7}$$

giving an additional expression for the dependant pyroelectric effect vector, all at constant B and σ.

But it is easily verified that three other interaction diagrams shown in Figure 5.2 can also be used to describe h_i , leading to the three additional equations that follow, all at constant B and σ.

$$\left[-h_i=\kappa_0 p_j^{-1}\chi_{ji}=q_j^{-1}\lambda_{ji}=\alpha_{jk}^{-1}d_{jki}\right]_{B,\sigma} \tag{5.8}$$

Similarly, the interaction diagram shown in Figure 5.3 represents the Maxwell relation in Eq. (5.4) for the dependent coupled effect $-\nu_{ij} = (\partial E_i / \partial B_j)_P$. From this diagram, there results the equation

$$\left[-\nu_{ij}=p_i^{-1}q_j\right]_{T,\sigma} \tag{5.9}$$

at constant T and σ and involving the outer or dyadic product $p_i^{-1}q_j$.

However, it is clear that three other equations for ν_{ij} can be derived from the three interaction diagrams given in Figure 5.4. Three additional equations are

$$-\nu_{ij}=\kappa_0^{-1}\chi_{ik}^{-1}\lambda_{kj}=\mu_0^{-1}\lambda_{ik}^{-1}\psi_{kj}=d_{ikl}^{-1}Q_{klj} \tag{5.10}$$

all at constant T and σ.

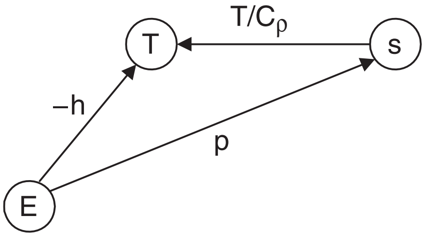


FIGURE 5.1: Interaction diagram for dependent coupled effect h in Eq. (5.1) at constant B and σ.

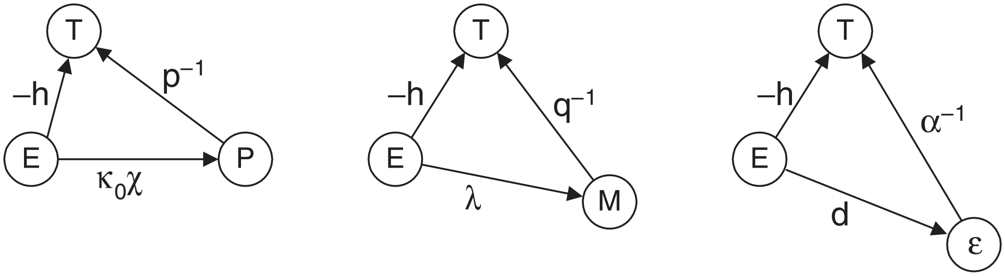


FIGURE 5.2: Additional interaction diagrams representing the dependent coupled effect h in Eq (5.1), all at constant B and σ.

Following the same procedure, the four expressions for each of the remaining four dependent coupled effects are readily obtained. These, together with those illustrated previously, are given by the following six sets of equations all given in conformable matrix order:

$$-h = (T/C_\sigma)\,p = \kappa_0\chi p^{-1} = \tilde{\lambda} q^{-1} = d\alpha^{-1} \qquad (B,\sigma \text{ constant}) \tag{5.11}$$

$$-\eta = (C_\sigma/T)q^{-1} = \lambda^{-1}p = \mu_0\psi^{-1}q = Q^{-1}\alpha \qquad (E,\sigma \text{ constant}) \tag{5.12}$$

$$-t = (C_\sigma/T)\alpha^{-1} = \tilde{d}^{-1}p = \tilde{Q}^{-1}q = s^{-1}\alpha \qquad (E,\ B \text{ constant}) \tag{5.13}$$

$$-\nu = p^{-1}\tilde{q} = \kappa_0^{-1}\chi^{-1}\lambda = \mu_0^{-1}\lambda^{-1}\psi = d^{-1}\tilde{Q} \qquad (T,\sigma \text{ constant}) \tag{5.14}$$

$$-\varepsilon = p^{-1}\tilde{\alpha} = \kappa_0^{-1}\chi^{-1}d = \lambda^{-1}Q = d^{-1}s \qquad (T,\ B \text{ constant}) \tag{5.15}$$

$$-m = q^{-1}\tilde{\alpha} = \lambda^{-1}d = \mu_0\psi^{-1}Q = Q^{-1}s \qquad (T,\ E \text{ constant}) \tag{5.16}$$

The various tensor properties are used in the above six sets of equations to represent the dependent coupled effects defined by Eqs. (5.1)–(5.6) in Section 5.1. The tilde (~) appearing above some of

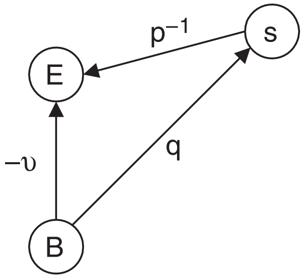


FIGURE 5.3: Interaction diagram for dependent coupled effect υ in Eq. (5.4) at constant T and σ.

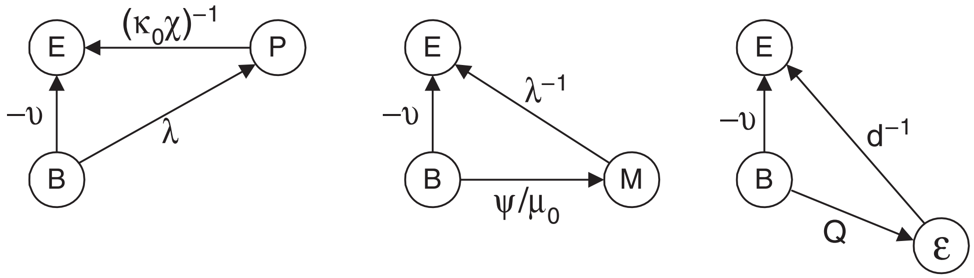


FIGURE 5.4: Additional interaction diagrams representing the dependent coupled effect υ in Eq (5.4), all at constant T and σ.

the property symbols indicates the transpose of the normal matrix form of the tensor. The normal matrix dimensions (rows × columns) for first- and third-rank tensors are (3 × 1) and (3 × 6), respectively. The normal matrix dimensions for a second-rank tensor property are either (3 × 3) or (6 × 1), the latter being the column form of symmetrical second-rank tensor properties such as α, χ and ψ, all of which are polar in character. As defined by Eqs. (4.57) in Section 4.5, the magnetoelectric susceptibility λ is an asymmetrical axial–magnetic second-rank tensor and has normal matrix dimensions of (3 × 3). However, unfolded according to arrays given by Eqs. (4.59) and (4.60), it would be represented as a (9 × 1) column matrix with axial character. Because the properties q, λ, and Q are axial–magnetic (first-, second-, and third-rank tensors, respectively), the dependent coupled effects η, ν, and m are also axial–magnetic in tensor character. The three remaining dependent coupled effects are polar tensors.

The six sets of equations, Eqs. (5.11) to (5.16), have some important uses. First they can be used to obtain the components for any dependent coupled tensor property from known components of the more common first-order properties defined in Section 4.5. As an example, suppose it is desired to know the six components of the isometric thermal stress coefficient t_{ij} given by Eqs. (5.13) and determined at constant E and B fields subjected to a particular crystal. If the heat capacity C^σ and coefficients for thermal expansion α_{ij} are known for the crystal, as they commonly are, or if the piezoelectric moduli d and the pyroelectric coefficients p are known, then Eqs. (5.13) give two alternatives for the determination of t_{ij} at constant E and B.

$$-\begin{bmatrix} t_1 \\ t_2 \\ t_3 \\ t_4 \\ t_5 \\ t_6 \end{bmatrix} = \frac{C_\sigma}{T}\begin{bmatrix} \alpha_1^{-1} \\ \alpha_2^{-1} \\ \alpha_3^{-1} \\ \alpha_4^{-1} \\ \alpha_5^{-1} \\ \alpha_6^{-1} \end{bmatrix} = \begin{bmatrix} d_{11}^{-1} & d_{12}^{-1} & d_{13}^{-1} \\ d_{21}^{-1} & d_{22}^{-1} & d_{23}^{-1} \\ d_{31}^{-1} & d_{32}^{-1} & d_{33}^{-1} \\ d_{41}^{-1} & d_{42}^{-1} & d_{43}^{-1} \\ d_{51}^{-1} & d_{52}^{-1} & d_{53}^{-1} \\ d_{61}^{-1} & d_{62}^{-1} & d_{63}^{-1} \end{bmatrix}\begin{bmatrix} p_1 \\ p_2 \\ p_3 \end{bmatrix} \tag{5.17}$$

Here, it should be understood that quantities such as $\tilde{d}^{-1}$ represent the component inverse (reciprocal) of its transpose, a two-stage operation from the normal (3 × 6) form.

There are many other such examples, including the inverse of the six dependent coupled effects given by Eqs. (5.11)–(5.16). For example, with reference to Eq. (5.3), the components of the effect $(\partial T_i / \partial \sigma_{ij})_s$, which describes the adiabatic application of stress, can be obtained by taking the inverse of Eq. (5.17) to give $(\partial T_i / \partial \sigma_{ij})_s = -(T / C_\sigma)\alpha_{ij}$ all at constant E and B. These same results can also be obtained from the application of Stoke's theorem to the generalized enthalpy, $\phi_5 = h$ given in Table 4.2, followed by the appropriate interaction diagram.

Another important use of the six sets of equations, Eqs. (5.11)–(5.16), is to interrelate the various first-order effects. Suppose, as a typical example, it is desired to find the components of the magnetoelectric susceptibility λ for a particular crystal under conditions of constant T and σ. If the components of the dielectric susceptibility χ, those of the piezoelectric coefficient d, and those of the piezomagnetic coefficient Q are all known for a particular crystal, Eqs. (5.14) yield the result

$$\kappa_0^{-1}\chi^{-1}\lambda = d^{-1}\tilde{Q} \tag{5.18}$$

Then, solving for λ gives

$$\lambda = \kappa_0 \begin{bmatrix} \chi_{11} & \chi_{12} & \chi_{31} \\ \chi_{12} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{23} & \chi_{33} \end{bmatrix} \begin{bmatrix} d_{11}^{-1} & d_{12}^{-1} & d_{13}^{-1} & d_{14}^{-1} & d_{15}^{-1} & d_{16}^{-1} \\ d_{21}^{-1} & d_{22}^{-1} & d_{23}^{-1} & d_{24}^{-1} & d_{25}^{-1} & d_{26}^{-1} \\ d_{31}^{-1} & d_{32}^{-1} & d_{33}^{-1} & d_{34}^{-1} & d_{35}^{-1} & d_{36}^{-1} \end{bmatrix} \begin{bmatrix} Q_{11} & Q_{12} & Q_{13} \\ Q_{21} & Q_{22} & Q_{23} \\ Q_{31} & Q_{32} & Q_{33} \\ Q_{41} & Q_{42} & Q_{43} \\ Q_{51} & Q_{52} & Q_{53} \\ Q_{61} & Q_{62} & Q_{63} \end{bmatrix} \tag{5.19}$$

where λ is given generally as an asymmetrical (3 × 3) matrix. If, however, all components of the four effects are known, then Eq. (5.18) could be used to check the internal consistency of the tensor properties involved. This internal consistency check can be used on other interrelated first-order effects.

5.3 THE GRÜNEISEN TENSOR

There are other interaction effects that may be deduced from the interaction diagram in Figure 1.1, and the Grüneisen tensor is one such example. The Grüneisen parameter can be used to show that the quantity $(C_\varepsilon)^{-1}c\alpha$ remains constant as the temperature T is changed. In its classical form, the Grüneisen parameter is represented by the relation

$$\gamma = -V\left(\frac{\partial P}{\partial U}\right)_V \tag{5.20}$$

Here, P is the pressure, U is the internal energy, and V is the volume, which is held constant. This equation may be written in a more general form, applicable to crystal systems, if $-P$ is replaced by σ_{ij}, dU is replaced by Vdu, and V is replaced by strain to give the Grüneisen tensor as

$$\gamma_{ij} = \left(\frac{\partial \sigma_{ij}}{\partial u}\right)_{\varepsilon}. \tag{5.21}$$

But in the absence of any polarization and magnetization (P and M are zero under constant E and B) and at constant strain, such that no mechanical work is done, we recognize that $\mathrm{d}u = T\mathrm{d}s$ for any process in which reversible heat is absorbed by the system. Therefore, Eq. (5.21) becomes

$$\gamma_{ij} = \frac{1}{T}\left(\frac{\partial \sigma_{ij}}{\partial s}\right)_{\varepsilon} = \gamma_{ji}, \tag{5.22}$$

indicating that the Grüneisen tensor is proportional to the inverse of the isometric piezocaloric coefficient α_{ij}^{-1} (see Eqs. (4.55)), which is symmetrical.

Shown in Figure 5.5 is the interaction diagram that is descriptive of the Grüneisen parameter as presented in Eq. (5.22). Here, as before, the arrows point toward the dependent variable. From the diagram, there results the tensor equation (note that the T's cancel)

$$\gamma_{ij} = \frac{1}{T}\left(\frac{\partial \sigma_{ij}}{\partial s}\right)_{\varepsilon} = \left(1/C_{\varepsilon}\right) c_{ijkl} \alpha_{kl} \tag{5.23}$$

all taken at constant E, B, and ε, and where C_{ε} represents the heat capacity at constant strain, α_{kl} is the thermal expansion tensor, and c_{ij} represents the elastic stiffness moduli. The properties C_{ε}, α_{kl}, and c_{ijkl} can all be obtained in the region of zero strain, P and M, which satisfies the condition of constant strain, and constant E and B.

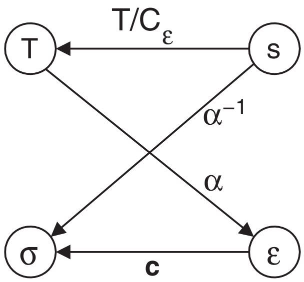


FIGURE 5.5: Interaction diagram descriptive of the Grüneisen parameter.

Equation (5.23) may be represented in matrix form by

$$\gamma_i = (C_\varepsilon)^{-1} c_{ij} \alpha_j \tag{5.24}$$

or in expanded form shown in Eq. (5.25). This holds generally for any of the seven crystal systems with the proper choice of c_{ij} and α_j,.

$$\begin{bmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \\ \gamma_4 \\ \gamma_5 \\ \gamma_6 \end{bmatrix} = (C_\varepsilon)^{-1} \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ & & c_{33} & c_{34} & c_{35} & c_{36} \\ & & & c_{44} & c_{45} & c_{46} \\ & Sym & & & c_{55} & c_{56} \\ & & & & & c_{66} \end{bmatrix} \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \\ \alpha_5 \\ \alpha_6 \end{bmatrix} \tag{5.25}$$

Of particular interest is the Grüneisen tensor specified for the cubic crystal system. See Section 6.2.5 and Table 6.3 for cubic elastic stiffness moduli. In expanded form, we can write

$$\gamma = \begin{bmatrix} \gamma_1 \\ \gamma_2 \\ \gamma_3 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \frac{1}{C_\varepsilon} \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{44} & 0 \\ & & & & & c_{44} \end{bmatrix} \begin{bmatrix} \alpha \\ \alpha \\ \alpha \\ 0 \\ 0 \\ 0 \end{bmatrix} = \frac{\alpha\left(c_{11} + 2c_{12}\right)}{C_\varepsilon} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \tag{5.26}$$

giving the six components of γ. From Eq. (5.26), it follows that the Grüneisen invariant is

$$\gamma = \frac{\gamma_1}{3} = \frac{\alpha\left(c_{11} + 2c_{12}\right)}{3C_\varepsilon} = \frac{\alpha}{3C_\varepsilon\left(s_{11} + 2s_{12}\right)} = \frac{\alpha K}{C_\varepsilon} \tag{5.27}$$

which is the classical result, with $K = (c_{11} + 2c_{12}) / 3$ being the bulk elastic modulus for the cubic crystal system. The quantity K is also the reciprocal of the volume compressibility.

Because of its close relationship with stress (or strain), the Grüneisen parameter may be decomposed into spherical and deviatoric components given by

$$\gamma_{ij} = \gamma\delta_{ij} + \gamma^*_{ij} \tag{5.28}$$

where $\gamma^*_{ij} = \lambda_{ij} - \gamma$ is the Grüneisen deviator.

There are other ways of representing the Grüneisen parameter as can be seen from five of the six dependent coupled effects given by Eqs. (5.11)–(5.13), (5.15), and (5.16). Keep in mind from Figure 5.5 that the Grüneisen tensor is the inverse of the piezocaloric coefficient, α_{ij}^{-1}. However, most of these other expressions involve axial–magnetic and/or first-rank property tensors that greatly restrict their application in obtaining the components of γ_{ij} for many crystals. Eqs. (5.11) and (5.13) would appear to be the most useful as alternative means of representing the Grüneisen tensor.

• • • •

CHAPTER 6

Third- and Fourth-Rank Tensor Properties—Symmetry Considerations

Before we can discuss the second- and higher-order effects presented in the next chapter, it is necessary to lay a proper foundation for that discussion. The best means of accomplishing this is to revisit the third- and fourth-rank tensor properties defined earlier in Section 4.5. We do this by considering, as good examples, the piezoelectric and elastic effects.

6.1 DIRECT AND CONVERSE PIEZOELECTRIC EFFECTS

Beyond mere definitions as in Eqs. (4.61) and (4.62), little was said about the direct or converse piezoelectric coefficient. It is important that these subjects be covered at this time because they illustrate the typical symmetry and transformation characteristics displayed by several other third-rank polar tensor properties.

6.1.1 Direct Piezoelectric Effect

When a stress σ_{ij} is applied to certain crystals, they will develop a total electric dipole moment per unit volume (*polarization*) P_i proportional to that stress as represented in tensor subscript notation by

$$P_i = d_{ijk}\sigma_{jk} \qquad (i, j, k = 1-3) \tag{6.1}$$

The effect represented by Eq. (6.1) is called the *direct piezoelectric effect*, and d_{ijk} are the piezoelectric moduli. Thus, d_{ijk} is a third-rank polar tensor property relating a vector to a second-rank tensor, hence, a vector-tensor property.

If only "pure" stresses (no body torques) are applied, then $\sigma_{jk} = \sigma_{kj}$, which allows $d_{ijk} = d_{ikj} = d_{im}$ and permits us to write the direct piezoelectric effect in the contracted form

$$P_i = d_{im}\sigma_m \qquad (i = 1\text{–}3;\ m = 1\text{–}6), \tag{6.2}$$

thereby reducing the number of independent components of d_{ijk} from 27 to 18 according to Eq. (2.30). Thus, to convert between tensor subscript notation and matrix notation, the stress components become

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{31} \\ & \sigma_{22} & \sigma_{23} \\ \text{Sym.} & & \sigma_{33} \end{bmatrix} \leftrightarrow \begin{bmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ & \sigma_2 & \sigma_4 \\ \text{Sym.} & & \sigma_3 \end{bmatrix}. \tag{6.3}$$

However, because stress is a symmetric second-rank tensor $\sigma_{jk} = \sigma_{jk}$, we follow the tensor-to-matrix conversion rule (recommended in "Standards on Piezoelectric Crystals," see Endnotes)

$$\begin{Bmatrix} d_{ijk} = d_{im} & \text{for} & m = 1-3 \\ 2d_{ijk} = d_{im} & \text{for} & m = 4-6 \end{Bmatrix} \tag{6.4}$$

to avoid the appearance of factors of 2 in Eq. (6.2) in terms for which m = 4, 5, and 6. As a result, we represent Eq. (6.2) as $P = d{:}\sigma$ or in matrix notation as

$$P = d\sigma. \tag{6.5}$$

Recall that the double dot (:) indicates a double contraction product as in Eq. (2.47). In expanded form, the three components of P in Eq. (6.5) can be written in the conformable matrix array form given by

$$\begin{bmatrix} P_1 \\ P_2 \\ P_3 \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix}. \tag{6.6}$$

Here, σ_1, σ_2, and σ_3 are the tensile stresses (positive by convention), and σ_4, σ_5, and σ_6 are shear stresses, with the understanding that $\sigma_{23} = \sigma_{32} = \sigma_4$, $\sigma_{31} = \sigma_{13} = \sigma_5$, and $\sigma_{12} = \sigma_{21} = \sigma_6$. Shown in Table 6.1 are five common stress arrays. Note that for hydrostatic pressure $p = -\sigma$ applied on each of the axis normals.

The transformation law for piezoelectric moduli, d, can now be established. First, let $P = d\sigma$ be true relative to the "old" axes and let $P' = d'\sigma'$ hold relative to a "new" set of axes. Then, because P and σ transform as $P' = aP$ and $\sigma' = \alpha\sigma$ or $\sigma = \alpha^{-1}\sigma'$, respectively, it follows that

TABLE 6.1: Sample stress arrays assuming a symmetric stress tensor $\sigma_{ij} = \sigma_{ji}$

UNIAXIAL STRESS	BIAXIAL STRESS	HYDROSTATIC PRESSURE	PURE SHEAR STRESS
$\begin{bmatrix} \sigma_1 & 0 & 0 \\ & 0 & 0 \\ \text{Sym.} & & 0 \end{bmatrix}$	$\begin{bmatrix} \sigma_1 & 0 & 0 \\ & \sigma_2 & 0 \\ \text{Sym.} & & 0 \end{bmatrix}$	$\begin{bmatrix} -\sigma & 0 & 0 \\ & -\sigma & 0 \\ \text{Sym.} & & -\sigma \end{bmatrix}$	$\begin{bmatrix} -\sigma & 0 & 0 \\ & \sigma & 0 \\ \text{Sym.} & & 0 \end{bmatrix} = \begin{bmatrix} 0 & \sigma & 0 \\ & 0 & 0 \\ \text{Sym.} & & 0 \end{bmatrix}$

$$P' = aP = a\mathrm{d}\sigma = a\mathrm{d}\alpha^{-1}\sigma' = \mathrm{d}'\sigma'$$

from which we conclude that

$$\mathrm{d}' = a\mathrm{d}\alpha^{-1}, \tag{6.7}$$

where α is the quadratic transformation form as presented in Eq. (2.22). Equation (6.7) is the appropriate transformation law for the piezoelectric moduli and is identical to Eq. (2.31), assuming that stress is a symmetrical second-rank field tensor, $\sigma = \tilde{\sigma}$.

6.1.2 Converse Piezoelectric Effect

When an arbitrarily oriented electric field E_i is applied to a piezoelectric crystal, the shape of the crystal changes slightly, that is, a strain is produced that is proportional to the electric field strength. This is the *converse piezoelectric effect* expressed by

$$\varepsilon_{jk} = d_{ijk}E_i \qquad (i, j, k = 1\text{–}3). \tag{6.8}$$

As a result, Eq. (6.8) is succinctly represented by $\varepsilon = d \cdot E$ or simply as

$$\varepsilon = \tilde{d}E \tag{6.9}$$

in conformable matrix form. The single dot (·) indicates a single contraction product as in Eq. (2.46). The converse piezoelectric effect is also called the *first-order electrostrictive effect*, and d_{ijk} are the first-order electrostrictive moduli. From Eqs. (4.61) and (4.62), it is clear that the direct and converse piezoelectric moduli are numerically equal.

Because strain is usually a symmetrical second-rank tensor, $\varepsilon_{jk} = \varepsilon_{jk}$, the tensor symmetry for d_{ijk} becomes $d_{ijk} = d_{ikj} = d_{im}$, which permits Eq. (6.8) to be written as

$$\varepsilon_m = d_{im} E_i \qquad (i = 1 - 3;\ m = 1 - 6). \tag{6.10}$$

The transpose of d, expressed as $\tilde{d}$ in Eq. (6.9), indicates that its rows and columns of the normal form in Eq. (2.30) must be interchanged to a 6×3 matrix if the product of Eq. (6.9) is to be conformable. Thus, Eq. (6.9) is written in extended matrix form as

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} = \begin{bmatrix} d_{11} & d_{21} & d_{31} \\ d_{12} & d_{22} & d_{32} \\ d_{13} & d_{23} & d_{33} \\ d_{14} & d_{24} & d_{34} \\ d_{15} & d_{25} & d_{35} \\ d_{16} & d_{26} & d_{36} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} = \tilde{d} E. \tag{6.11}$$

Equation (6.11) is valid because the symmetric part of the strain tensor ε_{jk}, defined by Eq. (2.17), is

$$\varepsilon_{jk} = \tfrac{1}{2}\left(\varepsilon_{jk} + \varepsilon_{kj} \right), \tag{6.12}$$

which, in turn, permits the strain matrix to be given by

$$\begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{31} \\ & \varepsilon_{22} & \varepsilon_{23} \\ \text{Sym.} & & \varepsilon_{33} \end{bmatrix} = \begin{bmatrix} \varepsilon_{11} & \tfrac{1}{2}(\varepsilon_{12} + \varepsilon_{21}) & \tfrac{1}{2}(\varepsilon_{31} + \varepsilon_{13}) \\ & \varepsilon_{22} & \tfrac{1}{2}(\varepsilon_{23} + \varepsilon_{32}) \\ \text{Sym.} & & \varepsilon_{33} \end{bmatrix}. \tag{6.13}$$

The tensor-to-matrix conversion scheme for strain now becomes

$$\begin{bmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{31} \\ & \varepsilon_{22} & \varepsilon_{23} \\ \text{Sym.} & & \varepsilon_{33} \end{bmatrix} \to \begin{bmatrix} \varepsilon_1 & \tfrac{1}{2}\varepsilon_6 & \tfrac{1}{2}\varepsilon_5 \\ & \varepsilon_2 & \tfrac{1}{2}\varepsilon_4 \\ \text{Sym.} & & \varepsilon_3 \end{bmatrix}, \tag{6.14}$$

where ε_1, ε_2, and ε_3 are the elastic tensile strains or stretches, and the three remaining, ε_4, ε_5, and ε_6, are the elastic shear strains. As a result of the conversion scheme of Eq. (6.14), the shear strain components of Eq. (6.10) will have factors of ½ on both sides of the equations that cancel. This permits Eq. (6.11) to be written in simple two-subscript form exclusive of the factors of 2 in the shear components that would otherwise be present. As it turns out, matrix shear strain is identical to engineering shear strain (i.e., $\varepsilon_4 = \gamma_{yz}$, $\varepsilon_5 = \gamma_{zx}$, and $\varepsilon_6 = \gamma_{xy}$). The antisymmetrical part of ε_{jk} is the axial second-rank tensor given by $\varpi_{jk} = \frac{1}{2}(\varepsilon_{jk} - \varepsilon_{kj})$ which is the rotation resulting from elastic shear.

The transformation law for converse piezoelectric moduli, *d*, is now established in a manner similar to that for the direct effect given earlier. First, let $\varepsilon = \tilde{d}E$ be true relative to the "old" axes and let $\varepsilon' = \tilde{d}'E'$ hold relative to a "new" set of axes. Now, because ε and E transform as $\varepsilon' = \tilde{\alpha}^{-1}\varepsilon$ and $E' = aE$ or $E = \tilde{a}E'$ $(a^{-1} = \tilde{a})$, respectively, it follows that $\varepsilon' = \tilde{\alpha}^{-1}\varepsilon = \tilde{\alpha}^{-1}\tilde{d}E = \tilde{\alpha}^{-1}\tilde{d}\tilde{a}E' = \tilde{d}'E'$, from which we conclude that

$$\tilde{d}' = \tilde{\alpha}^{-1}\tilde{d}\,\tilde{a}\,. \tag{6.15}$$

The transformation for matrix shear strain, $\varepsilon' = \tilde{\alpha}^{-1}\varepsilon$, results from the tensor-to-matrix conversion rule given by Eq. (6.14). Note that $\tilde{\alpha}^{-1}$ requires two separate operations because $\tilde{\alpha} \neq \alpha^{-1}$ in general.

6.1.3 Crystal Symmetry Considerations

The method of direct inspection can be used to determine the effect of crystal symmetry on the components of the third-rank tensor properties. To do this, the full tensor subscript notation must be used and then only on crystal systems other than the trigonal and hexagonal crystal systems as explained in Section 3.6. Application of Neumann's principle to the direct (or converse) piezoelectric moduli, d_{ijk}, results in

$$\left\{\begin{matrix} d_{ijk} = d_{ijk} \\ d_{ijk} = -d_{ijk} = 0 \end{matrix}\right\}. \tag{6.16}$$

For example, all holohedral crystal systems, those represented as $\|X\|$ in Table 3.6, are centrosymmetrical, and as a result, $d_{ijk} = -d_{ijk} = 0$. Thus, the 11 centrosymmetrical crystal groups will be lacking in all piezoelectric moduli.

To illustrate, we apply Neumann's principle to the *222* crystal group. By using Table 3.6, we observe that the *222* group requires the use of generating matrices $s^{(2)}$ and $s^{(3)}$. From Table 3.5, the transform of axes are given in compact form according to

$$s^{(2)} \rightarrow \left\{\begin{matrix} 1 & \rightarrow & -1 \\ 2 & \rightarrow & 2 \\ 3 & \rightarrow & -3 \end{matrix}\right\} \text{ and } s^{(3)} \rightarrow \left\{\begin{matrix} 1 & \rightarrow & -1 \\ 2 & \rightarrow & -2 \\ 3 & \rightarrow & 3 \end{matrix}\right\} \tag{6.17}$$

and are applied in any sequence. Applying $s^{(2)}$ first, it is clear that $d_{ijk} = 0$ for all moduli containing an odd number of 1's and/or 3's. Application of $s^{(3)}$ requires that $d_{ijk} = 0$ for all moduli for which there is an odd number of 1's and/or 2's. Therefore, the only moduli to survive are those containing all three, 1, 2, and 3 in any order. As a result, the array of piezoelectric moduli becomes

$$\begin{bmatrix} d_{111} & d_{122} & d_{133} & d_{123} & d_{131} & d_{112} \\ d_{211} & d_{222} & d_{233} & d_{223} & d_{231} & d_{212} \\ d_{311} & d_{322} & d_{333} & d_{323} & d_{331} & d_{312} \end{bmatrix}$$
$$\Downarrow$$
$$\begin{bmatrix} 0 & 0 & 0 & d_{123} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{231} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{312} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix} \qquad (6.18)$$

in both three- and two-suffix notation. Application of Neumann's principle to the trigonal or hexagonal crystal systems requires the "brute-force" method involving Eq. (6.7) for all threefold and sixfold rotations.

6.1.4 Brute-Force Method for the Trigonal and Hexagonal Classes—The Piezoelectric Moduli

1. If generating matrices other than $s^{(7)}$ are involved in the particular crystal class, apply them first each in turn by using the method of direct inspection to obtain a simplified array of the moduli.
2. By using the appropriate transformation law, for example, Eq. (6.7), complete the matrix calculations with the generating matrices $s^{(7)}$ and $\sigma^{(7)}$ to obtain a set of equations for the new property moduli.
3. As a final sep, equate each old modulus with the new and solve the resulting equations simultaneously for the moduli appropriate for the given crystal class.

As an example, let us apply Neumann's principle to the hexagonal class *6*. From Table 3.6, we see that this requires the application of generating matrices $s^{(3)} \cdot s^{(7)} = s^{(14)}$. To simplify the calculations, it is advantageous to apply $s^{(3)}$ first, then follow with $s^{(7)}$ as required by the brute-force method. From generating matrices given by Eq. (6.17), application of $s^{(3)}$ allows the d_{ijk} to survive only for moduli with an odd number of 3's, a total number of eight independent moduli. When this is done, application of $s^{(7)}$ to the piezoelectric transformation law given by Eq. (6.7) takes the form

$$d' = \overset{s^{(7)}}{\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}} \overset{[d_{ijk}]^{s^{(3)}}}{\begin{bmatrix} 0 & 0 & 0 & d_{123} & d_{131} & 0 \\ 0 & 0 & 0 & d_{223} & d_{231} & 0 \\ d_{311} & d_{322} & d_{333} & 0 & 0 & d_{312} \end{bmatrix}} \overset{(\sigma^{(7)})^{-1}}{\begin{bmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & -\frac{\sqrt{3}}{2} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} & 0 & 0 & 0 & -\frac{1}{2} \end{bmatrix}}. \qquad (6.19)$$

When the matrix multiplication operations of Eq. (6.19) are carried out, there result the following equations relating the old moduli to the new moduli:

$$d_{123} = \frac{d_{123}}{4} - \frac{\sqrt{3}}{4} d_{223} - \frac{1}{2}\left(\frac{-d_{131}}{2} + \frac{\sqrt{3}}{2} d_{231}\right)\sqrt{3} \qquad d_{311} = \frac{d_{311}}{4} + \frac{3}{4} d_{322} - \frac{\sqrt{3}}{4} d_{312}$$

$$d_{131} = \frac{1}{2}\left(\frac{-d_{123}}{2} + \frac{\sqrt{3}}{2} d_{223}\right)\sqrt{3} + \frac{d_{131}}{4} - \frac{\sqrt{3}}{4} d_{231} \qquad d_{322} = \frac{3}{4} d_{311} + \frac{d_{322}}{4} + \frac{\sqrt{3}}{4} d_{312}$$

$$d_{223} = \frac{\sqrt{3}}{4} d_{123} + \frac{d_{223}}{4} - \frac{1}{2}\left(\frac{-\sqrt{3}}{2} d_{131} - \frac{d_{231}}{2}\right)\sqrt{3} \qquad d_{333} = d_{333}$$

$$d_{231} = \frac{1}{2}\left(\frac{-\sqrt{3}}{2} d_{123} - \frac{d_{223}}{2}\right)\sqrt{3} + \frac{\sqrt{3}}{4} d_{131} \frac{d_{231}}{4} \qquad d_{312} = \frac{\sqrt{3}}{2} d_{311} - \frac{\sqrt{3}}{2} d_{322} - \frac{d_{312}}{2}$$

Solving these eight equations simultaneously gives the following class *6* piezoelectric moduli in both three- and two-suffix notation where the eight independent moduli in Eq. (6.19) have been reduced to four in Eq. (6.20).

$$\begin{bmatrix} 0 & 0 & 0 & d_{123} & d_{131} & 0 \\ 0 & 0 & 0 & d_{131} & -d_{123} & 0 \\ d_{311} & d_{311} & d_{333} & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \qquad (6.20)$$

From Table 3.6, we note that the generating matrices for class *622* are $s^{(12)}$ and $s^{(14)}$. Because the moduli arrays of Eq. (6.20) result from the application of $s^{(14)}$, there remains only the application of $s^{(12)} = s^{(1)} \cdot s^{(4)}$ to the three-suffix form of Eq. (6.20) to obtain the moduli for class *622*. From Table 3.5 for $s^{(12)}$ and using the method of direct inspection, it is clear that the only moduli to survive are those for which an odd number of 1's exists. Thus, $d_{131} = d_{311} = d_{333} = 0$, resulting in the array for class *622* given by

$$\begin{bmatrix} 0 & 0 & 0 & d_{123} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{123} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}. \tag{6.21}$$

Continuing on to class *6mm*, we see from Table 3.6 that the generation matrices required for this crystal class are $s^{(3)}$, $s^{(4)}$, and $s^{(7)}$. So there remains only the application of $s^{(4)}$ in Table 3.5 to the three-suffix result of matrix arrays (6.20). When this is done, the only moduli to survive are those for which an even number of 1's or no 1's exist. Thus, $d_{123} = 0$ in arrays (6.19) resulting in the moduli arrays for class *6mm* given by

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{131} & 0 \\ 0 & 0 & 0 & d_{131} & 0 & 0 \\ d_{311} & d_{311} & d_{333} & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \tag{6.22}$$

By applying similar analyses to the 32 crystal classes, there result the matrices for the direct and converse piezoelectric moduli given in Table 6.2 where $d_{ijk} = 0$ for all centrosymmetrical classes.

TABLE 6.2: Piezoelectric moduli for both the direct and converse effects

Triclinic

Class 1

$$\begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix}$$

Class $\|\bar{1}\|$ centrosymmetrical, $d_{ijk} = 0$

Monoclinic

Class 2 $(2 \parallel x_2)$

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{bmatrix}$$

Class *m* $(m \perp x_2)$

$$\begin{bmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{bmatrix}$$

Class $\|2/m\|$ centrosymmetrical, $d_{ijk} = 0$

TABLE 6.2: (continued)

Orthorhombic

Class 2*mm*

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Class 222

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix}$$

Class $\| mmm \|$ centrosymmetrical, $d_{ijk} = 0$

Tetragonal

Class 4

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Class $\bar{4}$

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & -d_{15} & d_{14} & 0 \\ d_{31} & -d_{31} & 0 & 0 & 0 & d_{36} \end{bmatrix}$$

Class $\|4/m\|$ centrosymmetrical, $d_{ijk} = 0$

Class 4*mm*

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Class $\bar{4}2m$

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix}$$

Class *422*

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Class $\|4/mmm\|$ centrosymmetrical, $d_{ijk} = 0$

TABLE 6.2: (continued)

Trigonal

Class 3

$$\begin{bmatrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Class $3m$ $(m \perp x_1)$

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Class $\|\bar{3}\|$ centrosymmetrical, $d_{ijk} = 0$

Class 32 (quartz)

$$\begin{bmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Class $\|\bar{3}m\|$ centrosymmetrical, $d_{ijk} = 0$

Hexagonal

Class 6

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Class $\bar{6}$

$$\begin{bmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Class $\|\bar{6}\|$ centrosymmetrical, $d_{ijk} = 0$

Class $6mm$ (same as $4mm$)

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Class 622 (same as 422)

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Class $\bar{6}2m$

$$\begin{bmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Class $\|\bar{6}\,mmm\|$ centrosymmetrical, $d_{ijk} = 0$

TABLE 6.2: (continued)

Cubic	
Class 23 and $\bar{4}3m$	Class 432
$\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$
Class $\|m3\|$ centrosymmetrical, $d_{ijk} = 0$	
Class $\|m3\,m\|$ centrosymmetrical, $d_{ijk} = 0$	

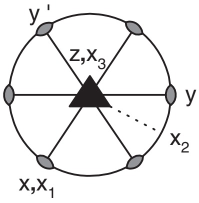
To demonstrate the use of the piezoelectric moduli in Table 6.2, we will work a couple of problems involving quartz, which belongs to the crystal class *32*. Consider the direct piezoelectric effect represented by Eq. (6.2) as applied to class *32* and the application of normal and shear stresses. Shown in Figure 6.1(a) is the array of piezoelectric moduli for class *32* together with the corresponding polarization and stress components. In Figure 6.1(b) is the stereogram for class *32* giving the x_1 and x_2 axes in the (0001) plane with its normal along the threefold (optic) axis, x_3. Clearly, there are only two independent piezoelastic moduli, d_{11} and d_{14}.

Referring to Figure 6.1 for quartz, a polarization P_1 can be produced along the x_1 direction under the following conditions:

1. By a tensile stress σ_1 applied along the x_1, resulting in $P_1 = d_{11}\sigma_1$, where $P_2 = P_3 = 0$.
2. By a compressive stress σ_2 applied along x_1, resulting in $P_1 = -d_{11}\sigma_2$ where $P_2 = P_3 = 0$.
3. By a shear stress $\sigma_4 = \sigma_{23}$, resulting in $P_1 = d_{14}\sigma_4$, where $P_2 = P_3 = 0$.

$$\begin{array}{r|cccccc|l} & \overbrace{\sigma_1 \quad \sigma_2 \quad \sigma_3}^{Normal} & & & \overbrace{\sigma_4 \quad \sigma_5 \quad \sigma_6}^{Shear} & & & \\ P_1 & d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 & Along\ x_1 \\ d = P_2 & 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} & Along\ x_2 \\ P_3 & 0 & 0 & 0 & 0 & 0 & 0 & Along\ x_3 \end{array}$$

(a)



(b)

FIGURE 6.1: (a) Piezoelectric moduli for quartz (class *32*) and the corresponding polarization and stress components. (b) Stereogram for class *32*.

A polarization P_2 along x_2 can be produced only by negative shear stresses σ_{31} and σ_{12} giving $P_2 = -d_{14}\sigma_{31}$ and $P_2 = -2d_{11}\sigma_{12}$, where for both $P_1 = P_3 = 0$. From Figure 6.1(a), it is evident that a polarization P_3 along x_3 is not possible under any set of conditions.

6.1.5 Longitudinal Piezoelectric Effect

The polarization can be found in an arbitrary direction P'_1 according to

$$P'_1 = d'_{111}\sigma'_{11} = d'_{11}\sigma'_1. \tag{6.23}$$

Here, d'_{11}, measures the longitudinal piezoelectric effect in the x_1x_2 plane, meaning the charge per unit area on the surface of a plate divided by the force per unit area applied normal to that surface, which is in the $0x_3$ direction. To find d'_{11}, we will need to find α^{-1} by making use of the equations $\sigma = \tilde{a}\ \sigma' a = \alpha^{-1}\sigma'$, which are the inverse of Eqs. (2.21) and (2.22). Recall that the stress tensor is a symmetric second-rank tensor. Once α^{-1} is known, then d'_{11}, can be found from the transformation equation $d' = ad\alpha^{-1}$, where a given moduli array is chosen from Table 6.2. As an example, we will find d'_{11} for a quartz crystal. Shown in Figure 6.2 is the longitudinal direction $0x'_1$ and direction cosines relative to a set of coordinate axes such that lie in the (0001) plane of a quartz crystal. Thus, as required, the surface of the crystal must conform to the point group symmetry.

Because a polarization cannot be produced alone $0x_3$, a direction $0x'_1$ out of the x_1x_2 plane will produce a polarization only due to the projection of $0x'_1$ onto the x_1x_2 plane. Thus, we are entitled, but not required, to set $a_{13} = l_3 = 0$, not shown in Figure 6.2. To facilitate the calculations, we will make the following transformation simplifications: $a_{11} = l_1$, $a_{12} = l_2$, $a_{13} = l_3$, with m_i and n_i used for the remaining direction cosines following Eq. (3.24). First, we will find α^{-1} as follows:

$$\sigma = \tilde{a}\sigma' a = \begin{bmatrix} l_1 & m_1 & n_1 \\ l_2 & m_2 & n_2 \\ l_3 & m_3 & n_3 \end{bmatrix} \begin{bmatrix} \sigma'_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{bmatrix} = \begin{bmatrix} l_1^2 & l_1 l_2 & l_3 l_1 \\ l_1 l_2 & l_2^2 & l_2 l_3 \\ l_3 l_1 & l_2 l_3 & l_3^2 \end{bmatrix} \sigma'_1. \tag{6.24}$$

Then, reconfiguring yields the result

$$\sigma = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} l_1^2 & 0 & 0 & 0 & 0 & 0 \\ l_2^2 & 0 & 0 & 0 & 0 & 0 \\ l_3^2 & 0 & 0 & 0 & 0 & 0 \\ l_2 l_3 & 0 & 0 & 0 & 0 & 0 \\ l_3 l_1 & 0 & 0 & 0 & 0 & 0 \\ l_1 l_2 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \sigma'_1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \alpha^{-1}\sigma'. \tag{6.25}$$

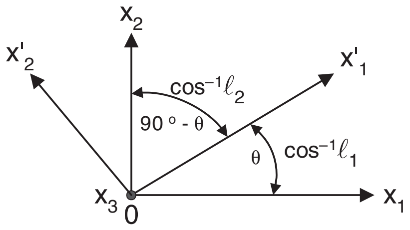


FIGURE 6.2: Longitudinal direction x_1 relative to a set of coordinate axes, where x_1 and x_2 lie in the (0001) plane of crystal class 32.

Now with α^{-1} known, we will set up the matrix equation for $d' = ad\alpha^{-1}$ where d is the class 32 array obtained from Table 6.2. Thus, there results

$$d' = \begin{bmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{bmatrix} \begin{bmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \alpha^{-1} = a\,d\,\alpha^{-1}$$

$$= \begin{bmatrix} l_1 d_{11} & -l_1 d_{11} & 0 & l_1 d_{14} & -l_2 d_{14} & -2l_2 d_{11} \\ m_1 d_{11} & -m_1 d_{11} & 0 & m_1 d_{14} & -m_2 d_{14} & -2m_2 d_{11} \\ n_1 d_{11} & -n_1 d_{11} & 0 & n_1 d_{14} & -n_2 d_{14} & -2n_2 d_{11} \end{bmatrix} \begin{bmatrix} l_1^2 & 0 & 0 & 0 & 0 & 0 \\ l_2^2 & 0 & 0 & 0 & 0 & 0 \\ l_3^2 & 0 & 0 & 0 & 0 & 0 \\ l_2 l_3 & 0 & 0 & 0 & 0 & 0 \\ l_3 l_1 & 0 & 0 & 0 & 0 & 0 \\ l_1 l_2 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} . \tag{6.26}$$

Therefore,

$$\begin{aligned} d'_{11} &= l_1^3 d_{11} - l_1 l_2^2 d_{11} + l_1 l_2 l_3 d_{14} - l_1 l_2 l_3 d_{14} - 2 l_1 l_2^2 d_{11} \\ &= l_1^3 d_{11} - 3 l_1 l_2^2 d_{11} = l_1 (l_1^2 - 3 l_2^2) d_{11}, \end{aligned} \tag{6.27}$$

which is seen to depend only on d_{11}. Furthermore, from Figure 6.2, it follows that $l_1 = \cos\theta$ and $l_2 = \cos(90° - \theta) = \sin\theta$. Therefore, with the help of trigonometric identities, we find

$$\begin{aligned} d'_{11} &= d_{11} \cos\theta(\cos^2\theta - 3\sin^2\theta) \\ &= d_{11} \cos\theta(\cos^2\theta + 3\cos^2\theta - 3) \\ &= d_{11}(4\cos^3\theta - 3\cos\theta) = d_{11}\cos 3\theta . \end{aligned} \tag{6.28}$$

The result $d'_{11} = d_{11} \cos 3\theta$ forms a three-petal (each almond shaped) rosette in the (0001) plane, indicating that the polarization is a maximum along the directions x, y, and y' spaced 120° apart (see Figure 6.1(b)) and that it is zero at 60° intervals between the x, y, and y' directions.

6.1.6 Transverse Piezoelectric Effect

A similar procedure to that used for the longitudinal piezoelectric effect can be used for the transverse piezoelectric effect. However, the calculations are necessarily made more complex because the direction cosines l_i, m_j, and n_k $(i, j, k = 1, 2, 3)$ will, in general, be involved. To demonstrate, let us set up the equations $\sigma = \tilde{a}\sigma' a = \alpha^{-1}\sigma'$ for the case of a shear stress $\sigma'_6 = \sigma'_{12}$ applied to a quartz crystal relative to axes x'_1 and x'_2. The results become

$$\sigma = \tilde{a}\sigma' a = \begin{bmatrix} l_1 & m_1 & n_1 \\ l_2 & m_2 & n_2 \\ l_3 & m_3 & n_3 \end{bmatrix} \begin{bmatrix} 0 & \sigma'_6 & 0 \\ \sigma'_6 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_1 & l_2 & l_3 \\ m_3 & m_3 & m_3 \\ n_3 & n_3 & n_3 \end{bmatrix} = \begin{bmatrix} 2\,l_1 m_1 & l_1 m_2 + l_2 m_1 & l_3 m_1 + l_1 m_3 \\ & 2\,l_2 m_2 & l_2 m_3 + l_3 m_2 \\ \text{Sym.} & & 2\,l_3 m_3 \end{bmatrix} \sigma'$$

$$\sigma = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 2l_1 m_1 \\ 0 & 0 & 0 & 0 & 0 & 2l_2 m_2 \\ 0 & 0 & 0 & 0 & 0 & 2l_3 m_3 \\ 0 & 0 & 0 & 0 & 0 & l_2 m_3 + l_3 m_2 \\ 0 & 0 & 0 & 0 & 0 & l_3 m_1 + l_1 m_3 \\ 0 & 0 & 0 & 0 & 0 & l_1 m_2 + l_2 m_1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ \sigma'_6 \end{bmatrix} = \alpha^{-1}\sigma' \tag{6.29}$$

Knowing α^{-1} permits us to evaluate $d' = ad\,\alpha^{-1}$, which will be more complex to evaluate than in the case of the longitudinal effect given by Eqs. (6.26), (6.27), and (6.28).

6.2 ELASTICITY

The concept of elasticity can best be understood by considering a one-dimensional lattice shown in Figure 6.3. Here, the equilibrium condition is demonstrated in Figure 6.3(a), where the lattice parameter is given by a_0. Then, if a tensile force is applied along the 0x direction the atoms are displaced by an amount $l = a - a_0$ to an atom separation of a as in Figure 6.3(b). At a state of equi-

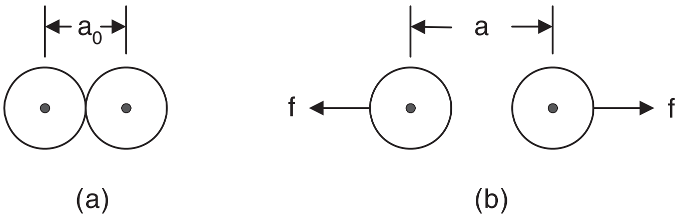


FIGURE 6.3: A one-dimensional lattice. (a) Atoms at equilibrium with lattice parameter a_0. (b) Atoms reversibly displaced after the application of a tensile force f along the 0x direction.

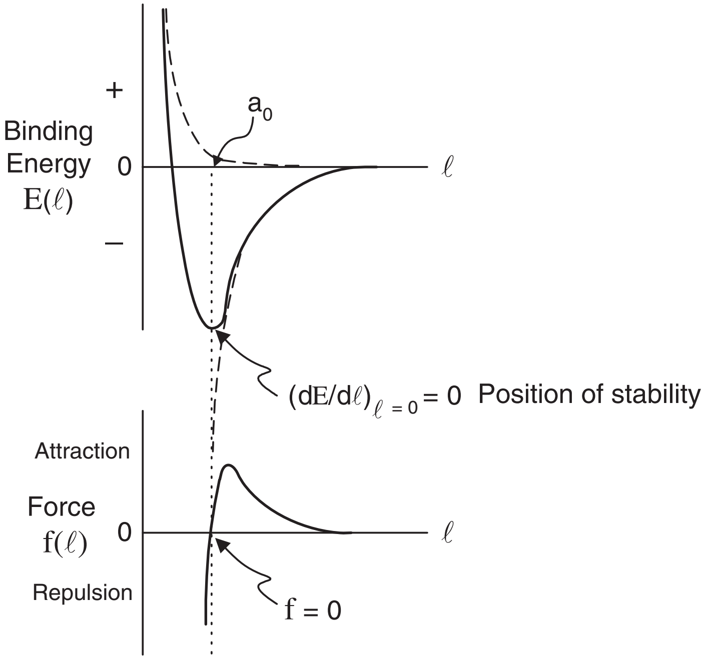


FIGURE 6.4: Binding energy and tensile force showing position of stability in a one-dimensional lattice.

librium, the force f_0 would represent a short-ranged attractive force between atoms along 0*x* where the lattice parameter between atoms is maintained at a_0.

The binding energy of the atoms in the one-dimensional lattice is a function of the atom displacement *l* and is shown in Figure 6.4. Here, at static equilibrium, the minimum in the energy curve occurs at

$$(\mathrm{d}E / \mathrm{d}l)_{l=0} = 0, \tag{6.30}$$

for which the applied tensile force $f = 0$ and where $a = a_0$. So, as $f \to 0$, a position of stability between the atoms is approached. Of course, the force *f* can be either a tensile force r a compressive force. The convention followed in this text is as follows:

If $f > 0$ tensile $a > a_0$ and $l > 0$

If $f < 0$ compressive $a < a_0$ and $l < 0.$

In any case, the cohesive force between atoms is a reversible function of displacement.

6.2.1 Hooke's Law

Assuming that the elastic strain energy E is everywhere a continuous function of displacement l, we can expand E in a Maclaurin series about the state of displacement $l = 0$, there results

$$E(l) = E_0 + \left(\frac{dE}{dl}\right)_{(0)} l + \frac{1}{2}\left(\frac{d^2E}{dl^2}\right)_{(0)} l^2 + \cdots. \tag{6.31}$$

For very small l, small linear strains exist, and applying Eq. (6.30), we have

$$E(l) \cong E_0 + \frac{1}{2}\left(\frac{d^2E}{dl^2}\right)_{(0)} l^2 + \cdots. \tag{6.32}$$

Taking the derivative of Eq. (6.32) with respect to displacement l leads to Hooke's law given as

$$f = \frac{d\,E(l)}{dl} = \left(\frac{d^2\,E}{dl^2}\right)_{(0)} l = Y \cdot l\,, \tag{6.33}$$

where

$$Y = \left(\frac{d^2\,E}{dl^2}\right)_{(0)} = \text{Young's Modulus.} \tag{6.34}$$

Here, Young's modulus ($d^2 E / dl^2$) is the curvature of the $E(l)$ versus l curve in Figure 6.4. Thus, the sharper the minimum in the $E(l)$ versus l curve, the greater will be the Young's modulus, Y, and vice versa.

6.2.2 Bulk Elastic Behavior

Up to this point, we have dealt with a one-dimensional lattice to express the simplest form of Hooke's law. Now we must move to bulk elastic representations that have practical application. To expand the one-dimensions model to bulk elastic behavior require summing all individual elastic deformations between atoms (neighbors, next nearest neighbors, etc.) taken over all directions in the crystal. Clearly, $\Sigma_i(f_i = Yl_i)$ applied in this manner would be an impossible task. This apparent dilemma can be overcome by making the following transformations:

$$\begin{aligned} f &\Rightarrow \sigma = \text{stress} \\ l &\Rightarrow \varepsilon = \text{strain.} \end{aligned} \tag{6.35}$$

Now, the two alternative forms of Hooke's law may be expressed in terms of the new parameters, σ and ε, as

$$\begin{matrix}\sigma = c\,\varepsilon \\ \varepsilon = s\,\sigma\end{matrix}, \tag{6.36}$$

where

$$\begin{aligned} c &= Elastic\ stiffness\ coefficient\ (\mathrm{N/m^2}) \\ s &= Elastic\ compliance\ coefficient = c^{-1}. \end{aligned} \tag{6.36a}$$

Following the developments given in Section 6.1 with regard to stress and strain, we can express Hooke's law $\sigma = c\varepsilon$ in tensor and matrix form, respectively, as

$$\sigma_{ij} = c_{ijkl}\,\varepsilon_{kl} \qquad (i, j, k, l = 1-3) \tag{6.37}$$

and

$$\sigma_m = c_{mn}\,\varepsilon_n \qquad (m, n = 1-6). \tag{6.38}$$

Here, the first and last suffix pairs of c_{ijkl} permit the c_{mn} coefficients to be unfolded according to the following scheme.

$$\begin{array}{rcccccc} \text{Tensor Notation} & 11 & 22 & 33 & 23,32 & 31,13 & 12,21 \\ \text{Matrix Notation} & 1 & 2 & 3 & 4 & 5 & 6 \end{array} \tag{6.39}$$

Then, by thermodynamic arguments presented in Section 4.4, we can write

$$c_{mn} = c_{nm}. \tag{6.40}$$

In expanded matrix form, Eq. (6.38) becomes

$$\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ & & c_{33} & c_{34} & c_{35} & c_{36} \\ & & & c_{44} & c_{45} & c_{46} \\ & \text{Sym.} & & & c_{55} & c_{56} \\ & & & & & c_{66} \end{bmatrix} \cdot \begin{bmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{bmatrix} \tag{6.41}$$

where, as before in Section 6.1, σ_1, σ_2, and σ_3 are the tensile stresses (positive by convention) and σ_4, σ_5, and σ_6 are shear stresses, with the understanding that $\sigma_{23} = \sigma_{32} = \sigma_4$, $\sigma_{31} = \sigma_{13} = \sigma_5$, and $\sigma_{12} = \sigma_{21} = \sigma_6$. With the convention used in Eq. (6.14), the strains ε_1, ε_2 and ε_3 are the elastic tensile strains or stretches, and the three remaining, ε_4, ε_5 and ε_6, are the elastic shear strains.

The alternative form of Hooke's law $\varepsilon = s\sigma$ is presented in the tensor form as

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}, \tag{6.42}$$

which represents nine equations each with nine terms—a total of 81 s_{ijkl} coefficients. Equation (6.42) can be represented in the simplified matrix form

$$\varepsilon_m = s_{mn}\sigma_n \qquad (m, n = 1 - 6), \tag{6.43}$$

provided that 2's and 4's are introduced into the definitions of s_{imn} according to the following:

$$\begin{aligned} s_{ijkl} &= s_{mn} \text{ when } m \text{ and } n \text{ are 1, 2, or 3} \\ 2s_{ijkl} &= s_{mn} \text{ when either } m \text{ and } n \text{ are 4, 5, or 6} \\ 4s_{ijkl} &= s_{mn} \text{ when either } m \text{ and } n \text{ are 4, 5, or 6.} \end{aligned}$$

These definitions avoid the appearance of the 2's and 4's in Eq. (6.42), thereby making the simplified matrix form possible. Note that in the case of Eq. (6.38), no introductions of 2's and 4's were necessary to allow Eq. (6.41).

By the thermodynamic arguments presented in Section 4.4, we can write

$$s_{mn} = s_{nm}, \tag{6.44}$$

giving the expanded matrix form of Eq. (6.43) as

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} = \begin{bmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} & s_{16} \\ & s_{22} & s_{23} & s_{24} & s_{25} & s_{26} \\ & & s_{33} & s_{34} & s_{35} & s_{36} \\ & & & s_{44} & s_{45} & s_{46} \\ & \text{Sym.} & & & s_{55} & s_{56} \\ & & & & & s_{66} \end{bmatrix} \cdot \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \tag{6.45}$$

6.2.3 Transformation Laws

The transformation laws for the elastic stiffness coefficients and elastic compliances are easily determined by using matrix notation together with the quadratic transformation matrix, α. The reader may find it helpful to review Section 6.1 because it pertains to the transformation laws for the direct and converse piezoelectric effects.

Beginning with the stiffness coefficients, the procedure is as follows: Let $\sigma = c\varepsilon$ be true relative to the "old" axes and let $\sigma' = c'\varepsilon'$ hold relative to the "new" axes. Stress transforms to the "new" axes as

$\sigma' = \alpha\sigma$. Then referring to the developments leading to Eq. (6.15), the strain transforms to the new axes as $\varepsilon' = \tilde{\alpha}^{-1}\varepsilon$ or $\varepsilon = \tilde{\alpha}\ \varepsilon'$. Therefore, it follows that $\sigma' = \alpha\sigma = \alpha c\varepsilon = \alpha c\tilde{\alpha}\ \varepsilon' = c'\varepsilon'$, or finally,

$$c' = \alpha c \tilde{\alpha}\,. \tag{6.46}$$

A procedure similar to that for the stiffness coefficients is followed for the elastic compliance coefficients. Let $\varepsilon = s\sigma$ and $\varepsilon' = s'\sigma'$ be valid for the old and new axes, respectively. From the preceding, $\sigma = \alpha^{-1}\sigma'$, such that we can write $\varepsilon' = \tilde{\alpha}^{-1}\varepsilon = \tilde{\alpha}^{-1}s\sigma = \tilde{\alpha}^{-1}s\alpha^{-1}\sigma' = s'\sigma'$ from which results

$$s' = \tilde{\alpha}^{-1}s\alpha^{-1}, \tag{6.47}$$

where it is understood that $\alpha^{-1} \neq \tilde{\alpha}$. Here, $\tilde{\alpha}^{-1}$ is the transpose of the inverse of α, two operations.

6.2.4 Elastic Strain Energy Density

Referring to the thermodynamic potentials in Table 4.2, the elastic strain energy density can be given by

$$df = dw = \sigma_i d\varepsilon_i = c_{ij}\varepsilon_j d\varepsilon_i \qquad (i, j = 1-6) \tag{6.48}$$

or

$$-dg = \varepsilon_i d\sigma_i = s_{ij}\sigma_j d\sigma_i \qquad (i, j = 1-6) \tag{6.49}$$

for a reversible, isothermal deformation in the absence of all electrical and magnetic fields and their conjugate effects. For a linear elastic solid under these conditions, $\sigma_i d\varepsilon_i = \varepsilon_i d\sigma_i$.

Making use of the *substitution property of the Kronecker delta* δ_{ij} (see Section 2.6.3), there results $\varepsilon_j = \delta_{ij}\varepsilon_i$ permitting Eq. (6.48) to be integrated for the elastic strain energy density

$$\begin{aligned} w_{\text{Elastic}} &= \int c_{ij}(\delta_{ij}\varepsilon_i)\,d\varepsilon_i = \tfrac{1}{2}c_{ij}(\delta_{ij}\varepsilon_i^2) + C \\ &= \tfrac{1}{2}c_{ij}\varepsilon_i\varepsilon_j = \tfrac{1}{2}\sigma_i\varepsilon_i \qquad (i = 1-6), \end{aligned} \tag{6.50}$$

where the constant of integration $C = 0$ because $w_{\text{elastic}} = 0$ if $\varepsilon_i\varepsilon_j = 0$. For the total strain energy, Eq. (6.50) must be integrated over the volume of the deformed crystal,

$$E_{\text{Total}} = \int_V \sigma_i\varepsilon_i dV. \tag{6.51}$$

6.2.5 Effect of Crystal Symmetry

Because the procedure to be followed here is similar to that used in Section 6.1 for the piezoelectric moduli, the reader may find it useful to review that material. First of all, it should be recalled that all polar tensors of *even* rank are "centrosymmetrical." This means that by Neumann's principle, their property coefficients are left unchanged by the transformation operation of a center of symmetry.

The procedure to be followed for property coefficients of polar fourth-rank tensor properties is as follows:

1. Use the *method of direct inspection* for all crystal classes for which the s generating matrices, other than $s^{(7)}$, are required as indicated in Table 3.6. This method provides the easiest means of obtaining the independent coefficients of polar fourth-rank tensors. The 10 possible generating matrices are given in Table 3.5 for both s and quadratic σ forms. In applying the direct inspection method to the two suffix coefficient arrays in Eqs. (6.41) and (6.45), the four suffix notation they represent must be kept in mind. Remember that it is actually the four suffix notation to which the method of direct inspection is applied via the tensor/matrix notation of Eq. (6.39).
2. The *brute-force method* must be used in applying the generating matrix $\sigma^{(7)}$ to the trigonal and hexagonal crystal systems of polar fourth-rank tensor properties. However, if generating matrices other than $s^{(7)}$ are involved in the particular crystal class, apply them first each in turn by using the method of direct inspection to obtain a simplified array of the moduli. By using the appropriate transformation law, $c' = \alpha\, c\, \tilde{\alpha}$ or $s' = \tilde{\alpha}^{-1} s \alpha^{-1}$, complete the matrix calculations with the generating matrix $\sigma^{(7)}$, together with its inverse and transpose as needed, to obtain a set of equations for the new property moduli. As a final step, equate each of the old moduli with the new and solve the resulting set of equations simultaneously for the moduli appropriate for the given crystal class. It is strongly recommended that application of the brute-force method be computer assisted.

As an example, let us apply the method of direct inspection to the centrosymmetrical cubic crystal class $\|m3\|$ having the generating (s) matrices $s^{(4)}$ and $s^{(10)}$ given in Table 3.6 and their respective generation operators provided in Table 3.5. Referring to the tensor/matrix suffix notations of Eq. (6.39), we apply the transformation of axes for the generating matrices $s^{(4)}$ and $s^{(10)}$ as follows:

$$s^{(4)} = (m \perp x) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Direct inspection method: $1 \to -1,\ 2 \to 2,\ 3 \to 3$.

This means that all c stiffness moduli in Eq. (6.41) containing a single 5 or single 6 (but not containing both) are zero. As examples, $c_{15} = c_{1131} = 0$, $c_{25} = c_{2231} = 0$, $c_{46} = c_{2312} = 0$, and so forth, for a total of eight vanishing coefficients. Application of $s^{(10)}$ then follows accordingly:

$$s^{(10)} = (3_{[111]}) = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}$$

Direct inspection method: $1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 1$ and $4 \rightarrow 5, 5 \rightarrow 6, 6 \rightarrow 4$.

Together with $s^{(4)}$, this means that $c_{16} = c_{24} = c_{2223} = 0$, $c_{36} = c_{14} = c_{1123} = 0$, and so forth. Also, $c_{11} = c_{22} = c_{33}$, $c_{44} = c_{55} = c_{66}$, and $c_{12} = c_{23} = c_{31}$.

If, for class $\|m3m\|$, the transformation of axes for $s^{(4)}$ and $s^{(9)}$ together with that for $s^{(10)}$ is applied to the remainder of the cubic classes, the results are found to be the same as above. Thus, the elastic stiffness and compliance coefficients for all classes of the cubic system are given by the following arrays in which there are three independent coefficients, c_{11}, c_{12}, c_{44}, and s_{11}, s_{22}, s_{44}:

$$c = \begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{44} & 0 \\ & & & & & c_{44} \end{bmatrix} \quad \text{and} \quad s = \begin{bmatrix} s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\ & s_{11} & s_{12} & 0 & 0 & 0 \\ & & s_{11} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & \text{Sym.} & & & s_{44} & 0 \\ & & & & & s_{44} \end{bmatrix}$$

Continuing in this way, the independent elastic stiffness coefficients are identified for the remainder of the seven crystal systems and are presented in Table 6.3. The case of an isotropic solid is added for completeness and will be considered separately below as an extension of the cubic crystal system.

TABLE 6.3: The independent elastic stiffness coefficients for the seven crystal systems with the addition of the case for the isotropic solid

Triclinic

$1, \|\bar{1}\|$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ & & c_{33} & c_{34} & c_{35} & c_{36} \\ & & & c_{44} & c_{45} & c_{46} \\ & \text{Sym.} & & & c_{55} & c_{56} \\ & & & & & c_{66} \end{bmatrix}$$

TABLE 6.3: (continued)

Monoclinic

$m, 2, \|2/m\|$ for diad parallel to x_2

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & c_{15} & 0 \\ & c_{22} & c_{23} & 0 & c_{25} & 0 \\ & & c_{33} & 0 & c_{35} & 0 \\ & & & c_{44} & 0 & c_{46} \\ & \text{Sym.} & & & c_{55} & 0 \\ & & & & & c_{66} \end{bmatrix}$$

Orthorhombic

$2mm, 222, \|mmm\|$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{22} & c_{23} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{55} & 0 \\ & & & & & c_{66} \end{bmatrix}$$

Tetragonal

$4, \bar{4}, \|4/m\|$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & c_{16} \\ & c_{11} & c_{13} & 0 & 0 & -c_{16} \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{44} & 0 \\ & & & & & c_{66} \end{bmatrix}$$

$4mm, \bar{4}2m, 422, \|4/mmm\|$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{11} & c_{13} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{44} & 0 \\ & & & & & c_{66} \end{bmatrix}$$

TABLE 6.3: (continued)

Trigonal

$3, \|\bar{3}\|$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & -c_{25} & 0 \\ & c_{11} & c_{13} & -c_{14} & c_{25} & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & (c_{25}) \\ & \text{Sym.} & & & c_{44} & (c_{14}) \\ & & & & & \left\{\frac{1}{2}(c_{11}-c_{12})\right\} \end{bmatrix}$$

$3m, 32, \|\bar{3}m\|$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{44} & (c_{14}) \\ & & & & & \left\{\frac{1}{2}(c_{11}-c_{12})\right\} \end{bmatrix}$$

$$(c_{25}) \to 2s_{25}\ ,\ (c_{14}) \to -2s_{14}$$

$$\left\{\frac{1}{2}(c_{11}-c_{12})\right\} \to 2(s_{11}-s_{12})$$

Hexagonal

$6, \bar{6}, \|6/m\|, 6mm, 622, \bar{6}2m, \|6/mmm\|$

$$\begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{11} & c_{13} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{44} & 0 \\ & & & & & \left\{\frac{1}{2}(c_{11}-c_{12})\right\} \end{bmatrix}$$

Cubic

$23, \|m3\|, \bar{4}32, 432, \|m3m\|,$

$$\begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & \text{Sym.} & & & c_{44} & 0 \\ & & & & & c_{44} \end{bmatrix}$$

TABLE 6.3: (continued)

Isotropic

$$\begin{bmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & \left\{\frac{1}{2}(c_{11}-c_{12})\right\} & 0 & 0 \\ & \text{Sym.} & & & \left\{\frac{1}{2}(c_{11}-c_{12})\right\} & 0 \\ & & & & & \left\{\frac{1}{2}(c_{11}-c_{12})\right\} \end{bmatrix}$$

$$\left\{\frac{1}{2}(c_{11}-c_{12})\right\} \to 2(s_{11}-s_{12})$$

The classes to which a given coefficient array belongs are indicated above the array. **Note** that the elastic compliance coefficients s_{ij} are obtained from the elastic stuffiness coefficients by replacing c by s except where noted by parentheses and braces $\{x\}$.

6.2.6 Homogeneous Elastically Isotropic Solids

Consider the application of a pure shear stress $\sigma'_{12} = \sigma'_{21} = \sigma'_6$ to the cubic system, where $x'_1, = [110]$ and $x'_2, = [\bar{1}10]$ as shown by the 45° rotation in Figure 6.5. In the absence of all other stresses, $\sigma'_1 = \sigma'_2 = \sigma'_3 = \sigma'_4 = \sigma'_5 = 0$, the stress tensor transforms as the inverse of Eq. (2.13) or

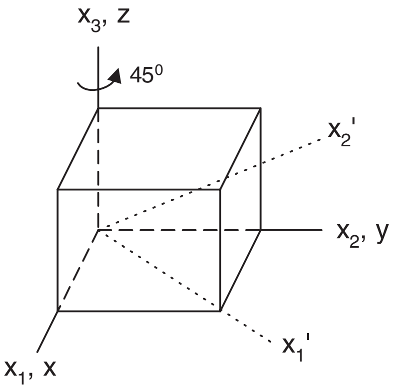


FIGURE 6.5: Rotation of 45° about the z axis.

$$\sigma = \tilde{a}\,\sigma'\,a = \begin{bmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & \sigma'_6 & 0 \\ \sigma'_6 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \sigma'_6 \tag{6.52}$$

Introducing the results of Eq. (6.52) into Eq. (6.43) for the cubic system yields

$$\varepsilon'_m = s_{mn}\,\sigma'_n = \begin{bmatrix} s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\ & s_{11} & s_{12} & 0 & 0 & 0 \\ & & s_{11} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & \text{Sym.} & & & s_{44} & 0 \\ & & & & & s_{44} \end{bmatrix} \begin{bmatrix} -1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \sigma'_6 = \begin{bmatrix} -(s_{11} - s_{12}) \\ (s_{11} - s_{12}) \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \sigma'_6 \tag{6.53}$$

Then, transforming shear strain to the new axes gives

$$\varepsilon'_{ij} = a_{ik}a_{jl}\varepsilon_{kl} \quad \text{or} \quad \varepsilon'_{12} = a_{11}a_{21}\varepsilon_{11} + a_{12}a_{22}\varepsilon_{22} = -\varepsilon_{11}/2 + \varepsilon_{22}/2.$$

Therefore, by Eq. (6.53), we have $\varepsilon'_{12} = [(s_{11} - s_{12})/2 + (s_{11} - s_{12})/2]\,\sigma'_{12} = (s_{11} - s_{12})\,\sigma'_{12}$ where use of the matrix-to-tensor strain conversion of Eq. (6.14) yields the results

$$\varepsilon'_6 = 2\varepsilon'_{12} = 2(s_{11} - s_{12})\sigma'_6 = s_{44}\sigma'_6 \quad \text{or} \quad s_{44} = 2(s_{11} - s_{12}) \tag{6.54}$$

as the necessary and sufficient condition for elastic isotropy, in agreement with Table 6.3. Obviously, the application of any other pure shear stress, σ'_4 or σ'_5, would lead to the same result.

Let us now compare the elastically isotropic compliance array in Table 6.3 with those frequently found in engineering textbooks:

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} = \begin{bmatrix} s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\ & s_{11} & s_{12} & 0 & 0 & 0 \\ & & s_{11} & 0 & 0 & 0 \\ & & & 2(s_{11} - s_{12}) & 0 & 0 \\ & \text{Sym.} & & & 2(s_{11} - s_{12}) & 0 \\ & & & & & 2(s_{11} - s_{12}) \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \tag{6.55}$$

$$\begin{bmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{bmatrix}=\begin{bmatrix}1/Y & -\nu/Y & -\nu/Y & 0 & 0 & 0\\ & 1/Y & -\nu/Y & 0 & 0 & 0\\ & & 1/Y & 0 & 0 & 0\\ & & & 1/G & 0 & 0\\ & \text{Sym.} & & & 1/G & 0\\ & & & & & 1/G\end{bmatrix}\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{bmatrix} \tag{6.56}$$

A comparison of Eqs. (6.55) and (6.56) indicates the following relationships:

$$s_{11}=1/Y \qquad s_{12}=-\nu/Y \qquad \text{and} \qquad 2(s_{11}-s_{12})=1/G, \tag{6.57}$$

where Y is *Young's modulus*, ν is *Poisson's ratio*, and G is thes *modulus of rigidity* with the combined relation, derived from Eq. (6.57), given by

$$G=Y/\{2(1+\nu)\}\,. \tag{6.58}$$

Here, Y is a measure of the elongation of an elastically isotropic solid under tension, and ν is a measure of the transverse contraction (at right angles to the elongation). The rigidity modulus measures the stuffiness to shear.

6.2.7 Young's Modulus in a Particular Direction

Consider a bar-shaped crystal of axis $0x_1'$, along which is applied a unit tensile stress σ_1' as shown in Figure 6.6.

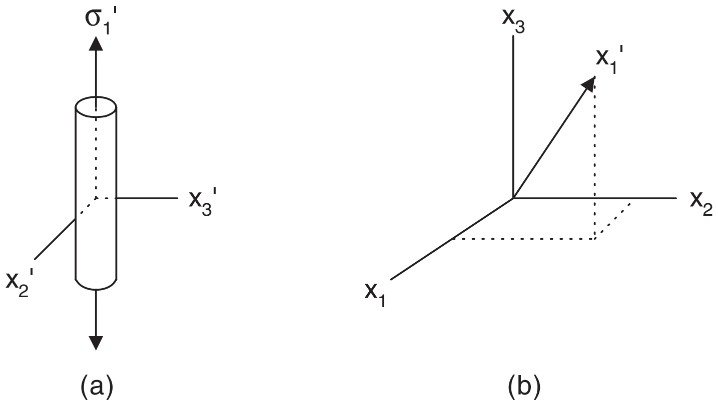


FIGURE 6.6: (a) Application of a unit tensile stress to a crystal rod along the $0x_1'$ direction. (b) Orientation of the rod axis $0x_1'$ relative to reference axes $0x_i$.

From Eq. (6.57), Young's modulus can be defined in the $0x'_1$ direction as

$$s'_{11} = 1/Y = \varepsilon'_1/\sigma'_1 \tag{6.59}$$

where it is understood that σ'_1 is a unit tensile stress applied along the $0x'_1$ axis of the rod such that $\sigma'_2 = \sigma'_3 = \sigma'_4 = \sigma'_5 = \sigma'_6 = 0$. Referring to Figure 2.1, let the direction cosines for $0x'_1$ in Figure 6.6(b) relative to reference axes $0x_i$ be represented as follows: $a_{11} = l_1$, $a_{12} = l_2$, and $a_{13} = l_3$. Then, s'_{11} is found for any crystal system by Eq. (6.47), which is

$$s' = \tilde{\alpha}^{-1} s \alpha^{-1} \tag{6.60}$$

where α^{-1} is found from $\sigma = \tilde{a}\sigma'\ a = \alpha^{-1}\sigma'$ as in Eq. (6.25).

Proceeding, having determined α^{-1}, we apply Eq. (6.60) to the cubic system to give

$$s' = \begin{bmatrix} l_1^2 & l_2^2 & l_3^2 & l_2 l_3 & l_3 l_1 & l_1 l_2 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} s_{11} & s_{12} & s_{12} & 0 & 0 & 0 \\ & s_{11} & s_{12} & 0 & 0 & 0 \\ & & s_{11} & 0 & 0 & 0 \\ & & & s_{44} & 0 & 0 \\ & \text{Sym.} & & & s_{44} & 0 \\ & & & & & s_{44} \end{bmatrix} \begin{bmatrix} l_1^2 & 0 & 0 & 0 & 0 & 0 \\ l_2^2 & 0 & 0 & 0 & 0 & 0 \\ l_3^2 & 0 & 0 & 0 & 0 & 0 \\ l_2 l_3 & 0 & 0 & 0 & 0 & 0 \\ l_3 l_1 & 0 & 0 & 0 & 0 & 0 \\ l_1 l_2 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

or

$$s'_{11} = s_{11}(l_1^4 + l_2^4 + l_3^4) + s_{44}(l_2^2 l_3^2 + l_3^2 l_1^2 + l_1^2 l_2^2) + 2s_{12}(l_2^2 l_3^2 + l_3^2 l_1^2 + l_1^2 l_2^2).$$

But $(l_1^4 + l_2^4 + l_3^4) = (l_1^2 + l_2^2 + l_3^2) - 2(l_2^2 l_3^2 + l_3^2 l_1^2 + l_1^2 l_2^2)$ which, when introduced into the equation for s'_{11}, yields the well-known result

$$s'_{11} = \frac{1}{Y} = s_{11} + \left\{s_{44} - 2(s_{11} - s_{12})\right\}\left(l_2^2 l_3^2 + l_3^2 l_1^2 + l_1^2 l_2^2\right), \tag{6.61}$$

which is not isotropic. Now, as examples, let $0x'_1 = [uvw]$, such that

$$l_1 = u/\sqrt{u^2 + v^2 + w^2},\ \ l_2 = v/\sqrt{u^2 + v^2 + w^2},\ \ l_3 = w/\sqrt{u^2 + v^2 + w^2}$$

where $\left(l_2^2 l_3^2 + l_3^2 l_1^2 + l_1^2 l_2^2\right) = \left(u^2 v^2 + v^2 w^2 + w^2 u^2\right)/\left(u^2 + v^2 + w^2\right)$ which is always positive.

Along <100> $(l_2^2 l_3^2 + l_3^2 l_1^2 + l_1^2 l_2^2) = 0$ and $Y_{<100>} = 1/s_{11} = Y_{\min}$

Along <111> $(l_2^2 l_3^2 + l_3^2 l_1^2 + l_1^2 l_2^2) = 1/3$ and $1/Y_{<111>} = s_{11} + (s_{44} - s_{44}')/3$; $Y_{<111>} = Y_{\max}$.

Also, because $(s_{44} - s_{44}') = 3(Y^{-1}_{<111>} - Y^{-1}_{<100>})$, then

$$Y^{-1}_{<uvw>} = Y^{-1}_{<100>} + 3\left(Y^{-1}_{<111>} - Y^{-1}_{<100>}\right). \tag{6.62}$$

The results for other crystal systems can be found in Nye cited in Endnotes.

6.2.8 Shear Modulus and Poisson's Ratio

The analysis for the shear modulus follows in a similar manner to that for Young's Modulus. Consider the application of a shear stress σ_6' in the $0x_1'$ direction on a plane whose normal is the $0x_2'$ direction. Thus, we define

$$\frac{1}{G} = \frac{\varepsilon_6'}{\sigma_6'}. \tag{6.63}$$

The method of solution is the same as for Young's modulus, namely, $s' = \tilde{\alpha}^{-1} s \alpha^{-1}$, where α^{-1} is found from $\sigma = \tilde{a}\sigma' a$ and $\sigma = \alpha^{-1}\sigma'$. After simplifying the result, the rigidity modulus is

$$1/G = s_{44} - 2\{(s_{44} - 2(s_{11} - s_{12})\}\left(a_{11}^2 a_{21}^2 + a_{12}^2 a_{22}^2 + a_{13}^2 a_{33}^2\right), \tag{6.64}$$

which is easily seen not to be isotropic. If we take $[uvw] = 0x_1'$ and $[hkl] = 0x_2'$, then

$$\left(a_{11}^2 a_{21}^2 + a_{12}^2 a_{22}^2 + a_{13}^2 a_{33}^2\right) = \left\{(uh)^2 + (vk)^2 + (wl)^2\right\} / (u^2 + v^2 + w^2)(h^2 + k^2 + l^2)$$

Poisson's ratio, defined as $v = -\varepsilon_2' / \varepsilon_1' = -\varepsilon_3' / \varepsilon_1'$, is more difficult to obtain by using the procedure above. However, knowing Y and G, it is easily found from Eq. (6.58) to be

$$\nu = Y/2G - 1. \tag{6.65}$$

* * *

CHAPTER 7

Second- and Higher-Order Effects—Symmetry Considerations

First, as we move into a discussion of the second- and higher-order effects, it quickly becomes apparent that their number is far too large for a detailed inclusion in this text. However, we will give specific examples, for instructional purposes, and then provide a generalized approach to their development. Second, it is often the case that the second-order effects do not depend strongly on the magnitudes of the intensive and extensive parameters and may be regarded as weak correction terms (if they exist at all) to the first-order effects under a given set of small intensive or extensive fields. Remember that the first-order effects were developed under the assumption of infinitesimally small fields. However, some second-order effects may actually dominate the first-order effects particularly under field strengths that are not infinitesimally small. If the second-order effects are but weak correction terms to the first-order effects, then it is safe to say that the third- and higher-order effects may be disregarded as we do in our treatment.

7.1 ELECTROSTRICTION AND MORPHIC EFFECTS

Recall that the piezoelectric moduli were given earlier by Eq. (4.62) as $C^{P,\sigma})_{T,E,B} = \tilde{C}^{\varepsilon,E})_{T,B,\sigma} = d_{T,B}$. Here, the converse piezoelectric effect is the first-order electrostriction effect expressed in integrated tensor form as

$$\varepsilon_{ij} = d_{ijk} E_k = \varepsilon_{ji}, \tag{7.1}$$

which applies for very small electric fields and very small stresses and strains all at constant T, B, and σ. At large stresses and strains, quadratic (second-order) terms must be introduced. To do this, we can expand d_{ijk} in a Taylor series to give

$$d_{ijk} = d^0_{ijk} + \left(\frac{\partial d_{ijk}}{\partial E_l}\right)_{T,B,\sigma} E_l + \frac{1}{2}\left(\frac{\partial^2 d_{ijk}}{\partial E_l \, \partial E_m}\right)_{T,B,\sigma} E_l E_m + \cdots, \tag{7.2}$$

where d^0_{ijk} is the value for d_{ijk} at infinitesimal field strength. Introducing Eq. (7.2) into Eq. (7.1) gives the result

$$\varepsilon_{ij} = \left\{ d^0_{ijk} + \gamma_{ijkl} E_l + \cdots \right\} E_k, \tag{7.3}$$

where the third-rank tensor terms $\gamma_{ijkl} E_l + \cdots$ are the correction terms to d^0_{ijk} proportional to field strength and that must conform to both tensor and crystal symmetry.

All electrostrictive moduli d^0_{ijk} vanish for the 11 centrosymmetrical crystal classes given in Table 3.4. However, the correction terms $\gamma_{ijkl} E_l + \cdots$ are not centrosymmetrical and can create new electrostrictive moduli proportional to the field strength E and a strain proportional to E^2. These new moduli create what is called a *morphic effect*. Thus, an electrostrictive effect in a centrosymmetrical class can exist but only as a morphic effect.

7.1.1 Symmetry and Transformation Considerations of Fourth-Rank Tensors

Given the second-order electrostrictive effect from Eq. (7.3),

$$\varepsilon_{ij} = \gamma_{ijkl} E_l E_k, \qquad xxx(7.4)$$

it follows that the symmetry for γ becomes

$$\gamma_{ijkl} = \gamma_{jikl} = \gamma_{ijlk} = \gamma_{jilk} = \gamma_{mn}, \tag{7.5}$$

since strain is commonly taken to be symmetrical, $\varepsilon_{ij} = \varepsilon_{ji}$. Therefore, we can write

$$\varepsilon_m = \gamma_{mn} (EE)_n \quad \text{or} \quad \varepsilon = \gamma(EE) \quad \text{where} \quad \gamma_{mn} \neq \gamma_{nm}. \tag{7.6}$$

Now, the transformation law for γ can be determined in matrix form from Eqs. (6.46), (7.5), and (7.6) as follows: First, we recognize that all principal compliance and rigidity effects, respectively, those along the leading diagonals in Eqs. (4.29) and (4.33), exhibit thermodynamic symmetry as illustrated by Eqs. (4.48) to (4.50). Accordingly, the elastic stiffness tensor c_{ijkl} (a property rigidity) is symmetrical to the extent that $c_{mn} = c_{nm}$, which derives from the fact that both stress and strain are taken to be symmetrical second-rank tensors. Thus, c_{ijkl} transforms in matrix notation as in Eq. (6.46) or $c' = \alpha c \tilde{\alpha}$, where α is the quadratic transformation form discussed in Section 2.2. In matrix notation, we can write that $\sigma = c\varepsilon$ with respect to the "old" set of axes $0x_i$ and that $\sigma' = c'\varepsilon'$ with respect to the "new" set of axes $0x'_i$. Now, with appropriate substitutions we write

$$\sigma' = \alpha\sigma = c'\varepsilon' = \alpha c \tilde{\alpha}\varepsilon' = \alpha c \varepsilon$$

Solving for ε' by acknowledging the transformation for the dyadic EE and using Eq. (7.6), there results

$$\varepsilon' = \tilde{\alpha}^{-1}\varepsilon \quad \text{and} \quad (EE)' = \alpha(EE) \quad \text{or} \quad (EE) = \alpha^{-1}(EE)'$$

Therefore, $\varepsilon' = \tilde{\alpha}^{-1}\varepsilon = \tilde{\alpha}^{-1}\gamma(EE) = \tilde{\alpha}^{-1}\gamma\alpha^{-1}(EE)' = \gamma(EE)'$, resulting in the transformation form

$$\gamma' = \tilde{\alpha}^{-1}\gamma\alpha^{-1}, \tag{7.7}$$

which transforms exactly like the elastic compliance coefficient, $s' = \tilde{\alpha}^{-1} s\alpha^{-1}$ given in Eq. (6.47).

7.2 GENERALIZED DEVELOPMENT OF THE SECOND-ORDER EFFECTS

Let the intensive parameters be represented by α, β, γ, ... and their conjugate extensive parameters represented by a, b, c, ... , such that the state equations for the extensive parameters are

$$\begin{aligned} a &= a(\alpha,\beta,\gamma,\ldots)_{b,c,\ldots} \\ b &= b(\alpha,\beta,\gamma,\ldots)_{a,c,\ldots} \\ \vdots & \quad \vdots \end{aligned} \tag{7.8}$$

Similarly, the state equations for the intensive parameters are

$$\begin{aligned} \alpha &= \alpha(a,b,c,\ldots)_{\beta,\gamma,\ldots} \\ \beta &= \beta(a,b,c,\ldots)_{\alpha,\gamma,\ldots} \\ \vdots & \quad \vdots \end{aligned} \tag{7.9}$$

We now expand each state equation in Eqs. (7.8) in a differential Taylor's series with the result

$$\begin{aligned} \mathrm{d}a &= \sum_{n=1}^{\infty}\frac{1}{n!}\left(\mathrm{d}\alpha\frac{\partial}{\partial\alpha} + \mathrm{d}\beta\frac{\partial}{\partial\beta} + \mathrm{d}\gamma\frac{\partial}{\partial\gamma} + \cdots\right)^n_{b,c,\ldots} a(\alpha,\beta,\gamma,\ldots) \\ \mathrm{d}b &= \sum_{n=1}^{\infty}\frac{1}{n!}\left(\mathrm{d}\alpha\frac{\partial}{\partial\alpha} + \mathrm{d}\beta\frac{\partial}{\partial\beta} + \mathrm{d}\gamma\frac{\partial}{\partial\gamma} + \cdots\right)^n_{a,c,\ldots} b(\alpha,\beta,\gamma,\ldots) \\ \vdots & \qquad\qquad \vdots \end{aligned} \tag{7.10}$$

Similarly, the Taylor series expansion of the intensive state equations in (7.9) become

$$\begin{aligned} \mathrm{d}\alpha &= \sum_{n=1}^{\infty}\frac{1}{n!}\left(\mathrm{d}a\frac{\partial}{\partial a} + \mathrm{d}b\frac{\partial}{\partial b} + \mathrm{d}c\frac{\partial}{\partial c} + \cdots\right)^n_{\beta,\gamma,\ldots} \alpha(a,b,c,\ldots) \\ \mathrm{d}\beta &= \sum_{n=1}^{\infty}\frac{1}{n!}\left(\mathrm{d}a\frac{\partial}{\partial a} + \mathrm{d}b\frac{\partial}{\partial b} + \mathrm{d}c\frac{\partial}{\partial c} + \cdots\right)^n_{\alpha,\gamma,\ldots} \beta(a,b,c,\ldots) \\ \vdots & \qquad\qquad \vdots \end{aligned} \tag{7.11}$$

Now, for the sake of illustration, consider any two intensive parameters α and β and their corresponding (conjugate) extensive parameters a and b with all other extensive parameters held constant, i.e., $\gamma, \delta, \ldots =$ constant. Then, if Eqs. (7.10) apply to the compliance effects as in Eq. (4.26), we can use Taylor's expansions to evaluate the integrals $\int \mathrm{d}a$ and $\int \mathrm{d}b$, giving

$$\Delta a = \left(C^{a,\alpha}\right)_\beta \Delta\alpha + \left(C^{a,\beta}\right)_\alpha \Delta\beta + \frac{1}{2}\frac{\partial\left(C^{a,\alpha}\right)_\beta}{\partial\alpha}(\Delta\alpha)^2 + \frac{1}{2}\frac{\partial\left(C^{a,\beta}\right)_\alpha}{\partial\beta}(\Delta\beta)^2 + \cdots \tag{7.12}$$

$$\Delta b = \left(C^{b,\alpha}\right)_\beta \Delta\alpha + \left(C^{b,\beta}\right)_\alpha \Delta\beta + \frac{1}{2}\frac{\partial\left(C^{b,\alpha}\right)_\beta}{\partial\alpha}(\Delta\alpha)^2 + \frac{1}{2}\frac{\partial\left(C^{b,\beta}\right)_\alpha}{\partial\beta}(\Delta\beta)^2 + \cdots, \tag{7.13}$$

where now $\Delta\alpha = \alpha - \alpha$ and $\Delta\beta = \beta - \beta$, indicating that the Taylor series (7.12) and (7.13) are to be evaluated around initial values α_0 and β_0 that become vanishingly small. After differentiating Eqs. (7.12) and (7.13), there results

$$\mathrm{d}a = \left(C^{a,\alpha}\right)_\beta \mathrm{d}\alpha + \left(C^{a,\beta}\right)_\alpha \mathrm{d}\beta + \frac{\partial\left(C^{a,\alpha}\right)_\beta}{\partial\alpha}\alpha\,\mathrm{d}\alpha + \frac{\partial\left(C^{a,\beta}\right)_\alpha}{\partial\beta}\beta\,\mathrm{d}\beta + \cdots \tag{7.14}$$

$$\mathrm{d}b = \left(C^{b,\alpha}\right)_\beta \mathrm{d}\alpha + \left(C^{b,\beta}\right)_\alpha \mathrm{d}\beta + \frac{\partial\left(C^{b,\alpha}\right)_\beta}{\partial\alpha}\alpha\,\mathrm{d}\alpha + \frac{\partial\left(C^{b,\beta}\right)_\alpha}{\partial\beta}\beta\,\mathrm{d}\beta + \cdots, \tag{7.15}$$

where use was made of

$$\mathrm{d}\left[\lim_{\alpha_0\to 0}(\Delta\alpha)^2\right] = 2\alpha\,\mathrm{d}\alpha \quad \text{and} \quad \mathrm{d}\left[\lim_{\beta_0\to 0}(\Delta\beta)^2\right] = 2\beta\,\mathrm{d}\beta. \tag{7.16}$$

If only the first- and second-order effects are considered, Eqs. (7.14) and (7.15) can be represented approximately in the matrix form

$$\begin{bmatrix}\mathrm{d}a\\ \mathrm{d}b\end{bmatrix} = \begin{bmatrix} \left\{\left(C^{a,\alpha}\right)_\beta + \alpha\left(\dfrac{\partial C^{a,\alpha}}{\partial\alpha}\right)_\beta\right\} & \left\{\left(C^{a,\beta}\right)_\alpha + \beta\left(\dfrac{\partial C^{a,\beta}}{\partial\beta}\right)_\alpha\right\} \\ \left\{\left(C^{b,\alpha}\right)_\beta + \alpha\left(\dfrac{\partial C^{b,\alpha}}{\partial\alpha}\right)_\beta\right\} & \left\{\left(C^{b,\beta}\right)_\alpha + \beta\left(\dfrac{\partial C^{b,\beta}}{\partial\beta}\right)_\alpha\right\} \end{bmatrix} \begin{bmatrix}\mathrm{d}\alpha\\ \mathrm{d}\beta\end{bmatrix}. \tag{7.17}$$

Here, other second-order terms such as $\partial^2 a / \partial\alpha\partial\beta$ and $\partial^2 b / \partial\alpha\partial\beta$ together with the third- and higher-order terms have been neglected. We will revisit the issue of first- and second-order terms later when we consider the phenomenological development of the optical effects.

Assuming that Eqs. (7.17) are a valid approximate representation of the extensive differentials da and db as functions of the intensive α and β, then an interesting and useful relationship between the second-order terms can be derived. Since from the application of Stoke's theorem in Eq. (4.38), we established the symmetrical nature of the compliance effects given by $C_{mn} = C_{nm}$, it follows that a symmetrical relationship can also be established between the second-order effects in Eqs. (7.17). Thus,

$$\left(C^{a,\beta}\right)_{\alpha}=\left(\frac{\partial a}{\partial \beta}\right)_{\alpha}=\left(\frac{\partial b}{\partial \alpha}\right)_{\beta}=\left(C^{b,\alpha}\right)_{\beta} \tag{7.18}$$

permits

$$\left(\frac{\partial C^{a,\beta}}{\partial \beta}\right)_{\alpha}=\left(\frac{\partial}{\partial \beta}\right)_{\alpha}\left(\frac{\partial b}{\partial \alpha}\right)_{\beta}=\left(\frac{\partial\left(C^{b,\beta}\right)_{\alpha}}{\partial \alpha}\right)_{\beta} \tag{7.19}$$

and

$$\left(\frac{\partial C^{b,\alpha}}{\partial \alpha}\right)_{\beta}=\left(\frac{\partial}{\partial \alpha}\right)_{\beta}\left(\frac{\partial a}{\partial \beta}\right)_{\alpha}=\left(\frac{\partial\left(C^{a,\alpha}\right)_{\beta}}{\partial \beta}\right)_{\alpha} \tag{7.20}$$

because the order of differentiation is immaterial. The meaning of $(\partial(C^{b,\beta})_{\alpha}/\partial\alpha)_{\beta}$ in Eq. (7.19) is that $C^{b,\beta}$ is evaluated at constant α and that its change with α is evaluated at constant β. The expressions in Eqs. (7.19) and (7.20) are *second-order Maxwell relations*. Introducing these expressions into Eqs. (7.17) gives the results

$$\begin{bmatrix}\mathrm{d}a\\ \mathrm{d}b\end{bmatrix}=\begin{bmatrix}\left\{\left(C^{a,\alpha}\right)_{\beta}+\alpha\left(\dfrac{\partial C^{a,\alpha}}{\partial \alpha}\right)_{\beta}\right\} & \left\{\left(C^{a,\beta}\right)_{\alpha}+\beta\left(\dfrac{\partial\left(C^{b,\beta}\right)_{\alpha}}{\partial \alpha}\right)_{\beta}\right\}\\ \left\{\left(C^{b,\alpha}\right)_{\beta}+\alpha\left(\dfrac{\partial\left(C^{a,\alpha}\right)_{\beta}}{\partial \beta}\right)_{\alpha}\right\} & \left\{\left(C^{b,\beta}\right)_{\alpha}+\beta\left(\dfrac{\partial C^{b,\beta}}{\partial \beta}\right)_{\alpha}\right\}\end{bmatrix}\begin{bmatrix}\mathrm{d}\alpha\\ \mathrm{d}\beta\end{bmatrix}. \tag{7.21}$$

By thermodynamic symmetry, the Maxwell relations lead to the equality of cross (bracketed) terms

$$\left(C^{a,\beta}\right)_{\alpha}+\beta\left(\frac{\partial\left(C^{b,\beta}\right)_{\alpha}}{\partial \alpha}\right)_{\beta}=\left(C^{b,\alpha}\right)_{\beta}+\alpha\left(\frac{\partial\left(C^{a,\alpha}\right)_{\beta}}{\partial \beta}\right)_{\alpha}, \tag{7.22}$$

where it follows that

$$\beta\left(\frac{\partial\left(C^{b,\beta}\right)_{\alpha}}{\partial \alpha}\right)_{\beta}=\alpha\left(\frac{\partial\left(C^{a,\alpha}\right)_{\beta}}{\partial \beta}\right)_{\alpha}. \tag{7.23}$$

Note that the expressions in Eq. (7.23) result from the symmetry expressed by Eq. (7.18) and that the second-order cross terms in Eqs. (7.21), (7.22), and (7.23) are no longer multiplied by an intensive parameter that is not held constant as in the case of Eqs. (7.17).

Consider the use of Eqs. (7.21) to develop the first- and second-order electrostrictive effects as was done in Section 7.1, but from a different approach. To do this, we select the following extensive and intensive parameters:

$$\begin{Bmatrix} a = \varepsilon & \alpha = \sigma \\ b = P & \beta = E \end{Bmatrix}. \tag{7.24}$$

Equations (7.21) now become

$$\begin{bmatrix} \mathrm{d}\varepsilon \\ \mathrm{d}P \end{bmatrix} = \begin{bmatrix} \left\{ \left(C^{\varepsilon,\sigma}\right)_E + \sigma\left(\dfrac{\partial C^{\varepsilon,\sigma}}{\partial E}\right)_E \right\} & \left\{ \left(C^{\varepsilon,E}\right)_\sigma + E\left(\dfrac{\partial \left(C^{P,E}\right)_\sigma}{\partial \sigma}\right)_E \right\} \\ \left\{ \left(C^{P,\sigma}\right)_E + \sigma\left(\dfrac{\partial \left(C^{\varepsilon,\sigma}\right)_E}{\partial E}\right)_\sigma \right\} & \left\{ \left(C^{P,E}\right)_\sigma + E\left(\dfrac{\partial C^{P,E}}{\partial E}\right)_\sigma \right\} \end{bmatrix}_{T,B} \begin{bmatrix} \mathrm{d}\sigma \\ \mathrm{d}E \end{bmatrix}, \tag{7.25}$$

where it is understood that T and B are held constant. By thermodynamics symmetry, the cross (braced) terms are equal giving the results

$$\left(C^{\varepsilon,E}\right)_\sigma + E\left(\frac{\partial \left(C^{P,E}\right)_\sigma}{\partial \sigma}\right)_E = \left(C^{P,\sigma}\right)_E + \sigma\left(\frac{\partial \left(C^{\varepsilon,\sigma}\right)_E}{\partial E}\right)_\sigma, \tag{7.26}$$

where it follows that

$$E\left(\frac{\partial \left(C^{P,E}\right)_\sigma}{\partial \sigma}\right)_E = \sigma\left(\frac{\partial \left(C^{\varepsilon,\sigma}\right)_E}{\partial E}\right)_\sigma, \tag{7.27}$$

because $(C^{\varepsilon,E})_\sigma = (C^{P,\sigma})_E$. The compliances $C^{P,E}$ and $C^{\varepsilon,\sigma}$ are defined by Eqs. (4.45) and (4.47), respectively. Written in tensor notation, Eq. (7.27) becomes

$$\kappa_0\left(\frac{\partial \chi_{ij}}{\partial \sigma_{kl}}\right)_E E_l = \left(\frac{\partial s_{ijkl}}{\partial E_m}\right)_\sigma \sigma_{lm} = \psi_{ijk}. \tag{7.28}$$

What Eq. (7.28) indicates is that the components of the polar third-rank tensor ψ_{ijk} on left side of the equation are numerical equal to those on the right side or vice versa. However, the frequency of the E and σ field changes must be the same if the equality of Eq. (7.28) is to be valid.

As another approach to the evaluation of second-order effects, consider the application of the parameter selection in Eq. (7.24) to Eqs. (7.17) expressed as

$$\begin{bmatrix} \mathrm{d}\varepsilon \\ \mathrm{d}P \end{bmatrix} = \begin{bmatrix} \left\{ \left(C^{\varepsilon,\sigma}\right)_E + \sigma\left(\frac{\partial C^{\varepsilon,\sigma}}{\partial\sigma}\right)_E \right\} & \left\{ \left(C^{\varepsilon,E}\right)_\sigma + E\left(\frac{\partial C^{\varepsilon,E}}{\partial E}\right)_\sigma \right\} \\ \left\{ \left(C^{P,\sigma}\right)_E + \sigma\left(\frac{\partial C^{P,\sigma}}{\partial\sigma}\right)_E \right\} & \left\{ \left(C^{P,E}\right)_\sigma + E\left(\frac{\partial C^{P,E}}{\partial E}\right)_\sigma \right\} \end{bmatrix} \begin{bmatrix} \mathrm{d}\sigma \\ \mathrm{d}E \end{bmatrix}. \tag{7.29}$$

The first- and second-order converse piezoelectric (electrostrictive) effects are represented by the equation for $\mathrm{d}\varepsilon$ under constant stress σ given in tensor notation by

$$\mathrm{d}\varepsilon_{ij} = (\mathrm{d}_{ijk})_\sigma \mathrm{d}E_k + \left(\frac{\partial d_{ijk}}{\partial E_l}\right)_\sigma E_k \mathrm{d}E_l$$

or in integrated form

$$\varepsilon_{ij} = \left\{d_{ijk} + \gamma_{ijkl}E_l\right\}_\sigma E_k, \tag{7.30}$$

which is the same as Eq. (7.3). Here, d_{ijk} are the converse piezoelectric moduli or the first-order electrostrictive moduli, and γ_{ijkl} are second-order electrostrictive moduli. In conformable matrix form, q. (7.30) is given by $\varepsilon = \tilde{d}E + \lambda(\boldsymbol{EE}_c)$, where $(\boldsymbol{EE}_c)$ is the self-conjugate (dyadic) product of electric fields. In expanded matrix form, the strain matrix of Eq. (7.30) becomes

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} = \begin{bmatrix} d_{11} & d_{21} & d_{31} \\ d_{12} & d_{22} & d_{32} \\ d_{13} & d_{23} & d_{33} \\ d_{14} & d_{24} & d_{34} \\ d_{15} & d_{25} & d_{35} \\ d_{16} & d_{26} & d_{36} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} + \begin{bmatrix} \gamma_{11} & \gamma_{12} & \gamma_{13} & \gamma_{14} & \gamma_{15} & \gamma_{16} \\ \gamma_{21} & \gamma_{22} & \gamma_{23} & \gamma_{24} & \gamma_{25} & \gamma_{26} \\ \gamma_{31} & \gamma_{32} & \gamma_{33} & \gamma_{34} & \gamma_{35} & \gamma_{36} \\ \gamma_{41} & \gamma_{42} & \gamma_{43} & \gamma_{44} & \gamma_{45} & \gamma_{46} \\ \gamma_{51} & \gamma_{52} & \gamma_{53} & \gamma_{54} & \gamma_{55} & \gamma_{56} \\ \gamma_{61} & \gamma_{62} & \gamma_{63} & \gamma_{64} & \gamma_{65} & \gamma_{66} \end{bmatrix} \begin{bmatrix} E_1E_1 \\ E_2E_2 \\ E_3E_3 \\ E_2E_3 \\ E_3E_1 \\ E_1E_2 \end{bmatrix} \tag{7.31}$$

where it is recalled from Section 7.1 that $\gamma_{mn} \neq \gamma_{nm}$.

7.3 PHENOMENOLOGICAL DEVELOPMENT OF THE OPTICAL EFFECTS

In the presence of external fields, the *dielectric constant* (relative permittivity) $K_{ij} = \kappa_{ij} / \kappa_0$ and, hence, the refractive index of a crystal may change. For example, in the presence of an external electric field, an isotropic solid may become optically anisotropic, a uniaxial crystal may become biaxial, and so forth. The effect of the external electric field on the optical symmetry of the crystal is commonly called the *electro-optical* effect. Similar effects are obtained by the application of other external fields such as magnetic, stress, and temperature changes. The corresponding effects are referred to as magneto-optical, piezo-optical, and thermo-optical effects, respectively.

There are several ways to phenomenologically develop the previously mentioned optical effects. For example, we could expand the relative permittivity tensor, K_{ij} in a power series as a function of electric field E, magnetic field H, and stress σ. Two of the coefficients resulting from this expansion would be called the electro-optical and piezo-optical coefficients. Alternatively, we could expand the electric field strength E as a function of the polarization P, magnetic flux density B, and strain ε,thereby obtaining the electro-optical, magneto-optical, and elasto-optical coefficients, and so forth, the choice being arbitrary and a matter of convenience.

For our purposes, we will choose as the dependent variable the *dielectric impermeability tensor* defined as

$$B_{ij} = K_{ij}^{-1} = \kappa_0 \left(\partial E_i / \partial D_j \right) = B_{ji}, \tag{7.32}$$

where D_j is the electric flux density given vectorially as $\vec{D} = \kappa_0 \vec{E} + \vec{P}$. The refractive index of a crystal is specified generally by an ellipsoid called the *indicatrix* whose coefficients at optical frequencies are the components of the dielectric impermeability tensor B_{ij} given by $B_{ij} x_i x_j = 1$.

Expansion of the dielectric impermeability in a Taylor's series about the state of a reference temperature T^0, zero electric field, zero magnetic flux density, and zero stress yields

$$\begin{aligned} B_{ij}(T, E_k, B_l, \sigma_{mn}) &= \sum_{n=0}^{\infty} \frac{1}{n!} \left((T - T^0) \frac{\partial}{\partial T} + E_k \frac{\partial}{\partial E_k} + B_l \frac{\partial}{\partial B_l} + \sigma_{mn} \frac{\partial}{\partial \sigma_{mn}} \right)^n B_{ij}(T^0, 0, 0, 0) \\ &= B_{ij}(T^0,\ 0,\ 0,\ 0) + \left(\frac{\partial B_{ij}}{\partial T} \right) \Delta T + \left(\frac{\partial B_{ij}}{\partial E_k} \right) E_k + \left(\frac{\partial B_{ij}}{\partial B_l} \right) B_l + \left(\frac{\partial B_{ij}}{\partial \sigma_{mn}} \right) \sigma_{mn} \end{aligned} \tag{7.33}$$

$$\begin{aligned} &+ \frac{1}{2!} \left[\left(\frac{\partial^2 B_{ij}}{\partial T^2} \right) (\Delta T)^2 + \left(\frac{\partial^2 B_{ij}}{\partial E_k \partial E_o} \right) E_k E_o + \left(\frac{\partial^2 B_{ij}}{\partial B_l \partial B_p} \right) B_l B_p + \left(\frac{\partial^2 B_{ij}}{\partial \sigma_{mn} \sigma_{qr}} \right) \sigma_{mn} \sigma_{qr} \right. \\ &+ 2 \left(\frac{\partial^2 B_{ij}}{\partial T \partial E_k} \right) E_k \Delta T + 2 \left(\frac{\partial^2 B_{ij}}{\partial T \partial B_l} \right) B_l \Delta T + 2 \left(\frac{\partial^2 B_{ij}}{\partial T \partial \sigma_{mn}} \right) \sigma_{mn} \Delta T + 2 \left(\frac{\partial^2 B_{ij}}{\partial E_k B_l} \right) E_k B_l \\ &\left. + 2 \left(\frac{\partial^2 B_{ij}}{\partial E_k \partial \sigma_{mn}} \right) E_k \sigma_{mn} + 2 \left(\frac{\partial^2 B_{ij}}{\partial B_l \sigma_{mn}} \right) B_l \sigma_{mn} \right] + \cdots. \end{aligned} \tag{7.34}$$

Here, $B_{ij}\,(T^0,0,0,0)$ and all coefficients (in parentheses) are evaluated at a reference temperature T^0 and at zero electric field, zero magnetic field, and zero stress. We now develop phenomenologically the 14 linear and quadratic optical effects expressed in Eq. (7.34).

$$\left(\frac{\partial B_{ij}}{\partial T}\right)_{(T^0,0,0,0)} = t_{ij} = \textit{linear thermo-optical effect}$$

$$\tfrac{1}{2}\left(\frac{\partial^2 B_{ij}}{\partial T^2}\right)_{(T^0,0,0,0)} = T_{ij} = \textit{quadratic thermo-optical effect}$$

$$\left(\frac{\partial B_{ij}}{\partial E_k}\right)_{(T^0,0,0,0)} = r_{ijk} = \textit{linear electro-optical effect}$$

$$\tfrac{1}{2}\left(\frac{\partial^2 B_{ij}}{\partial E_k \partial E_o}\right)_{(T^0,0,0,0)} = R_{ijko} = \textit{quadratic electro-optical (Kerr) effect}$$

$$\left(\frac{\partial B_{ij}}{\partial B_l}\right)_{(T^0,0,0,0)} = f_{ijl} = \textit{linear magneto-optical (Faraday) effect}$$

$$\tfrac{1}{2}\left(\frac{\partial^2 B_{ij}}{\partial B_l \partial B_p}\right)_{(T^0,0,0,0)} = F_{ijlp} = \textit{quadratic magneto-optical (Cotton–Mouton) effect}$$

$$\left(\frac{\partial B_{ij}}{\partial \sigma_{mn}}\right)_{(T^0,0,0,0)} = \pi_{ijmn} = \textit{linear piezo-optical effect}$$

$$\tfrac{1}{2}\left(\frac{\partial^2 B_{ij}}{\partial \sigma_{mn} \sigma_{qr}}\right)_{(T^0,0,0,0)} = \Pi_{ijmnqr} = \textit{quadratic piezo-optical effect}$$

$$\left(\frac{\partial^2 B_{ij}}{\partial T \partial E_k}\right)_{(T^0,0,0,0)} = r_{ijk}^{(T)} = \textit{thermoelectro-optical effect}$$

$$\left(\frac{\partial^2 B_{ij}}{\partial T \partial B_l}\right)_{(T^0,0,0,0)} = f_{ijl}^{(T)} = \textit{thermomagneto-optical effect}$$

$$\left(\frac{\partial^2 B_{ij}}{\partial T \partial \sigma_{mn}}\right)_{(T^0,0,0,0)} = \pi_{ijmn}^{(T)} = \textit{thermopiezo-optical effect}$$

$$\left(\frac{\partial^2 B_{ij}}{\partial E_k B_l}\right)_{(T^0,0,0,0)} = m_{ijkl} = \textit{magnetoelectro-optical effect}$$

$$\left(\frac{\partial^2 B_{ij}}{\partial E_k \partial \sigma_{mn}}\right)_{(T^0,0,0,0)} = z_{ijkmn} = \textit{piezoelectro-optical effect}$$

$$\left(\frac{\partial^2 B_{ij}}{\partial B_l \sigma_{mn}}\right)_{(T^0,0,0,0)} = w_{ijlmn} = \textit{piezomagneto-optical effect.}$$

Only a few of these effects have been experimentally investigated and their tensor rank and symmetry considered. In what follows, we will briefly examine a few of the more common effects.

7.3.1 Electro-Optical Effects

The linear and quadratic electro-optical effects can be obtained by applying very small electric fields to a crystal at constant reference temperature T^0 and zero magnetic field and stress. The Taylor's series expansion of the dielectric impermeability tensor reduces to

$$B_{ij}(E_k) = B_{ij}(0) + \left(\frac{\partial B_{ij}}{\partial E_k}\right) E_k + \tfrac{1}{2}\left(\frac{\partial^2 B_{ij}}{\partial E_k \partial E_o}\right) E_k E_o + \cdots \tag{7.35}$$

or

$$\Delta B_{ij} = r_{ijk} E_k + R_{ijko} E_k E_o + \cdots . \tag{7.36}$$

where r_{ijk} and R_{ijko} represent the linear and quadratic electro-optical effects, respectively.

The coefficients r_{ijk}, which describe the linear electro-optical effect in crystals, form a polar nonmagnetic third-rank tensor with symmetry $r_{ijk} = r_{jik} = r_{mk}$ such that the linear electro-optical effect can be written as

$$\Delta B_m = r_{mk} E_k \qquad (m = 1-6;\ k = 1-3). \tag{7.37}$$

In simplified notation, Eq. (7.37) can be expressed as $\Delta B = r \cdot E$ or simply as $\Delta B = \tilde{r}\, E$ in conformable matrix form. Thus, the matrix representation of Eq. (7.37) is the same as the converse piezoelectric effect given by Eq. (6.11). with ε replaced by ΔB and d replaced by r. Because r_{ijk} and d_{ijk} are both third-rank polar tensors, the symmetry restrictions on their coefficients must be the same. Thus, $r_{ijk} = 0$ for all 11 centrosymmetrical crystal classes and the r_{mk} for the linear electro-optical moduli are the same as those in Table 6.2 if the transpose of each array is taken with the subscripts *mk* reversed as in Eqs. (6.10) and (6.11). Remember that the *d* moduli arrays in Table 6.2 are given in normal form.

Because the linear electro-optical effect is possible only in piezoelectric crystals, the presence of an externally applied electric field will produce a slight change in the shape of the crystal by the converse piezoelectric effect. The change in crystal shape results in the elasto-optical effect, to be considered in Section 7.3.2. As a result, the electro-optical effect will consist of two components: 1) the true (primary) linear electro-optical effect and 2) the false (secondary) linear electro-optical effect. Combined, these effects are given by

$$\Delta B_{ij} = r_{ijk} E_k = r^{*}_{ijk} E_k + p_{ijlm} \varepsilon_{lm}, \tag{7.38}$$

where r^{*}_{ijk} are the true electro-optical coefficients and p_{ijlm} are the elasto-optical coefficients. The elasto-optical coefficients are related to the linear piezo-optical coefficients, as in Eqs. (7.50), by

$$p_{ijlm} = \pi_{ijrs} c_{rslm} \quad \text{and} \quad \pi_{ijlm} = p_{ijrs} s_{rslm}, \tag{7.39}$$

where c and s represent the elastic stiffness and elastic compliance moduli of a crystal, respectively. Equation (7.38) can be cast into an alternative form by using Eq. (6.8), yielding

$$\Delta B_{ij} = (r^{*}_{ijk} + p_{ijlm} d_{klm}) E_k \quad \text{or} \quad \Delta B_m = (r^{*}_{mk} + p_{mr} d_{kr}) E_k, \tag{7.40}$$

so that the product *pd* appears as a correction factor for the true linear electro-optical effect. At high-field frequencies, the *pd* correction factor is usually much smaller than the true linear electro-optical effect, but at low frequencies, it can become relatively important.

The quadratic electro-optical effect, or *Kerr effect*, is represented by the coefficients R_{ijko} in Eq. (7.36), which is a polar nonmagnetic fourth-rank tensor. Thus, contrary to the linear electro-optical effect, the quadratic effect may exist in all crystal classes. From its definition $\partial^2 B_{ij} / \partial E_k \partial E_o$ there exists symmetry in the subscript pairs (i, j) and (k, o) permitting the Kerr coefficients to be represented in either form

$$\Delta B_{ij} = R_{ijko} E_k E_o$$

or

$$\Delta B_m = R_{mn} E_n^2 \quad (m, n = 1-6), \quad \text{and} \quad R_{mn} \neq R_{nm}. \tag{7.41}$$

In expanded matrix form, Eq. (7.41) becomes

$$\begin{bmatrix} \Delta B_1 \\ \Delta B_2 \\ \Delta B_3 \\ \Delta B_4 \\ \Delta B_5 \\ \Delta B_6 \end{bmatrix} = \begin{bmatrix} R_{11} & R_{12} & R_{13} & R_{14} & R_{15} & R_{16} \\ R_{21} & R_{22} & R_{23} & R_{24} & R_{25} & R_{26} \\ R_{31} & R_{32} & R_{33} & R_{34} & R_{35} & R_{36} \\ R_{41} & R_{42} & R_{43} & R_{44} & R_{45} & R_{46} \\ R_{51} & R_{52} & R_{53} & R_{54} & R_{55} & R_{56} \\ R_{61} & R_{62} & R_{63} & R_{64} & R_{65} & R_{66} \end{bmatrix} \cdot \begin{bmatrix} E_1 E_1 \\ E_2 E_2 \\ E_3 E_3 \\ E_2 E_3 \\ E_3 E_1 \\ E_1 E_2 \end{bmatrix}. \tag{7.42}$$

Here, the R_{mn} coefficients are related to the R_{ijko} coefficients by the rules: $R_{mn} = R_{ijko}$ if $n = 1-3$, and $R_{mn} = 2R_{ijko}$ if $n = 4-6$. The restrictions imposed by crystal symmetry on the coefficients R_{mn} are exactly the same as those imposed on the linear piezo-optical coefficients considered in Section 7.3.2.

As in the case of the linear electro-optical effect, the quadratic effect will normally contain two parts: 1) the true (primary) quadratic electro-optical effect and 2) the false (secondary) quadratic electro-optical effect. This can be expressed as

$$\Delta B_{ij} = R_{ijko} E_k E_o = R^*_{ijko} E_k E_o + p_{ijlm} \varepsilon_{lm}, \tag{7.43}$$

where R^*_{ijko} are the coefficients for the true quadratic electro-optical effect and p_{ijlm} are the components for the elasto-optical effect. Equation (7.43) can be cast into an alternative form by use of second-order electrostrictive coefficients given in Eq. (7.4). When this is done, Eq. (7.43) becomes

$$\Delta B_{ij} = (R^*_{ijko} + p_{ijlm} \gamma_{lmko}) E_k E_o, \tag{7.44}$$

where now the $p\gamma$ product appears as a correction to the true quadratic electro-optical (Kerr) effect. The $p\gamma$ correction factor is usually weak but can become important in some ferroelectric crystals.

7.3.2 Piezo-Optical and Elasto-Optical Effects

The linear and quadratic piezo-optical effects can be obtained by applying small stress components to a crystal at a reference temperature T^0 under zero magnetic and electrical field conditions. The Taylor's series expansion of the dielectric impermeability tensor in Eq. (7.34) reduces to

$$B_{ij}(\sigma_{mn}) = B_{ij}(0) + \left(\frac{\partial B_{ij}}{\partial \sigma_{mn}} \right) \sigma_{mn} + \tfrac{1}{2} \left(\frac{\partial^2 B_{ij}}{\partial \sigma_{mn} \sigma_{qr}} \right) \sigma_{mn} \sigma_{qr} + \cdots$$

or

$$\Delta B_{ij} = \pi_{ijmn} \sigma_{mn} + \Pi_{ijmnqr} \sigma_{mn} \sigma_{qr} + \cdots, \tag{7.45}$$

where π_{ijmn} and $\prod_{ijmnqr}$ represent the linear and quadratic piezo-optical coefficients, respectively.

The coefficients π_{ijmn} represent a polar fourth-rank tensor with partial symmetry implied by B_{ij} and σ_{mn} thereby permitting the linear effect to be presented in reduced suffix notation as

$$\Delta B_o = \pi_{op} \sigma_p \quad (o,\ p = 1-6) \quad \text{and} \quad \pi_{op} \neq \pi_{po} \tag{7.46}$$

or in expanded matrix form

$$\begin{bmatrix} \Delta B_1 \\ \Delta B_2 \\ \Delta B_3 \\ \Delta B_4 \\ \Delta B_5 \\ \Delta B_6 \end{bmatrix} = \begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & \pi_{15} & \pi_{16} \\ \pi_{21} & \pi_{22} & \pi_{23} & \pi_{24} & \pi_{25} & \pi_{26} \\ \pi_{31} & \pi_{32} & \pi_{33} & \pi_{34} & \pi_{35} & \pi_{36} \\ \pi_{41} & \pi_{42} & \pi_{43} & \pi_{44} & \pi_{45} & \pi_{46} \\ \pi_{51} & \pi_{52} & \pi_{53} & \pi_{54} & \pi_{55} & \pi_{56} \\ \pi_{61} & \pi_{62} & \pi_{63} & \pi_{64} & \pi_{65} & \pi_{66} \end{bmatrix} \cdot \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix}, \tag{7.47}$$

The elasto-optical coefficients can be obtained in a similar manner by expressing the impermeability tensor as functions of the strain components of the crystal, as in Eq. (7.43), to give

$$\Delta B_{ij} = p_{ijlm}\varepsilon_{lm} \quad (i, j, m, n = 1-3) \tag{7.48}$$

or in reduced suffix notation

$$\Delta B_o = p_{op}\varepsilon_p \qquad (o, p = 1-6) \qquad \text{and} \qquad p_{op} \neq p_{po} \tag{7.49}$$

Now, $P_{op} = P_{ijlm}$ for all o and p with no factors of 2 or $\frac{1}{2}$ present. The elasto-optical and piezo-optical coefficients are related through the elastic moduli c and s, respectively, by the equations

$$p_{op} = \left(\frac{\partial B_o}{\partial \sigma_q}\right)\left(\frac{\partial \sigma_q}{\partial \varepsilon_p}\right) = \pi_{oq}\, c_{qp} \quad \text{and} \quad \pi_{oq} = \left(\frac{\partial B_o}{\partial \varepsilon_p}\right)\left(\frac{\partial \varepsilon_p}{\partial \sigma_q}\right) = p_{op}\, s_{pq}. \tag{7.50}$$

The effect of crystal symmetry on the piezo-optical coefficients π_{oq} can be determined by applying the direct inspection method to all crystal classes except the trigonal and hexagonal systems for which the "brute-force" method must be used. Thus, for the trigonal and hexagonal systems, the transformation equation must be used:

$$\pi' = \alpha\pi\alpha^{-1}. \tag{7.51}$$

which also applies to the quadratic electro-optical coefficients R given in Eq. (7.42). Note that Eq. (7.51) derives from $B' = \alpha B = \alpha\pi\sigma = \alpha\pi\alpha^{-1}\sigma' = \pi'\sigma'$ because $B = \pi\sigma$ applies to the old axes $0x_i$, whereas $B' = \pi'\sigma'$ applies to the new axes $0x_i'$. Here, the linear quadratic electro-optical coefficients R_{mn} will be affected by crystal symmetry exactly as will be π_{mn}. Shown in Table 7.1 are the piezo-optical coefficients π_{mn} for the seven crystal systems and the isotropic solid with the understanding that $\pi_{ij} \neq \pi_{ji}$. This table can also be applied to the elasto-optical coefficients with some minor changes.

7.3.3 Piezo-Optical Effect in Cubic Crystals Under Uniaxial Tension

Consider the application of a uniaxial stress on a cubic crystal of the class $\bar{4}32$, 432 or $m3m$. For any direction of stress, the matrix equation Eq. (7.46) becomes

$$\begin{bmatrix} \Delta B_1 \\ \Delta B_2 \\ \Delta B_3 \\ \Delta B_4 \\ \Delta B_5 \\ \Delta B_6 \end{bmatrix} = \begin{bmatrix} B_1 - B^0 \\ B_2 - B^0 \\ B_3 - B^0 \\ B_4 \\ B_5 \\ B_6 \end{bmatrix} = \begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{44} \end{bmatrix} \cdot \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix}, \tag{7.52}$$

where B^0 is the reference dielectric impermeability defined by the indicatrix sphere for the undeformed crystal in the absence of temperature, electric, and magnetic fields

$$B^0(x_1^2 + x_2^2 + x_3^2) = \left(\frac{x_1^2}{(n^0)^2} + \frac{x_2^2}{(n^0)^2} + \frac{x_3^2}{(n^0)^2} \right) = 1 \tag{7.53}$$

because $B^0 = 1(n^0)^2$. Here, n^0 is the refractive index in the absence of all external fields.

Now, let a uniaxial tensile stress σ_2 be applied along the $0x_2$ direction, with $0x_1$ and $0x_3$ being the other cubic unit cell axes. Because $\Delta B_4 = \Delta B_5 = \Delta B_6 = 0$, Eq. (7.52) reduces to

$$\begin{aligned} \Delta B_1 &= \pi_{12}\sigma_2 \\ \Delta B_2 &= \pi_{11}\sigma_2 \\ \Delta B_3 &= \pi_{12}\sigma_2 . \end{aligned} \tag{7.54}$$

The changes in the three principal refractive indices can be determined by noting, for example, that $B_i = 1/n_i^2$. Then, after differentiation, there results $\Delta B_i = -(2/n_i^3)\Delta n_i = B_i = B_i^0 \ll B_i^0$ along the principal axes. Thus, $n \cong n^0$, which gives the change in the three principal refractive indices as

$$\begin{aligned} \Delta n_1 &= -\frac{1}{2}(n^0)^3\, \Delta B_1 = -\frac{1}{2}(n^0)^3 \pi_{12}\sigma_2 \\ \Delta n_2 &= -\frac{1}{2}(n^0)^3\, \Delta B_2 = -\frac{1}{2}(n^0)^3 \pi_{11}\sigma_2 \\ \Delta n_3 &= -\frac{1}{2}(n^0)^3\, \Delta B_3 = -\frac{1}{2}(n^0)^3 \pi_{12}\sigma_2 . \end{aligned} \tag{7.55}$$

This shows that $\Delta n_1 = \Delta n_3$ and that the crystal has become uniaxial. Therefore, for light traveling along x_2, the birefringence (also called double refraction) is zero because $\Delta n_1 = \Delta n_3$. However, for light traveling along either x_1 or x_3, the birefringence becomes

TABLE 7.1: The independent piezo-optical coefficients π_{mn} and quadratic electro-optical coefficients R_{mn} are identical for the seven crystal systems and the isotropic solid

Triclinic

$1, \|\bar{1}\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & \pi_{15} & \pi_{16} \\ \pi_{21} & \pi_{22} & \pi_{23} & \pi_{24} & \pi_{25} & \pi_{26} \\ \pi_{31} & \pi_{32} & \pi_{33} & \pi_{34} & \pi_{35} & \pi_{36} \\ \pi_{41} & \pi_{42} & \pi_{43} & \pi_{44} & \pi_{45} & \pi_{46} \\ \pi_{51} & \pi_{52} & \pi_{53} & \pi_{54} & \pi_{55} & \pi_{56} \\ \pi_{61} & \pi_{62} & \pi_{63} & \pi_{64} & \pi_{65} & \pi_{66} \end{bmatrix}$$

Monoclinic

$m, 2, \|2/m\|$ for diad $\|$ to x_2

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & \pi_{15} & 0 \\ \pi_{21} & \pi_{22} & \pi_{23} & 0 & \pi_{25} & 0 \\ \pi_{31} & \pi_{32} & \pi_{33} & 0 & \pi_{35} & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & \pi_{46} \\ \pi_{51} & \pi_{52} & \pi_{53} & 0 & \pi_{55} & 0 \\ 0 & 0 & 0 & \pi_{64} & 0 & \pi_{66} \end{bmatrix}$$

Orthorhombic

$2mm, 222, \|mmm\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{21} & \pi_{22} & \pi_{23} & 0 & 0 & 0 \\ \pi_{31} & \pi_{32} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{66} \end{bmatrix}$$

TABLE 7.1: (continued)

Tetragonal

$4, \bar{4}, \|4/m\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & \pi_{16} \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & -\pi_{16} \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & \pi_{45} & 0 \\ 0 & 0 & 0 & -\pi_{45} & \pi_{44} & 0 \\ \pi_{61} & -\pi_{61} & 0 & 0 & 0 & \pi_{66} \end{bmatrix}$$

$4mm, \bar{4}2m, 422, \|4/mmm\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{66} \end{bmatrix}$$

Trigonal

$3, \|\bar{3}\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & -\pi_{25} & 2\pi_{62}^{*} \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & \pi_{25} & -2\pi_{62}^{*} \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & -\pi_{41} & 0 & \pi_{44} & \pi_{45} & 2\pi_{52}^{*} \\ -\pi_{52} & \pi_{52} & 0 & -\pi_{45} & \pi_{44} & 2\pi_{41}^{*} \\ -\pi_{62} & \pi_{62} & 0 & \pi_{25} & \pi_{14} & (\pi_{11}-\pi_{12})^{*} \end{bmatrix}$$

$3m, 32, \|\bar{3}m\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & -\pi_{14} & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ \pi_{41} & -\pi_{41} & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 2\pi_{41}^{*} \\ 0 & 0 & 0 & 0 & \pi_{14} & (\pi_{11}-\pi_{12})^{*} \end{bmatrix}$$

Hexagonal

$6, \bar{6}, \|6/m\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 2\pi_{62}^{*} \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & -2\pi_{62}^{*} \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & \pi_{45} & 0 \\ 0 & 0 & 0 & -\pi_{45} & \pi_{44} & 0 \\ -\pi_{62} & \pi_{62} & 0 & 0 & 0 & (\pi_{11}-\pi_{12})^{*} \end{bmatrix}$$

$6mm, 622, \bar{6}2m, \|6/mmm\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & 0 \\ \pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & (\pi_{11}-\pi_{12})^{*} \end{bmatrix}$$

TABLE 7.1: (continued)

Cubic

23, $\|m3\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\ \pi_{13} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{13} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{44} \end{bmatrix}$$

$\bar{4}32$, 432, $\|m3m\|$

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \pi_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \pi_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \pi_{44} \end{bmatrix}$$

Isotropic

$$\begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{11} & \pi_{12} & 0 & 0 & 0 \\ \pi_{12} & \pi_{12} & \pi_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & (\pi_{11}-\pi_{12})* & 0 & 0 \\ 0 & 0 & 0 & 0 & (\pi_{11}-\pi_{12})* & 0 \\ 0 & 0 & 0 & 0 & 0 & (\pi_{11}-\pi_{12})* \end{bmatrix}$$

To obtain p coefficients, multiply the $^*\pi$ coefficient entries by ½, all others directly convertible. The classes to which each coefficient array belongs is indicated above each array. The coefficient arrays for the elasto-optical coefficients p_{mn} are obtained by replacing π by p except as indicated by an asterisk *.

$$n_{||} - n_{\perp} = \Delta n_2 - \Delta n_1 = \Delta n_2 - \Delta n_3 = -\tfrac{1}{2}(n^0)^3(\pi_{11} - \pi_{12})\sigma_2, \tag{7.56}$$

giving the difference between the refractive index parallel and perpendicular to the stress direction. A similar uniaxial tensile stress analysis on a cubic crystal class *23* or *m3* will show that the crystal becomes biaxial. In short, a cubic crystal becomes optically uniaxial if a tensile stress is applied along any cubic axis but is optically biaxial if a uniaxial tensile stress is applied along any other axis (see Nye in Endnotes for a in-depth treatment of double refraction).

7.3.4 Magneto-Optical (Cotton–Mouton and Faraday) Effects

In the presence of a magnetic field, the dielectric impermeability tensor B_{ij} is no longer symmetrical relative to its subscripts i and j. If the subscripts are interchanged, then the direction of the B field must be reversed. As with any second-rank tensor, the dielectric impermeability tensor can be divided into symmetrical and antisymmetrical parts, B_{ij}^{S} and B_{ij}^{A}, as in Eqs. (2.16), (2.17), and (2.18), respectively. Thus,

$$B_{ij} = B_{ij}^{S} + B_{ij}^{A}. \tag{7.57}$$

This requires that

$$B_{ij}^{S}(B) = B_{ji}^{S}(-B) = B_{ij}^{S}(-B) \tag{7.58}$$

and

$$B_{ij}^{A}(B) = -B_{ji}^{A}(B) = B_{ji}^{A}(-B) = -B_{ij}^{A}(-B). \tag{7.59}$$

By definition, $B_{ij}^{S}(B)$ is an even function of the magnetic flux density B, whereas $B_{ij}^{A}(B)$ is an odd function of B. Given this, the *quadratic magneto-optical effect* can be obtained by expanding the symmetrical part of the dielectric impermeability B_{ij}^{S} in a Taylor's series as an even function of a small externally applied magnetic flux density B about the state of a reference temperature T^0 and zero electric field and zero stress. Thus, the expansion yields coefficients for $n = 0,2,4, \ldots$ in Eq. (2.52), with the result,

$$B_{ij}^{S}(B_k, B_l) = B_{ij}^{S}(0,0) + \frac{1}{2}\left(\frac{\partial^2 B_{ij}^{S}}{\partial B_k \partial B_l}\right) B_k B_l + \cdots \tag{7.60}$$

or

$$\Delta B_{ij}^{S} = F_{ijkl} B_k B_l, \tag{7.61}$$

where

$$F_{ijkl} = \frac{1}{2}\left(\frac{\partial^2 B_{ij}^{S}}{\partial B_k \partial B_l}\right) \tag{7.62}$$

as defined earlier in Section 7.3. Here, F_{ijkl} is a polar, nonmagnetic, fourth-rank tensor property representing the coefficients for the quadratic magneto-optical effect known as the *Cotton–Mouton effect.*

Because there is symmetry in both B_{ij} and the dyadic product $B_k B_l$, Eq. (7.61) can be cast in the form

$$\Delta B_{m}^{S} = F_{mn} B_{n}^{2}, \tag{7.63}$$

for which $B_1^2 = B_1B_1$, $B_2^2 = B_2B_2$, $B_3^2 = B_3B_3$, $B_4^2 = B_2B_3$, $B_5^2 = B_3B_1$, and $B_6^2 = B_1B_2$. Now, the F_{mn} coefficients are related to the F_{ijkl} coefficients by the rules

$$F_{mn} = F_{ijkl} \quad \text{if} \quad n = 1, 2, \text{or } 3$$

$$F_{mn} = 2F_{ijkl} \quad \text{if} \quad n = 4, 5, \text{or } 6.$$

The effects of crystal symmetry on the F_{mn} coefficients are exactly the same as those imposed on the piezo-optical coefficients π_{mn} given in Table 7.1 obtained by replacing π with F.

Qualitatively, the Cotton–Mouton effect can be explained in the following way. When a dielectric is placed in a magnetic field, it may undergo a phase difference or retardation between the velocity of the ordinary light wave and that of the extraordinary light wave. This retardation is proportional to the square of the magnetic flux density B, the difference between Cotton–Mouton moduli, and cube of the refractive index n_0. Thus, the phase difference is directly related to the dielectric impermeability tensor via Eq. (7.61) (for a further discussion, see Landau and Lifshitz in Endnotes).

The antisymmetrical part of B_{ij}, labeled B_{ij}^A, can be expanded in a Taylor's series as an odd function of a small B field about the state of a reference temperature T^0 and zero electric field and stress. This leads to the *linear magneto-optical effect* expressed as

$$B_{ij}^A(B_k) = B_{ij}^A(0) + \left(\frac{\partial B_{ij}^A}{\partial B_k}\right) B_k + \cdots, \tag{7.64}$$

where

$$\left(\frac{\partial B_{ij}^A}{\partial B_k}\right) = f_{ijk}, \tag{7.65}$$

Here, f_{ijk} represents the linear magneto-optical effect known as the *Faraday effect*. Because B_{ij}^A is an antisymmetrical, magnetic, second-rank tensor and B_k is an axial magnetic vector, then f_{ijk} must be an axial, antisymmetrical (in i and j), nonmagnetic tensor of rank three such that

$$f_{ijk}(B) = f_{ijk}(-B) \quad \text{and} \quad f_{ijk} = -f_{jik}. \tag{7.66}$$

However, every antisymmetrical second-rank tensor corresponds to an axial vector or vice versa (see Section 2.6.3). Therefore, by using the permutation tensor e_{lij}, discussed in Section 2.6.3, the combined Eqs. (7.64) and (7.65) can be written for small B fields as

$$\Delta B_{ij}^A = e_{lij}G_l = f_{ijk}B_k, \tag{7.67}$$

where G_l is the axial–magnetic vector corresponding to the antisymmetrical magnetic tensor ΔB_{ij}^{A}. This allows Eq. (7.67) to be presented in the form

$$G_l = \tfrac{1}{6} e_{lij} f_{ijk} B_k = f_{lk} B_k \quad (l, k = 1, 2, 3), \tag{7.68}$$

which results from multiplying both sides of Eq. (7.67) by e_{lij} since the value $e\tilde{e}$ = 2tr(ee) = 6. Here, $f_{lk} = {}^{1}\!/_{6} e_{lij} f_{ijk}$ is a polar, nonmagnetic second-rank tensor for which $f_{lk} \neq f_{kl}$ and is called the *Faraday tensor*. Thus, the third-rank, axial, antisymmetrical Faraday tensor f_{ijk} is related to the polar, asymmetrical, second-rank Faraday tensor f_{lk} via the permutation tensor e_{lij}. The effect of crystal symmetry on f_{lk} can be found by applying the transformation law $f' = af\tilde{a}$ to each crystal class. When this is done, the results are identical to those for the Seebeck effect in Table 9.1 as discussed in Section 9.1.

Qualitatively, the Faraday effect can be explained as follows: When a transparent isotropic magnetic material is subjected to a DC magnetic field and linear polarized light travels parallel or antiparallel to that magnetic field, the plane of polarization is rotated. The angle of rotation is called the *Faraday rotation angle* found to be proportional to the magnetic field strength, the thickness of the transparent medium along the optic axis, and the Faraday tensor considered to be a *Hermitian tensor*. In tensor notation, the Faraday rotation angle is given by

$$\theta_F = f_{lk} H_k x_l = V(\omega) B_i x_i . \tag{7.69}$$

along the optic axis say x_3 and where $B_i = \mu_{ik} H_k$, or for an isotropic material $B = \mu H$. Here, $V(\omega)$ is called the *Verdet coefficient*, which is a function of the frequency ω of the light wave. Further discussion of the Faraday effect is beyond the scope of this text and is left for further study by the reader (see Newnham in Endnotes for additional reading on the subject).

7.3.5 Thermo-Optical Effects

The *linear thermo-optical effect* can be obtained by expanding B_{ij} in a Taylor's series as a function of temperature T about the state of zero applied electric, magnetic, and stress fields. Referring to Eq. (7.34) and retaining only the first-order term in T, we have

$$B_{ij}(T) = B_{ij}(T^0) + \frac{\partial B_{ij}}{\partial T}\Delta T + \cdots \quad \text{or} \quad \Delta B_{ij} = \frac{\partial B_{ij}}{\partial T}\Delta T = t_{ij}\Delta T \tag{7.70}$$

where t_{ij} is the symmetrical, second-rank, linear thermo-optical property tensor that is affected by crystal symmetry according to Table 3.7.

Because the change in temperature of a crystal produces a thermal expansion, t_{ij} contains a *false* (secondary) thermo-optical part in addition to the *true* (primary) part. The two contributions can be expressed as

$$t_{ij} = t'_{ij} + \frac{\partial B_{ij}}{\partial \varepsilon_{kl}} \cdot \frac{\partial \varepsilon_{kl}}{\partial T} = t'_{ij} + p'_{ijkl}\alpha_{kl} = t_{true} + t_{false}. \tag{7.71}$$

Here, p' and α represent the photoelastic and thermal expansion coefficients, respectively. The effect of crystal symmetry on the p' coefficients is the same as the elasto-optical coefficients p obtained from Table 7.1 (see Newnham in Endnotes for additional reading on the subject).

In addition to the linear thermo-optical effect, there also exists the quadratic thermo-optical effect defined in Section 7.3. This effect can be obtained from the continued expansion of Eq. (7.70) given by

$$B_{ij}(T) = B_{ij}(T^0) + \frac{\partial B_{ij}}{\partial T}\Delta T + \tfrac{1}{2}\left(\frac{\partial^2 B_{ij}}{\partial T^2}\right)\Delta T^2 + \cdots$$

or

$$\Delta B_{ij} = \frac{\partial B_{ij}}{\partial T}\Delta T + \tfrac{1}{2}\left(\frac{\partial^2 B_{ij}}{\partial T^2}\right)\Delta T^2 = t_{ij}\Delta T + T_{ij}\Delta T^2 + \cdots. \tag{7.72}$$

The contribution of the $T_{ij}\Delta T^2$ term to the total thermo-optical effect will be, in most cases, negligible compared with the linear thermo-optical effect that will be present.

• • • •

PART II

Transport Properties of Solids

CHAPTER 8

Introduction to Transport Properties and the Thermodynamics of Irreversible Processes

Up to this point, we have concerned ourselves only with equilibrium properties, meaning those that are thermodynamically reversible. We now undertake the considerable task of presenting the concepts of irreversible thermodynamics that are fundamental to the general understanding of the transport properties. To do this will require a somewhat less tangible treatment than was used to discuss the equilibrium properties in Part I. However, every effort will be made to provide a lucid step-by-step presentation of the more complex concepts fundamental to irreversible thermodynamics.

8.1 GRADIENTS, CURRENT DENSITIES, AND THE CONDUCTIVITIES

The steady-state (nonequilibrium) properties are characterized by parameters called *gradients* or *driving forces* and *current densities* or *fluxes*. A list of such parameters is given in Table 8.1.

Here, the gradient of a scalar field $\nabla\phi^{\beta}$ is a vector given generally by

$$\nabla\phi = \text{grad}\phi = \left(\frac{\partial}{x_1}\vec{i} + \frac{\partial}{x_2}\vec{j} + \frac{\partial}{x_3}\vec{k}\right)\phi \quad , \tag{8.1}$$

where $\vec{i}$, $\vec{j}$, and $\vec{k}$ are the unit vectors along Cartesian axes x_1, x_2, and x_3, respectively. The ϕ'*s* are scalar field potentials representing electrostatic potential E, temperature T, and mass concentration C (not to be confused with the symbol C for coulombs). A potential gradient is assumed to be from low to high potential (or concentration). In the case of electrostatic potential gradient, we used the convention that high potential is more positive than low potential. The flux vectors $\vec{J}^{\alpha}$ represent the flow of number of positive test charges n, heat q, and mass m all per square meter per second (m^2/s). A positive test charge is taken to be the charge magnitude on an electron but taken as positive, hence, $+|e|$.

TABLE 8.1: Force–flux (cause–effect) vector parameters and dimensions in SI units for the flow of electric current, heat, and mass

Gradient or affinity (driving force), (cause)	$\nabla\phi^{\beta}$	**Current density (flux), (effect)**	$\vec{J}^{\alpha}$
Electric potential gradient (V/m)	$\nabla\phi^{E}$	Electron current density (no. electrons/m²/s)	$\vec{J}^{n}$
Temperature gradient (°K/m)	$\nabla\phi^{T}$	Heat current density (J/m²/s = W/m²)	$\vec{J}^{q}$
Concentration gradient (kg /m³/m)	$\nabla\phi^{C}$	Mass current density (kg/m²/s)	$\vec{J}^{m}$

Note that SI units are used for the forces and fluxes.

The principal steady-state properties relating cause and effect are given, generally, in tensor subscript notation by

$$-J_i^{\alpha} = K_{ij}^{\alpha\beta}\,\nabla_j\,\phi^{\beta} \tag{8.2}$$

or

$$-J = K \cdot \nabla\phi \tag{8.3}$$

as the single contraction product in vector notation. The minus sign is used to express flow from high to low potential (or from high to low concentration), with $\nabla\phi^{\beta}$ being the driving force. Thus, if a concentration increases in, say, the x direction, then the flow must be in the opposite ($-x$ direction). In the case of electric current flux, we take positive current flow from high to low electrostatic potential. These facts must be kept in mind as we progress through the remainder of this chapter.

We represent $[K_{ij}^{\alpha\beta}]$ as the matrix of conductivities K_{ij}, each of which is a second-rank tensor property. In expanded matrix form and in the absence of a magnetic field, the three equations representing Eq. (8.2) are given by

$$-\begin{bmatrix} J_i^{n} \\ J_i^{q} \\ J_i^{m} \end{bmatrix} = \begin{bmatrix} K_{ij}^{nE} & K_{ij}^{nT} & K_{ij}^{nC} \\ K_{ij}^{qE} & K_{ij}^{qT} & K_{ij}^{qC} \\ K_{ij}^{mE} & K_{ij}^{mT} & K_{ij}^{mC} \end{bmatrix} \begin{bmatrix} \nabla_j\,\phi^{E} \\ \nabla_j\,\phi^{T} \\ \nabla_j\,\phi^{C} \end{bmatrix} \tag{8.4}$$

where, in general, $K_{ij}^{\alpha\beta} \neq K_{ij}^{\beta\alpha}$, meaning that the matrix $[K_{ij}^{\alpha\beta}]$ is not symmetrical. We may take the inversion of Eq. (8.2) to express the matrix of *resistivities* given by

$$-\nabla_i \phi^\beta = (K_{ij}^{\alpha\beta})^{-1} J_j^\alpha = \rho_{ij}^{\beta\alpha} J_j^\alpha \tag{8.5}$$

where, in general, $\rho_{ij}^{\alpha\beta} \neq \rho_{ij}^{\beta\alpha}$ and where $\rho = K^{-1}$. Note that the superscripts in Eqs. (8.2) to (8.5) are for identification purposes only.

8.2 CONJUGATE OR PROPER CONDUCTIVITIES

The three well-known conductivities along the leading diagonal in Eq. 8.4 are presented below together with their corresponding and well-established phenomenological laws.

1. Electrical conductivity: K_{ij}^{nE} or σ_{ij} under constant T

   $$J_i^n = -K_{ij}^{nE} \nabla_j \phi^E \quad \text{or} \quad j_i = \sigma_{ij} E_j \quad (\textit{inverse Ohm's law}), \tag{8.6}$$

   where σ_{ij} is given in units of $(\Omega \cdot \text{m})^{-1}$ = (mho/m) and K_{ij}^{nE} in units of $(\text{m} \cdot \text{s} \cdot \text{V})^{-1}$, consistent with Table 8.1. Note that $E_i = \rho_{ij} j_j$ represents generalized Ohm's law where ρ_{ij} is the resistivity tensor in units of $(\Omega \cdot \text{m})$. It is an accepted common use that $E_j = -\nabla_j \phi^E$ as will be the case in this test.
2. Thermal conductivity: K_{ij}^{qT} or k_{ij} under condition $J^n = 0$

   $$J_i^q = -K_{ij}^{qT} \nabla_j \phi^T \quad \text{or} \quad h_i = -k_{ij} \nabla_j T \quad (\textit{Fourier's law}), \tag{8.7}$$

   where K_{ij}^{qT} and k_{ij} are given in units of (J/s/m °K) = (W/m °K), consistent with Table 8.1.
3. Diffusivity: K_{ij}^{mC} or D_{ij}

   $$J_i^m = -K_{ij}^{mC} \nabla_j \phi^C \quad \textit{or} \quad J_i^m = -D_{ij} \nabla_j C \quad (\textit{Fick's law}), \tag{8.8}$$

   where K_{ij}^{mC} and D_{ij} are given in units of (m²/s), consistent with Table 8.1.

8.3 CROSS OR INTERFERENCE CONDUCTIVITIES

From the matrix of conductivities given in Eq. (8.4), the cross or interference conductivities are given as follows:

1. Thermoelectric coefficients: K_{ij}^{nT} and K_{ij}^{qE}
2. Electrodiffusive coefficients: K_{ij}^{nC} and K_{ij}^{mE}
3. Thermodiffusive coefficients: K_{ij}^{qC} and K_{ij}^{mT}.

But $K_{ij}^{\alpha\beta} \neq K_{ij}^{\beta\alpha}$.

TABLE 8.2: Dimensions in SI units of the conjugate (flux) × (force) products from Table 8.1

$J^n \nabla \phi^E$	$J^q \nabla \phi^T$	$J^m \nabla \phi^C$
V/m^{3}s	W °K/m^3	(kg)^2/s · m^5/m

The fact that $(K^{\alpha\beta})$ and $(K^{\beta\alpha})$ do not produce symmetrical coefficients is not surprising. Recall that for the equilibrium compliances C_{mn} and rigidities R_{mn}, the products of the conjugate parameters $(I_i)(e_i)$ all have dimensions of energy density (energy per unit volume), which allowed, with help of Green's theorem, $C_{mn} = C_{nm}$ and $R_{mn} = R_{nm}$ as indicated in Section 4.4. An inspection of Table 8.2 makes it clear that the conjugate parameters $(J^\alpha)(\nabla\phi^\alpha)$ have no consistent dimensions.

Even if all $(J^\alpha)(\nabla\phi^\alpha)$ products had the dimensions of energy or energy density, it is not clear at this point what the criterion would be for the symmetry $K_{ij}^{\alpha\beta} = K_{ij}^{\beta\alpha}$. The following sections establish this criterion and the general method of representing properties of irreversible processes.

8.4 MARKOFFIAN SYSTEMS, MICROSCOPIC REVERSIBILITY, AND ONSAGER'S RECIPROCITY PRINCIPLE

Before we can discuss the transport properties of solids, we must first consider the fundamental principles of irreversible thermodynamics. The discussion that follows summarizes these principles.

8.4.1 Markoff Processes

For certain processes, the fluxes at any given instant depend on the values of the forces (affinities) at that instant. These processes have no memory and are called *Markoffian processes*. A non-Markoffian system or process has memory in the sense that the fluxes will depend on the forces applied at previous times as well as on those applied at the present. A resistor is an example of a Markoffian system, whereas a capacitor is non-Markoffian.

Generally, the fluxes J_i can be expanded in a power series as functions of the affinities with no constant terms—all J_i are known to vanish as the affinities (forces) X_j vanish. The results give

$$J_i = L_{ij} X_j + \frac{1}{2!} L_{ijk} X_j X_k + \frac{1}{3!} L_{ijkl} X_j X_k X_l + \ldots, \tag{8.9}$$

where $L_{ij} = (\partial J_i / \partial X_j)_{X=0}$ and $L_{ijk} = (\partial^2 J_i / \partial X_j \partial X_k)_{X=0}$ are the kinetic coefficients and second-order kinetic coefficients, respectively, and so forth.

Because the applied affinities are usually very small, a truncated form of the power series of Eq. (8.9) gives to a very good approximation the phenomenological relation

$$J_i^{\alpha} = L_{ij}^{\alpha\beta} X_j^{\beta}, \tag{8.10}$$

which represents a linear Markoff process. Here, J_i^{α} and X_j^{β} are the fluxes and driving forces (affinities), respectively. The $L_{ij}^{\alpha\beta}$ are the *phenomenological coefficients* that are related to the conductivities $K_{ij}^{\alpha\beta}$ but will not, in general, be identical to them. This relationship may be classified by the following:

$L^{\alpha\alpha}$ Related to the conjugate or proper conductivities σ,k, D

$L^{\alpha\beta}(\alpha \neq \beta)$ Related to the cross or interference conductivities as, for example, thermoelectric, electrodiffusive, and thermodiffusive coefficients.

8.4.2 Principle of Microscopic Reversibility

The gap between thermodynamic equilibrium and an irreversible (steady-state) process is bridged by considering the microfluctuations in a system at local equilibrium. With this, we may state the *principle of microscopic reversibility* as follows.

> *For a system in thermodynamic equilibrium, every type of micromotion occurs just as often as its reverse.*

Using fluctuation theory for the small spontaneous motions around thermodynamic equilibrium, Onsager (after Lars Onsager, 1903–1976) proved what is now referred to as Onsager's principle.

8.4.3 Onsager's Reciprocity Principle

A simple statement of *Onsager's theorem* is given as follows:

> *Provided a proper choice is made for the fluxes J_i and driving forces (affinities) X_j, the matrix of phenomenological coefficients (L_{ij}) is symmetrical, that is*

$$L_{ij}^{\alpha\beta} = L_{ji}^{\beta\alpha} \quad \text{and} \quad L_{ij}^{\alpha\alpha} = L_{ji}^{\alpha\alpha} \quad (i, j = 1, 2, \ldots n), \tag{8.11}$$
$$\text{but } L_{ij}^{\alpha\beta} = L_{ji}^{\alpha\beta}.$$

The relationships, Eqs. (8.11), are called *Onsager's reciprocal relations* in the absence of a magnetic field. Note that only the $L^{\alpha\alpha}$ phenomenological coefficients have *self symmetry* in the sense of $L_{ij}^{\alpha\alpha} = L_{ji}^{\alpha\alpha}$.

In a magnetic field, the reciprocal relations for $L^{\alpha\beta}$ that are *even functions* of H must be modified according to

$$L_{ij}^{\alpha\beta}(\vec{H}) = L_{ji}^{\beta\alpha}(-\vec{H}) \quad \text{and} \quad L_{ij}^{\alpha\alpha}(\vec{H}) = L_{ji}^{\alpha\alpha}(-\vec{H}) \quad (i, j = 1, 2, \ldots n), \tag{8.12}$$

which means that $L_{ij}^{\alpha\beta}$ is the same function of $(\vec{H})$ as $L_{ji}^{\beta\alpha}$ is of $(-\vec{H})$. Similarly, $L_{ij}^{\alpha\alpha}$ is the same function of $(\vec{H})$ as $L_{ji}^{\alpha\alpha}$ is of $(-\vec{H})$. These results have their origin in the Lorentz force vector given by $\vec{F} = e(\vec{v} \times \vec{B})$, where e and $\vec{v}$ are the charge and velocity vector of a particle, respectively, $\vec{B}$ is the magnetic flux density vector, and $\vec{v} \times \vec{B}$ indicates the cross product between $\vec{v}$ and $\vec{B}$. The reciprocal relations require that both the velocity and magnetic field strength be reversed to ensure that all particles retrace their former paths. The $L_{ij}^{\alpha\beta}$ coefficients that are odd functions of the magnetic field will be discussed in Section 10.1.

8.4.4 Entropy Production

The criterion for Onsager's reciprocal relations is contained in the expression for entropy density production inside the system undergoing an irreversible process. This is expressed in quadratic form as

$$\dot{s} = \frac{\partial s}{\partial t} = \sum_{\alpha} J^{\alpha} X^{\alpha} = \sum_{\alpha\beta} L^{\alpha\beta} X^{\alpha} X^{\beta} > 0 \quad (\dot{s} \text{ in units of } Energy/l^3tT), \qquad (8.13)$$

where l is length (e.g., meter, m), t is time (e.g., second, s), and T is temperature (e.g., °K) as in the SI system of units for which energy is given in joules, (1 W = 1 J/s). Thus, we take entropy density production as the time variation of unrecoverable work per unit volume per unit temperature inside the system and whose quadratic form must be positive definite. In general, we assert the requirements that

$$\dot{s} = 0 \text{ (reversible process)}$$
$$\dot{s} > 0 \text{ (irreversible process)}$$
$$\dot{s} < 0 \text{ (a process that cannot occur without altering the system conditions).}$$

8.5 PROPER CHOICE OF PARAMETERS

The entropy production criterion allows for some latitude of "proper choice" for the fluxes J^{α} and affinities X^{α}. Thus, authors may differ in their choice for the fluxes and affinities. We will consider the conjugate parameters for the flow of electrical current, entropy (heat), and matter as they relate to reciprocal Ohm's, Fourier's, and Fick's laws, respectively, given in Section 8.1. But in doing this, we will require that the product of the conjugate parameters each have the units of entropy density production $\dot{s}$, that is, $\dot{s}$ in SI units of $Energy / l^3tT$ as in Eq. (8.13).

1. Flow of electronic charge:

$$J^1 = J_i^n = -J_i^e/e = \text{Electron flux (in units of no. electrons}/l^2t),$$

where J^e is the charged electron flux in the direction of the electrostatic potential gradient. The affinity (force) is given by

$$X^1 = \nabla_i \left(\bar{\mu} / T \right) = \left(\nabla_i \bar{\mu} / T \right) \text{ (in units of } Energy/lT\text{)},$$

where

$$\bar{\mu} = \mu_c + e\phi \tag{8.14}$$

is the *electrochemical potential* (total energy per particle, also called the *Fermi level* in the equilibrium state), μ_c is the chemical potential per particle, $e\phi$ is the electrostatic potential per particle, and e is the charge on the particle assumed to be a positive test charge equal to $+|e| = 1.60 \times 10^{-19}$ C. Thus, the inner product of the conjugate parameters for the flow of electronic charge gives the entropy density production per particle as

$$\dot{s} = -J_i^n \nabla_i \left(\bar{\mu} / T \right) \text{(in units of } Energy/l^3tT\text{)}, \tag{8.15}$$

which will later be shown to satisfy the corresponding reciprocity relations. Be aware of the fact that we are using the positive current convention and that high electrostatic potential is more positive than low electrostatic potential. Thus, J_i^n is always in a direction counter to the electrostatic potential gradient, which is from low potential to high potential.

2. Flow of entropy or heat:

$$J^2 = J_i^s = \text{Entropy flux} \quad \text{(in units of } Energy/l^2t\text{)}$$

$$X^2 = T\nabla_i \left(1/T \right) = -\frac{\nabla_i T}{T} \quad \text{(in units of } l^{-1}\text{)}.$$

The inner product of the conjugate parameters for the flow of entropy yields the entropy production as

$$\dot{s} = J_i^s T \nabla_i \left(1/T \right) \text{(in units of } Energy/l^3tT\text{)}, \tag{8.16}$$

which will be shown to satisfy the corresponding reciprocity relations. Alternatively, for our purpose, because $J^q = T J^s$, the conjugate parameters become

$$J^2 = J_j^q = \text{Heat flux (in units of } Energy\,/l^2t\text{)}$$

and

$$X^2 = \nabla_i \left(1/T \right) = -\left(\nabla_i T / T^2 \right) \quad \text{(in units of } (lT)^{-1}\text{,}$$

which gives the entropy density production

$$\dot{s} = J_i^q \, \nabla_i \left({}^{1}\!/_{T} \right) \quad \text{(in units of } \mathit{Energy}/l^3 tT\text{)}, \tag{8.17}$$

3. Flow of matter (uncharged single component):

$$J^3 = J^m = \text{Matter flux} \quad \text{(in units of mole number } N/l^2 t\text{)}$$

$$X^3 = \nabla_i \left({}^{\mu_c}\!/_{T} \right) = \left({}^{\nabla_i \mu_c}\!/_{T} \right) \quad \text{(in units of } \mathit{Energy}/lT\text{)}.$$

Here, the mole number N is defined as the actual number of the diffusing species divided by Avogadro's number. The inner product of the conjugate parameters for the flow of uncharged mass (kg-moles) counter to the concentration gradient of one component gives the entropy density production as

$$\dot{s} = -J_i^m \, \nabla_i \left({}^{\mu_c}\!/_{T} \right) \quad \text{(in units of } \mathit{Energy}/l^3 tT\text{)}, \tag{8.18}$$

which will also be shown to satisfy the corresponding reciprocity relations.

Combining Eqs. (8.15), (8.17), and (8.18) yields the total entropy density production for all three processes as

$$\dot{s} = \sum_i J_i^\alpha X_i^\alpha = -J_i^n \, \nabla_i \left({}^{\bar{\mu}}\!/_{T} \right) + J_i^q \, \nabla_i \left({}^{1}\!/_{T} \right) - J_i^m \nabla_i \left({}^{\mu_c}\!/_{T} \right), \tag{8.19}$$

which are each represented in units of $\mathit{Energy}/l^3 tT$). Thus, the phenomenological relations for the three types of flow can be written in the following matrix forms

$$\begin{bmatrix} -J_i^n \\ J_i^q \\ -J_i^m \end{bmatrix} = \begin{bmatrix} L_{ij}^{11} & L_{ij}^{12} & L_{ij}^{13} \\ L_{ij}^{21} & L_{ij}^{22} & L_{ij}^{23} \\ L_{ij}^{31} & L_{ij}^{32} & L_{ij}^{33} \end{bmatrix} \begin{bmatrix} \nabla_j \left(\bar{\mu}/T \right) \\ \nabla_j \left(1/T \right) \\ \nabla_j \left(\mu_c /T \right) \end{bmatrix}. \tag{8.20}$$

Here, diagonal $L_{ij}^{\alpha\alpha}$ are the principal phenomenological coefficients and the $L_{ij}^{\alpha\beta}$ are the cross or interference coefficients. Onsager's reciprocity theorem permits the following relationships between the phenomenological coefficients in the absence of a magnetic field

$$L_{ij}^{\beta\alpha} = L_{ji}^{\alpha\beta} \;\text{ or }\; L^{\beta\alpha} = \tilde{L}^{\alpha\beta} \;\text{ for } \alpha \neq \beta \;\text{ but }\; L^{\beta\alpha} \neq \tilde{L}^{\alpha\beta}, \;\text{ that is, }\; L_{ij}^{\alpha\beta} \neq L_{ji}^{\alpha\beta}$$

and

$$L_{ij}^{\alpha\alpha} = L_{ji}^{\alpha\alpha} \;\text{ or }\; L^{\alpha\alpha} = \tilde{L}^{\alpha\alpha} \;\text{ for } \alpha = \beta.$$

Thus, only the $L_{ij}^{\alpha\alpha}$ are self-symmetrical.

The reciprocal relations are best illustrated for a three-dimensional system in which only electric current and heat flow occurs. Accordingly, Eqs. (8.20) now become

$$\begin{bmatrix} -J_1^n \\ -J_2^n \\ -J_3^n \\ J_1^q \\ J_2^q \\ J_3^q \end{bmatrix} = \begin{bmatrix} L_{11}^{11} & L_{12}^{11} & L_{31}^{11} & L_{11}^{12} & L_{12}^{12} & L_{13}^{12} \\ L_{12}^{11} & L_{22}^{11} & L_{23}^{11} & L_{21}^{12} & L_{22}^{12} & L_{23}^{12} \\ L_{31}^{11} & L_{23}^{11} & L_{33}^{11} & L_{31}^{12} & L_{32}^{12} & L_{33}^{12} \\ L_{11}^{12} & L_{21}^{12} & L_{31}^{12} & L_{11}^{22} & L_{12}^{22} & L_{31}^{22} \\ L_{12}^{12} & L_{22}^{12} & L_{32}^{12} & L_{12}^{22} & L_{22}^{22} & L_{23}^{22} \\ L_{13}^{12} & L_{23}^{12} & L_{33}^{12} & L_{31}^{22} & L_{23}^{22} & L_{33}^{22} \end{bmatrix} \cdot \begin{bmatrix} \nabla_1 \left(\bar{\mu}/T \right) \\ \nabla_2 \left(\bar{\mu}/T \right) \\ \nabla_3 \left(\bar{\mu}/T \right) \\ \nabla_1 \left(1/T \right) \\ \nabla_2 \left(1/T \right) \\ \nabla_3 \left(1/T \right) \end{bmatrix}, \qquad (8.21)$$

where $L^{11} = \tilde{L}^{11}$, $L^{22} = \tilde{L}^{22}$, and $L^{21} = \tilde{L}^{12}$, meaning that $L_{ij}^{21} = L_{ji}^{12}$, but $L^{12} \neq \tilde{L}^{12}$.

8.5.1 Further Restrictions on the Phenomenological Coefficients

Relating the entropy production given in Equation (8.13) to the phenomenological coefficients provides a first step in formalizing a unified theory of the cross (interaction) effects as they relate to the conjugate effects for linear, first-order, irreversible processes. For conditions under which Eq. (8.10) is valid, the quadratic form of the entropy production as given earlier is

$$\dot{s} = \sum_{\alpha\beta} L^{\alpha\beta} X^{\alpha} X^{\beta} > 0, \qquad (8.22)$$

which is positive definite and implies that the matrix of phenomenological coefficients $L^{\alpha\beta}$ also be positive definite. For this to be so requires that that determinant of the $L^{\alpha\beta}$ matrix and all of its minors be positive definite. Take, for example, a two-flow process involving a two-dimensional matrix $L^{\alpha\beta}$ given by

$$\begin{bmatrix} J^1 \\ J^2 \end{bmatrix} = \begin{bmatrix} L^{11} & L^{12} \\ L^{21} & L^{22} \end{bmatrix} \begin{bmatrix} X^1 \\ X^2 \end{bmatrix}, \qquad (8.23)$$

where $L^{12} = L^{21}$ according to Onsager's principle. The necessary and sufficient condition for Eq. (8.23) to be positive definite is that the 2×2 determinant of $L^{\alpha\beta}$ be positive definite. Thus,

$$\begin{vmatrix} L^{11} & L^{12} \\ L^{21} & L^{22} \end{vmatrix} = L^{11} L^{22} - \left(L^{12} \right)^2 > 0. \qquad (8.24)$$

Generally, the diagonal coefficients $L^{\alpha\alpha} > 0$ (i.e., are positive), but the $L^{\alpha\beta}$ coefficients can be positive or negative. Applying Eq. (8.13) to the flow of electric charge and heat given in Eq. (8.20), we would write the entropy production for any two-flow process as

$$\dot{s} = \sum_{\alpha\beta} L^{\alpha\beta} X^{\alpha} X^{\beta} = \left(L^{\alpha\alpha} X^{\alpha} X^{\alpha} + 2L^{\alpha\beta} X^{\alpha} X^{\beta} + L^{\beta\beta} X^{\beta} X^{\beta}\right) > 0 \qquad (8.25)$$

or specifically for the flow of electric charge and heat

$$\dot{s} = L^{11}\left\{\nabla\left(\frac{\bar{\mu}}{T}\right)\right\}^{2} + 2L^{12}\left\{\nabla\left(\frac{\bar{\mu}}{T}\right)\cdot\nabla\left(\frac{1}{T}\right)\right\} + L^{22}\left\{\nabla\left(\frac{1}{T}\right)\right\}^{2} > 0, \qquad (8.26)$$

where each of the quadratic terms is given in units of $Energy/l^{3}tT$. Now back to Eq. (8.23), the value of the 2×2 determinant given by Eq. (8.24) requires that

$$L^{11}L^{22} > (L^{12})^{2}, \qquad (8.27)$$

which must be valid if the $L^{\alpha\beta}$ matrix is to obey Onsager's reciprocal relations $L^{12} = L^{21}$. Note that $L^{11}L^{22}$ and $(L^{12})^{2}$ both have units of $T^{2}(l \cdot t)^{-2}$ for the flow of electric charge and heat.

8.6 FLOW OF ELECTRONIC CHARGE AND HEAT—THE CONDUCTIVITIES

A basic postulate in irreversible thermodynamics states that "every observed flux depends on all the affinities (driving forces) applied." This means that the electronic and heat fluxes must depend on their conjugate affinities as well as the cross affinities. Thus, the flow of electrons not only transport charge but also heat (recall what Joule heat is when electric current flows through a resistor). The flow of mass in this case is considered negligible. With these concepts in mind, consider the simultaneous flow of electron current and heat in a system whose phenomenological equations for the thermoelectric effects are from Eq. (8.20) given by

$$-J_{i}^{n} = L_{ij}^{11}\nabla_{j}\left(\bar{\mu}/T\right) + L_{ij}^{12}\nabla_{j}\left(1/T\right) \qquad (8.28)$$

$$J_{i}^{q} = L_{ji}^{12}\nabla_{j}\left(\bar{\mu}/T\right) + L_{ij}^{22}\nabla_{j}\left(1/T\right) \qquad (8.29)$$

The phenomenological coefficients L_{ij} in Eqs. (8.28) and (8.29) can now be related to the familiar conductivities σ_{ij} and k_{ij}. We begin with the *electrical conductivity* σ_{ij}, which is defined as the electric current density $-eJ_{i}^{n}$ per unit potential gradient $\nabla\phi = \nabla\bar{\mu}/e$ in an isothermal system, the latter being essentially an electromotive force because $\nabla\mu_{c} = 0$, giving $\nabla\bar{\mu} = e\,\nabla\phi$. Therefore, under isothermal conditions, Eq. (8.28) becomes

$$-J_{i}^{n} = L_{ij}^{11}\left(1/T\right)\nabla_{j}\,\bar{\mu} = eL_{ij}^{11}\frac{\nabla_{j}\,\phi}{T} \quad \text{for } \nabla T = 0$$

and

$$\sigma_{ij} \equiv \frac{-eJ_i^n}{\nabla_j \phi} = e^2 L_{ij}^{11} / T = \sigma_{ji} \,, \tag{8.30}$$

which indicates symmetry of the electrical conductivity, $\sigma_{ij} = \sigma_{ji}$ because $L_{ij}^{11}\ \ L_{ji}^{11}$. Thus, the electrical conductivity is a symmetrical second-rank tensor with the component array given by Eq. (2.17). Solving for L_{ij}^{11} in Eq. (8.30) gives

$$L_{ij}^{11} = T\sigma_{ij} / e^2. \tag{8.31}$$

Next, we turn to the *heat conductivity* defined as the heat current density per unit temperature gradient for zero electric current, $J^n = 0$. For this purpose, Eqs. (8.28) and (8.29) become

$$0 = L_{ij}^{11} \nabla_j \left({}^{\bar{\mu}}\!/_{T} \right) - L_{ij}^{12} \left({}^{\nabla_j T}\!/_{T^2} \right) \tag{8.32}$$

and

$$J_i^q = L_{ji}^{12} \nabla_j \left({}^{\bar{\mu}}\!/_{T} \right) - L_{ij}^{22} \nabla_j \left({}^{\nabla_j T}\!/_{T^2} \right). \tag{8.33}$$

Solving for $\nabla_j \left({}^{\bar{\mu}}\!/_{T} \right)$ in Eq. (8.32) gives, with subscripts excluded for simplicity,

$$\nabla \left({}^{\bar{\mu}}\!/_{T} \right) = (L^{11})^{-1} L^{12} \left({}^{\nabla T}\!/_{T^2} \right), \text{ for } J^n = 0$$

which when substituted into Eq. (8.33) yields

$$J^q = \left\{ \tilde{L}^{12} (L^{11})^{-1} L^{12} - L^{22} \right\} \left({}^{\nabla T}\!/_{T^2} \right). \tag{8.34}$$

The thermal conductivity tensor, defined as the heat current density $-J_i^q$ per unit temperature gradient $\nabla_j T$, now becomes

$$k_{ij} = -\frac{J_i^q}{\nabla_j T} = \frac{1}{T^2} \left\{ L_{ij}^{22} - L_{ji}^{12} \left(L_{ij}^{11} \right)^{-1} L_{ij}^{12} \right\} = \frac{L_{ij}^{11} L_{ij}^{22} - (L^{12})^2}{L_{ij}^{11} T^2} = \frac{|D_L|}{L_{ij}^{11} T^2}, \tag{8.35}$$

where by Eq. (8.11) $L_{ji}^{12} = L_{ij}^{12} = \tilde{L}^{12}$, and $|D_L| > 0$ is the determinant of the phenomenological coefficients. Here, $(L^{12})^2$ is a symmetrical square matrix often represented as $L^{12}\tilde{L}^{12}$ in matrix symbology. Because L^{11}, L^{22}, and $(L^{12})^2$ are all symmetrical square matrices, we are permitted to state that

$$k_{ij} = k_{ji} \tag{8.36}$$

Thus, $k_{ij} = k_{ji}$ if $\left(\tilde{L}^{12}(L^{11})^{-1}L^{12}\right)^t = \tilde{L}^{12}(L^{11})^{-1}L^{12}$, which it does since $(ABC)^t = (\tilde{C}\tilde{B}\tilde{A})$ or in this case, $(\tilde{A}B^{-1}A)^t = \tilde{A}B^{-1}A$. A potential problem with this has been pointed out by Casimir in Nye's *Physical Properties of Crystals* (see Endnotes). Only if the antisymmetrical part of k_{ij} (see Eq. (2.16)) is negligibly small or unobservable can Eq. (8.36) be justified. Given the validity of Eq. (8.36), the component array for k_{ij} as a symmetrical second-rank tensor is given by Eq. (2.17).

Solving for L^{22}_{ij} in Eq. (8.35) and introducing Eq. (8.31) yields the results

$$L^{22}_{ij} = \left(L^{12}\right)^2 \left(L^{11}_{ij}\right)^{-1} + k_{ij}T^2 = \left({}^{e^2}\!/_{T} \right)\left(L^{12}\right)^2\left(\sigma_{ij}\right)^{-1} + T^2 k_{ij}. \tag{8.37}$$

We can now write Eqs. (8.28) and (8.29) in terms of the conductivities σ_{ij} and k_{ij} by introducing the expressions for L^{11}_{ij} and L^{22}_{ij} in Eqs. (8.31) and (8.37) with the results

$$-J^n_i = \left(\frac{T\sigma_{ij}}{e^2}\right)\nabla_j\left({}^{\bar{\mu}}\!/_{T} \right) + L^{12}_{ij}\nabla_j\left({}^{1}\!/_{T} \right) \tag{8.38}$$

$$J^q_i = L^{12}_{ji}\nabla_j\left({}^{\bar{\mu}}\!/_{T} \right) + \left[T^2 k_{ij} + \frac{e^2}{T}(L^{12})^2(\sigma_{ij})^{-1}\right]\nabla_j\left({}^{1}\!/_{T} \right), \tag{8.39}$$

where $(L^{12})^2 = L^{12}_{ji}L^{12}_{ij} = L^{12}\tilde{L}^{12}$. Equations (8.38) and (8.39) give the generalized force–flux expressions for the dual flows of electricity and heat in an anisotropic solid both in terms of the conductivities σ_{ij} and k_{ij} and the cross-coupled phenomenological coefficient L^{12}_{ij} yet to be determined in Section 9.1. By dropping the subscripts i and j, these equations can be applied to the one-dimensional flow of electricity and heat in a homogeneous isotropic wire or rod.

We end this section by defining *thermal resistivity tensor* r_{ij} as the inverse of the thermal conductivity tensor. Following Eq. (2.35), the inverse of k_{ij} is r_{ij} given by

$$r_{ij} = -\frac{\nabla_i T}{J^q_j} \tag{8.40}$$

or in matrix notation $r = k^{-1}$.

$$(k_{ij})^{-1} = \frac{(-1)^{(i+j)}\ |M_{ji}|}{|k_{ij}|} = r_{ij} = r_{ji}, \tag{8.41}$$

where $|M_{ji}|$ is the ji^{th} minor of $|k_{ij}|$, indicating that any individual component of r_{ij} is not the simple reciprocal of k_{ij} component. The same reasoning applies to the relationship between the electrical conductivity σ_{ij} and resistivity ρ_{ij} expressed by $(\sigma_{ij})^{-1} = \rho_{ij}$.

• • • •

CHAPTER 9

Thermoelectric, Piezothermoelectric, and Diffusive Effects in Solids

In previous sections, we dealt mainly with the conduction of electricity and heat as two separate processes. This was done to formalize the conductivity definitions and define the phenomenological coefficients L_{ij}^{11} and L_{ij}^{22} in terms of the proper conductivities σ_{ij} and k_{ij}. Now we will consider the simultaneous flow of electricity and heat usually referred to as the thermoelectric effects or, more specifically, the Seebeck, Peltier, and Thomson effects. In doing this, we will recognize that the irreversible processes involved interfere with one another. Thus, we will have to take into account the cross coupled or interference effects by making use of the developments given in Section 8.4. To simplify the treatment given here, we will begin with the isotropic case and then move to the generalized case of the anisotropic solids. In fact, it will be instructive to switch back and forth between the isotropic and anisotropic nomenclature as needed.

9.1 SEEBECK EFFECT (THERMOCOUPLE EFFECT)

The Seebeck effect is defined as the production of an open-circuit voltage or thermoelectric electromotive force between two dissimilar conductors held at different temperatures under conditions of $J^n = 0$. This is, of course, the means by which one can measure a temperature difference by means of a calibrated thermocouple. The physical picture of the thermocouple is illustrated in Figure 9.1 where an ideal capacitor is placed in a circuit that consists of the two dissimilar conducting wires A and B attached to large heat reservoirs held at high and low temperatures designated as T_{H} and T_{L}. The presence of the ideal capacitor ensures that $J^n = 0$. The potential difference $\Delta\phi$ is the thermoelectric voltage difference between high and low potential measured across the capacitor held at the reference temperature T_0. High potential is taken as being more positive than low potential.

From Eq. (8.32), with subscripts removed and with $\nabla\mu_c = 0$, we have

$$\nabla\,\overline{\mu} = e\nabla\phi = \frac{L^{12}}{TL^{11}}\nabla T\,. \tag{9.1}$$

In a continuous conducting media, the *absolute thermoelectric power* Σ is defined generally as the electrostatic potential gradient per unit temperature gradient when $J^n = 0$. However, in the case of

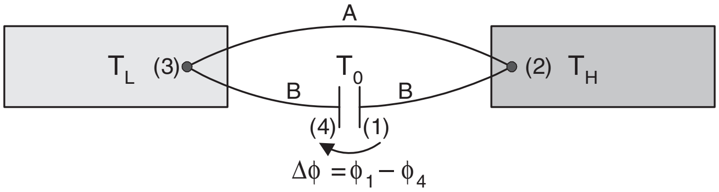


FIGURE 9.1: Thermocouple setup showing two dissimilar metals A and B joined at junctions that are maintained at different temperature T_H and T_L.

Figure 9.1, there can be no temperature gradient across the open circuit of the ideal capacitor. Thus, the absolute thermoelectric power Σ must be defined as the change in electrostatic voltage potential per unit change in temperature relative to the heat reservoirs. Thus, by using Eqs. (9.1) and (8.31), we have

$$\Sigma \equiv \frac{\nabla \phi}{\nabla T} = \frac{L^{12}}{eTL^{11}} = \frac{eL^{12}}{T^2\sigma} \text{ in units of (V/°K)} \tag{9.2}$$

in terms of L^{12} and σ. Solving for L^{12} then gives the result

$$L^{12} = \frac{T^2\sigma}{e}\Sigma. \tag{9.3}$$

From Figure 9.1, because there is no temperature gradient across the capacitor held at temperature T^0, we can sum the electrostatic potential differences as

$$\begin{aligned}\Delta\phi &= \phi_1 - \phi_4 = (\phi_1 - \phi_2) + (\phi_2 - \phi_3) + (\phi_3 - \phi_4) \\ &= \int_{T_\mathrm{H}}^{T_0} \Sigma_\mathrm{B}\, \mathrm{d}T + \int_{T_\mathrm{L}}^{T_\mathrm{H}} \Sigma_\mathrm{A}\, \mathrm{d}T + \int_{T_0}^{T_\mathrm{L}} \Sigma_\mathrm{B}\, \mathrm{d}T \\ &= \int_{T_\mathrm{L}}^{T_\mathrm{H}} (\Sigma_\mathrm{A} - \Sigma_\mathrm{B})\, \mathrm{d}T \cdot\end{aligned}$$

Therefore, the resulting absolute thermoelectric power for the thermocouple becomes

$$\Sigma_\mathrm{AB} = \frac{\Delta\phi_\mathrm{AB}}{\Delta T} = \left(\frac{L_\mathrm{A}^{12}}{eTL_A^{11}}\right) - \left(\frac{L_\mathrm{B}^{12}}{eTL_\mathrm{B}^{11}}\right) = \Sigma_\mathrm{A} - \Sigma_\mathrm{B} \tag{9.4}$$

In tensor notation, we write Eq. (9.2) applied to an anisotropic medium as

$$\Sigma_{ij} = \frac{\nabla_i \phi}{\nabla_j T} = \frac{L_{ij}^{12}(L_{ij}^{11})^{-1}}{eT} \neq \Sigma_{ji} \tag{9.5}$$

since $L_{ij}^{12} \neq L_{ji}^{12}$.

By introducing Eq. (9.3) into Eqs. (8.38) and (8.39), we can cast these thermoelectric equations into forms containing physically measurable quantities (σ, k, and Σ) as they apply to a thermoelectric junction composed of two different isotropic conductors. When this is done, the results are, excluding subscripts,

$$-J^n = \left(\frac{T\sigma}{e^2}\right)\nabla\left(\mu/T\right) + \frac{T^2\sigma\Sigma}{e}\nabla\left(1/T\right) \tag{9.6}$$

$$J^q = \frac{T^2\sigma\Sigma}{e}\nabla\left(\mu/T\right) + T^2\left[k + T\sigma\Sigma^2\right]\nabla\left(1/T\right). \tag{9.7}$$

Then, by eliminating $\nabla\left(\mu/T\right)$ between Eqs. (9.6) and (9.7), there results

$$\nabla\left(\mu/T\right) = -\frac{e^2 J^n}{T\sigma} + \frac{e\Sigma}{T}\nabla T. \tag{9.8}$$

Finally, by introducing Eq. (9.8) into Eq. (9.7) with $\nabla(1/T) = -\nabla T/T^2$ and with a little algebra, Eq. (9.7) can be written in the useful alternative form

$$J^q = -eT\Sigma J^n - k\nabla T = TJ^s \tag{9.9}$$

which provides another definition for the thermoelectric power given by

$$\Sigma \equiv -\frac{1}{eT}\left(\frac{J^q}{J^n}\right)_{\nabla T=0} = \left(\frac{J^s}{J^e}\right)_{\nabla T=0}, \tag{9.10}$$

where $J^n = -J^e/e$ and $J^q = TJ^s$.

TABLE 9.1: Effect of crystal symmetry on Σ_{ij} for the tetragonal, trigonal, and hexagonal systems, all others being the same as in Table 3.7 except that $\Sigma_{ij} \neq \Sigma_{ji}$

CLASSES	CLASSES
$4, \bar{4}, \Vert 4/m \Vert, 3, \Vert \bar{3} \Vert$ $6, \bar{6}, \Vert 6/m \Vert$	$4mm, \bar{4}2m, 422, \Vert 4/mmm \Vert, 3m, 32, \Vert \bar{3}m \Vert$ $\Vert \bar{6}m2 \Vert, 6mm, 622, \Vert 6/mmm \Vert$
$\begin{bmatrix} \Sigma_{11} & \Sigma_{12} & 0 \\ -\Sigma_{12} & \Sigma_{11} & 0 \\ 0 & 0 & \Sigma_{33} \end{bmatrix}$	$\begin{bmatrix} \Sigma_{11} & 0 & 0 \\ 0 & \Sigma_{11} & 0 \\ 0 & 0 & \Sigma_{33} \end{bmatrix}$

To apply Eqs. (9.6) and (9.7) to an anisotropic solid, one need only reinstall the subscripts and take into account the affect of crystal symmetry on the property tensors—all of which are second-rank tensors but only Σ_{ij} is nonsymmetrical.

The effect of crystal symmetry on the Σ_{ij} components follows Table 3.7 for S_{ij} with the following changes: 1) crystal systems are the same as S_{ij} except that $\Sigma_{ij} \neq \Sigma_{ji}$ and 2) the uniaxial group of tetragonal, trigonal, and hexagonal systems is given as in Table 9.1.

9.2 PELTIER EFFECT (THERMOELECTRIC HEATER/REFRIGERATOR EFFECT)

The Peltier effect is defined as the evolution or absorption of heat accompanying the flow of electric current across an isothermal junction between two dissimilar conductors or semiconductors. That is, when J^n flows across a junction, heat must be removed or added continuously to maintain the junction at constant temperature, T. This is illustrated in Figure 9.2.

Because $\nabla T = 0$ at the junction (the junction is at constant T), Eq. (9.9) applies as

$$J^q = -eT\Sigma J^n = TJ^s. \tag{9.11}$$

Then the difference in heat flow is

$$J^q_A - J^q_B = -eT(\Sigma_A - \Sigma_B)J^n = -eT\Sigma_{AB} J^n, \tag{9.12}$$

where Σ_{AB} is the thermoelectric power of the AB junction.

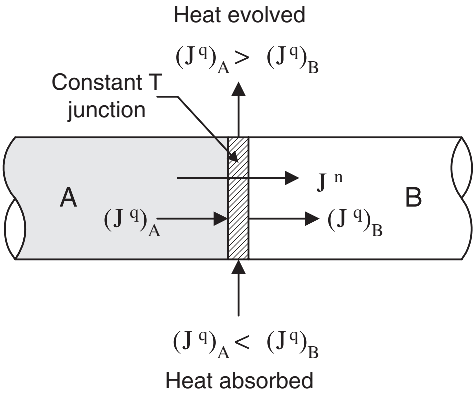


FIGURE 9.2: Schematic illustrating the Peltier effect.

By definition, the *Peltier coefficient* Π is the heat that must be removed from the isothermal junction AB per unit electric current flux from conductor A to conductor B as depicted in Figure 9.2. This is expressed by

$$\Pi_{\mathrm{AB}} \equiv \left(\frac{J^q_{\mathrm{B}} - J^q_{\mathrm{A}}}{eJ^n} \right)_{\nabla T = 0} = T\,\Sigma_{\mathrm{AB}}, \tag{9.13}$$

giving the relationship between the Peltier and Seebeck (thermoelectric power) coefficients. Equation (9.13) is known as the *first Kelvin relation*. Thus, if $(J^q_{\mathrm{A}} - J^q_{\mathrm{B}}) > 0$, heat must be issued from the isothermal junction AB to the surroundings (thermoelectric heating). Or if $(J^q_{\mathrm{A}} - J^q_{\mathrm{B}}) < 0$, heat must be supplied to (absorbed by) the isothermal junction from the surroundings (thermoelectric cooling) as illustrated in Figure 9.2.

In tensor notation, applicable to anisotropic crystals, the Peltier and Seebeck coefficients are related according to

$$\Pi_{ij} = T\Sigma_{ij} \neq \Pi_{ji} \ \text{ since } \Sigma_{ij} \neq \Sigma_{ji}, \tag{9.14}$$

where the effect of crystal symmetry for Π_{ij} is the same as that for Σ_{ij} given in Table 9.1. It should be noted that the developments presented by Eqs. (9.11), (9.12), and (9.13) apply to homogeneous isotropic conducting materials.

9.3 THOMSON EFFECT

Consider a homogeneous conducting rod of uniform cross section that has established a steady-state heat flow J^q in the absence of an electric current. Assume that the surroundings are heat reservoirs having the same temperature distribution as the rod. Now, if an electric current J^n is allowed to flow through this material, heat must be emitted to or absorbed from the surroundings

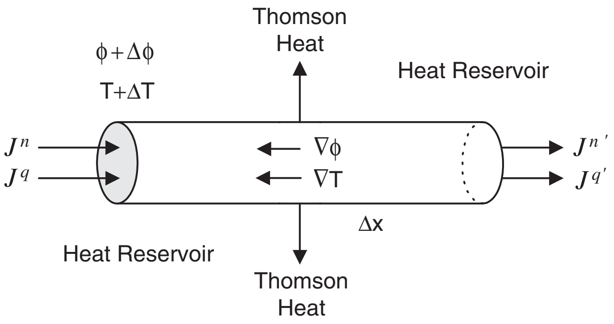


FIGURE 9.3: Schematic illustrating the Thomson effect in a homogenous rod element Δx of a constant cross section carrying heat and electric currents and surrounded by heat reservoirs.

to maintain the steady temperature distribution. This is what is called the *Thomson effect* (after Sir William Thomson, who later became Lord Kelvin), and the heat that is exchanged in this process is called the *Thomson heat* as depicted by the closed system in Figure 9.3. Whether the Thomson heat is emitted to or absorbed from the surroundings depends on the direction and magnitude of the electric current relative to the heat flow.

We now establish an energy flow balance given by fluxes

$$J_i^u = J_i^q + \bar{\mu} J_i^n , \tag{9.15}$$

where J_i^u is the total energy flow along the rod and $\bar{\mu}$ is the total energy carried per particle. Thus, as the electric current flows through the conducting rod, any change in the total energy flow must be supplied by a Thomson heat interchange with the surroundings. Introducing Eq. (9.9) into (9.15) yields

$$J_i^u = -eT\Sigma_{ji} J_j^n - k_{ij}\nabla_j T + \bar{\mu} J_i^n = (eT\Sigma_{ji} + \delta_{ji}\bar{\mu})\, J_j^n - k_{ij}\nabla_j T, \tag{9.16}$$

where the substitution property of the Kronecker delta δ_{ji} has been used (see Section 2.6.3). The rate at which energy is interchanged between the rod element and the surroundings in Figure 9.3 is the divergence (Section 2.6.2) of Eq. (9.16) represented by

$$\nabla_i J_i^u = -eT\nabla_i\,(J_j^n \Sigma_{ji}) - (e\,\Sigma_{ji}\nabla_i T - \delta_{ji}\nabla_i \bar{\mu})\, J_j^n - \nabla_i\,(k_{ij}\nabla_j T). \tag{9.17}$$

But from Eq. (9.8)

$$\nabla_j \bar{\mu} = T\nabla_j \left({}^{\bar{\mu}}\!/\!{}_{T} \right) = -e^2 J_i^n \sigma_{ji}^{-1} + e\Sigma_{ji}\nabla_i T \tag{9.18}$$

or

$$e^2 \sigma_{ji}^{-1} J_i^n = (e\Sigma_{ji}\nabla_i T - \delta_{ji}\nabla_i \bar{\mu}) \tag{9.19}$$

because $\delta_{ji}\nabla_i \bar{\mu} = \nabla_j \bar{\mu}$.

Introducing Eq. (9.19) into Eq. (9.17) yields

$$\nabla_i J_i^u = \underset{\text{Thermoelectric heat}}{-\,eT\nabla_i(J_j^n\,\Sigma_{ji})} \underset{\text{Joule heat}}{-\,e^2\rho_{ji} J_i^n J_j^n} \underset{\text{Conduction}}{-\,\nabla_i(k_{ij}\nabla_j T)}, \tag{9.20}$$

where $\sigma_{ij}^{-1} = \rho_{ij}$ and $e^2\rho_{ji} J_i^n J_j^n$ is the Joule (I^2R) heat that is generated by current flow through a conductor even in the absence of a temperature gradient. But for the steady-state conditions, $J^n = 0$ and $\nabla \cdot J^n = 0$, it follows that $\nabla \cdot J^u$ must vanish. If we set $\nabla \cdot J^n = 0$ and $\nabla \cdot J^u = 0$, we have

$$\left\{\nabla_i\,(k_{ji}\nabla_j T)\right\}_{\substack{\nabla\cdot J^n = 0 \\ \nabla\cdot J^u = 0}} = 0\,,$$

which gives the result

$$\nabla_i J_i^u = \underbrace{-eT\nabla_i(J_j^n \Sigma_{ji})}_{\text{Thermoelectric heat}} - \underbrace{e^2 \rho_{ji} J_i^n J_j^n}_{\text{Joule heat}} . \tag{9.21}$$

We now note that the thermoelectric power Σ_{ji} is a function of the local temperature represented as $\nabla_i\Sigma_{ji} / \nabla_i T = \partial\Sigma_{ji} / \partial T$, which allows

$$\nabla_i \Sigma_{ji} = \left(\frac{\partial \Sigma_{ji}}{\partial T}\right)\nabla_i T . \tag{9.22}$$

Introducing Eq. (9.22) into Eq. (9.21) yields

$$\begin{aligned} \nabla_i J_i^u &= \underbrace{-T\frac{\partial \Sigma_{ji}}{\partial T}\nabla_i TeJ_j^n}_{\text{Thomson heat}} - \underbrace{e^2\rho_{ji} J_i^n J_j^n}_{\text{Joule heat}} \\ &= \underbrace{-\tau_{ji}\nabla_i TeJ_j^n}_{\text{Thomson heat}} - \underbrace{e^2\rho_{ji} J_i^n J_j^n}_{\text{Joule heat}} \end{aligned} \tag{9.23}$$

Here,

$$\tau_{ji} = T\frac{\partial \Sigma_{ji}}{\partial T} \neq \tau_{ij} \tag{9.24}$$

is the Thomson heat coefficient, which is seen to be an asymmetrical second-rank tensor where the effect of crystal symmetry follows that for $\Sigma_{ji} \neq \Sigma_{ij}$ in Table 9.1. Equation (9.24) is known as the second Kelvin relation. Thus, the Thomson heat is the heat evolved or absorbed per unit volume per unit time depending on the direction and magnitude of the current J_i^n relative to the Joule heat it produces. The Thomson coefficient is usually (but not always) defined as positive if heat must be added to (absorbed by) the element in Figure 9.3 so as to maintain the steady-state temperature distribution in the element. Notice that the Thomson heat (proportional to J^n) changes sign when the current density is reversed but that the Joule heat does not because it is proportional to the square of the current density.

The foregoing results apply generally to an anisotropic conducting material. However, they can be applied to homogeneous isotropic conductors or semiconductors by dropping subscripts except for a suffix indicating a specific direction along which the heat effects are generated. When this is done, for example, Eq. (9.23) becomes

$$\nabla J^u = \underbrace{-\tau\nabla TeJ^n}_{\text{Thomson heat}} - \underbrace{e^2\rho\,(J^n)^2}_{\text{Joule heat}} . \tag{9.25}$$

This single direction would apply to one-dimensional flow in the longitudinal direction of the conducting rod (e.g., the x direction). In the isotropic case, the Thomson coefficient is given by the known isotropic value for τ when substituted for the S cubic (diagonal) values presented in Table 3.7.

9.4 PIEZOTHERMOELECTRIC AND ELASTOTHERMOELECTRIC EFFECTS

From what we have learned so far in this chapter, the thermoelectric power tensor Σ_{ij} is fundamental to a general description of the three thermoelectric effects discussed in Sections 9.1, 9.2, and 9.3. However, in practical experimental situations, both temperature and stress variation of the thermoelectric power may be involved. Assuming that Σ_{ij} is everywhere, a continuous function of temperature and stress and that its derivatives with respect to temperature T and stress σ_{kl} are real, we may expand Σ_{ij} in a Taylor's series about the state of reference temperature T_0 and zero applied stress (neglecting gravitational forces and body torques). When this is done, we have

$$\begin{aligned}\Sigma_{ij}(T,\sigma_{kl}) &= \sum_{n=0}^{\infty}\frac{1}{n!}\left\{(T-T_0)\frac{\partial}{\partial T}+\sigma_{kl}\frac{\partial}{\partial\sigma_{kl}}\right\}^n \Sigma_{ij}(T_0,0)\\ &= \Sigma_{ij}(T_0,0)+\left(\frac{\partial\Sigma_{ij}}{\partial T}\right)_{(T_0,0)}(T-T_0)+\left(\frac{\partial\Sigma_{ij}}{\partial\sigma_{kl}}\right)_{(T_0,0)}\sigma_{kl}\\ &\quad+\frac{1}{2!}\left[\left(\frac{\partial^2\Sigma_{ij}}{\partial T^2}\right)_{(T_0,0)}(T-T_0)^2+2\left(\frac{\partial^2\Sigma_{ij}}{\partial T\partial\sigma_{kl}}\right)_{(T_0,0)}(T-T_0)\sigma_{kl}\right.\\ &\quad\left.+\left(\frac{\partial^2\Sigma_{ij}}{\partial\sigma_{kl}\partial\sigma_{op}}\right)_{(T_0,0)}\sigma_{kl}\,\sigma_{op}\right]+\cdots,\end{aligned} \tag{9.26}$$

where Σ_{ij} $(T_0, 0)$ and all coefficients (in parentheses) are evaluated at temperature T_0 and zero stress.

Assuming that all measurements are to be conducted at a reference temperature of $T = T_0$ and that all second- and higher-order terms in stress can be neglected, Eq. (9.26) becomes

$$\Delta\Sigma_{ij}=\Sigma_{ij}(T_0,\sigma_{kl})-\Sigma_{ij}(T_0,0)=\left(\frac{\partial\Sigma_{ij}}{\partial\sigma_{kl}}\right)_{(T_0,0)}\sigma_{kl}=\Pi_{ijkl}\,\sigma_{kl}, \tag{9.27}$$

where Π_{ijkl} is a fourth-rank polar tensor called the *piezothermoelectric power tensor*, not to be confused with the Peltier coefficient Π. Because σ_{kl} is symmetrical but $\Delta\Sigma_{ij}$ is not, then $\Pi_{ijkl} = \Pi_{ijlk}$ or

$$\Delta\Sigma_i = \Pi_{ij}\,\sigma_j \quad (i = 1 - 9; j = 1 - 6) \tag{9.28}$$

in matrix subscript notation. Thus Π_{ij} in Eq. (9.28) is completely specified by 54 independent coefficients for the triclinic crystal system given by

$$\begin{bmatrix} \Delta\Sigma_1 \\ \Delta\Sigma_2 \\ \Delta\Sigma_3 \\ \Delta\Sigma_4 \\ \Delta\Sigma_5 \\ \Delta\Sigma_6 \\ \Delta\Sigma_7 \\ \Delta\Sigma_8 \\ \Delta\Sigma_9 \end{bmatrix} = \begin{bmatrix} \Pi_{11} & \Pi_{12} & \Pi_{13} & \Pi_{14} & \Pi_{15} & \Pi_{16} \\ \Pi_{21} & \Pi_{22} & \Pi_{23} & \Pi_{24} & \Pi_{25} & \Pi_{26} \\ \Pi_{31} & \Pi_{32} & \Pi_{33} & \Pi_{34} & \Pi_{35} & \Pi_{36} \\ \Pi_{41} & \Pi_{42} & \Pi_{43} & \Pi_{44} & \Pi_{45} & \Pi_{46} \\ \Pi_{51} & \Pi_{52} & \Pi_{53} & \Pi_{54} & \Pi_{55} & \Pi_{56} \\ \Pi_{61} & \Pi_{62} & \Pi_{63} & \Pi_{64} & \Pi_{65} & \Pi_{66} \\ \Pi_{71} & \Pi_{72} & \Pi_{73} & \Pi_{74} & \Pi_{75} & \Pi_{76} \\ \Pi_{81} & \Pi_{82} & \Pi_{83} & \Pi_{84} & \Pi_{85} & \Pi_{86} \\ \Pi_{91} & \Pi_{92} & \Pi_{93} & \Pi_{94} & \Pi_{95} & \Pi_{96} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \tag{9.29}$$

The transformation law for the piezothermoelectric power tensor Π is easily determined from the transformation laws for stress and thermoelectric power. These transformation laws are $\sigma' = \alpha\sigma$ or $\sigma = \alpha^{-1}\sigma'$, as given in Section 6.1.1, and Σ is $\Sigma' = \beta\Sigma$, where α is the quadratic transformation form for symmetrical second-rank polar tensors and β is the general quadratic transformation form for asymmetrical second-rank polar tensors. If $\Sigma' = \Pi'\sigma'$ relative to coordinate axes $0x'$ and $\Sigma = \Pi\sigma$ relative to axes $0x$, then it follows that

$$\Sigma' = \beta\Sigma = \beta\Pi\sigma = \beta\Pi\alpha^{-1}\sigma' = \Pi'\sigma'$$

or

$$\Pi' = \beta\Pi\alpha^{-1} \tag{9.30}$$

in matrix symbolic notation. The quadratic transformation form β is given by Eq. (9.31), where it is divided into nine 3×3 submatrices (numbered in parentheses), 4 of which are replicated as indicated by the symbols ↔ and ↕. Eq. (9.31) can be deduced from that of α given by Eq. (2.22).

$$\beta = \left[\begin{array}{ccccccccc}
 & (1) & & & (2) & & & (3) & \\
a_{11}^2 & a_{12}^2 & a_{13}^2 & a_{12}a_{13} & a_{13}a_{11} & a_{11}a_{12} & & & \\
a_{21}^2 & a_{22}^2 & a_{23}^2 & a_{12}a_{23} & a_{23}a_{21} & a_{21}a_{22} & & (2) \leftrightarrow (3) & \\
a_{31}^2 & a_{32}^2 & a_{33}^2 & a_{32}a_{33} & a_{33}a_{31} & a_{31}a_{32} & & & \\
 & (4) & & & (5) & & & (6) & \\
a_{21}a_{31} & a_{22}a_{32} & a_{23}a_{33} & a_{22}a_{33} & a_{21}a_{33} & a_{21}a_{32} & a_{23}a_{32} & a_{23}a_{31} & a_{22}a_{31} \\
a_{31}a_{11} & a_{32}a_{12} & a_{33}a_{13} & a_{12}a_{33} & a_{11}a_{33} & a_{11}a_{32} & a_{13}a_{32} & a_{13}a_{31} & a_{12}a_{31} \\
a_{11}a_{21} & a_{12}a_{22} & a_{13}a_{23} & a_{12}a_{23} & a_{11}a_{23} & a_{11}a_{22} & a_{13}a_{22} & a_{13}a_{21} & a_{12}a_{21} \\
 & (7) & & & (8) & & & (9) & \\
 & & & & & & & & \\
 & (4) \updownarrow (7) & & & (6) \leftrightarrow (8) & & & (5) \leftrightarrow (9) &
\end{array}\right] \tag{9.31}$$

The variation in thermoelectric power with strain can also be established. For this purpose, Eq. (9.27) is altered to give

$$\Delta\Sigma_{ij} = \left(\frac{\partial\Sigma_{ij}}{\partial\varepsilon_{mn}}\right)\left(\frac{\partial\varepsilon_{mn}}{\partial\sigma_{kl}}\right)\sigma_{kl} = \mathrm{E}_{ijmn}s_{mnkl}\sigma_{kl} \tag{9.32}$$

or

$$\Delta\Sigma_i = \mathrm{E}_{ik}s_{kj}\sigma_j = \mathrm{E}_{ik}\varepsilon_k \tag{9.33}$$

in matrix subscript notation. Here $\mathrm{E}_{ik} = (\partial\Sigma_i/\partial\varepsilon_k)$ is a polar fourth-rank tensor called the *elastothermoelectric power tensor* and s_{kj} is the elastic compliance tensor given by Eq. (4.47). By comparing Eqs. (9.28) and (9.33), the piezothermoelectric and elastothermoelectric power coefficients can be related by reciprocity

$$\Pi_{ij} = \mathrm{E}_{ik}s_{kj} \tag{9.34}$$

or its inverse

$$\mathrm{E}_{ij} = \Pi_{ik}c_{kj}, \tag{9.35}$$

where c_{kj} is the elastic stiffness modulus given by $c = s^{-1}$ as deduced from Eq. (6.36a) and thermodynamic symmetry discussed in Section 4.4.

The transformation law for the elastothermoelectric power tensor E is easily found from the transformation laws for strain and thermoelectric power. Strain transforms as $\varepsilon' = \tilde{\alpha}^{-1}\varepsilon$ or $\varepsilon = \tilde{\alpha}\varepsilon'$ (see Section 6.1.2) and Σ transforms as $\Sigma' = \beta\Sigma$. Because from Eq. (9.33) $\Sigma = \mathrm{E}s\sigma = \mathrm{E}\varepsilon$ relative to coordinate axes $0x_i$ and $\Sigma' = \mathrm{E}'\varepsilon'$ relative to axes $0x_i'$, it follows that

$$\Sigma' = \beta\,\Sigma = \beta\,\mathrm{E}\varepsilon = \beta\,\mathrm{E}\tilde{\alpha}\varepsilon' = \mathrm{E}'\varepsilon'$$

or

$$\mathrm{E}' = \beta\,\mathrm{E}\tilde{\alpha} \tag{9.36}$$

all in matrix notation.

A complete description of the first-order piezothermoelectric and elastothermoelectric properties must necessarily include the piezo- and elasto-Seebeck, Peltier, and Thomson effects. From Eq. (9.24) in contracted subscript form and using Eqs. (9.28) and (9.34), there results

$$\tau_i = T\frac{\partial \Sigma_i}{\partial T} = T\left(\frac{\partial \Pi_{ij}}{\partial T}\right)\sigma_j = T\left(\frac{\partial \mathrm{E}_{ik}\ s_{kj}}{\partial T}\right)\sigma_j\ , \tag{9.37}$$

giving the Thomson effect in terms of the piezothermoelectric and elastothermoelectric coefficients. Here, it has been assumed that all thermal stresses are absent and that the tensor character and aelotropism of $\prod$ and E are the same.

The anisotropy of the piezothermoelectric and elastothermoelectric coefficients $\prod$ and E is determined by the standard methods emphasized in this text. Consider the $\prod$ array in Eq. (9.29), which applies to the triclinic crystal system. The anisotropy of all crystal systems, other than the trigonal and hexagonal, can be determined by the method of direct inspection as was done for the piezoelectric moduli in Section 6.1.3. For the trigonal and hexagonal crystal systems, the "brute-force" method described in Section 6.1.4 must be used. Remember that the generalized quadratic transformation form β must be used together with α in Eqs. (9.30) and (9.36) when applying the brute-force method. For the coefficient arrays of $\prod$ and E, see Tinder in Endnotes, Section VII.

9.5 PIEZORESISTANCE EFFECT (STRAIN GAUGE EFFECT)

The application of a mechanical stress can significantly change the electrical resistivity of a given conducting medium. The calibrated sensitivity of piezoresistive elements made from metal or semiconductor thin wires are used as gauges to measure the surface strains resulting from a stressed solid member to which the strain gauges are firmly attached. The strain gauges can be aligned with specific crystallographic axes for meaningful measurements. Such measurements are usually in the form of a fractional change in the resistance associated with elongation or contraction of the piezoresistive elements. For cubic crystals, the piezoresistive sensitivity is similar to that discussed for Young's modulus in Section 6.2.7.

To determine the tensor nature of the piezoresistance effect, we can expand the resistivity tensor ρ_{ij} in a Taylor's series about the state of reference temperature T_0 and zero applied stress (neglecting gravitational forces and body torques) much the same as in the previous section for the piezothermoelectric effect. Here again, we assume that ρ_{ij} is everywhere a continuous function of temperature and stress and that its derivatives with respect to temperature T and stress σ_{kl} are real. The resulting expansion is

$$\begin{aligned}
\rho_{ij}(T,\sigma_{kl}) &= \sum_{n=0}^{\infty}\frac{1}{n!}\left\{(T-T_0)\frac{\partial}{\partial T}+\sigma_{kl}\frac{\partial}{\partial\sigma_{kl}}\right\}^{n}\rho_{ij}(T_0,0)\\
&= \rho_{ij}(T_0,0)+\left(\frac{\partial\rho_{ij}}{\partial T}\right)_{(T_0,0)}(T-T_0)+\left(\frac{\partial\rho_{ij}}{\partial\sigma_{kl}}\right)_{(T_0,0)}\sigma_{kl}\\
&\quad+\frac{1}{2!}\left[\left(\frac{\partial^2\rho_{ij}}{\partial T^2}\right)_{(T_0,0)}(T-T_0)^2+2\left(\frac{\partial^2\rho_{ij}}{\partial T\partial\sigma_{kl}}\right)_{(T_0,0)}(T-T_0)\sigma_{kl}\right.\\
&\quad\left.+\left(\frac{\partial^2\rho_{ij}}{\partial\sigma_{kl}\,\partial\sigma_{op}}\right)_{(T_0,0)}\sigma_{kl}\,\sigma_{op}\right]+\cdots,
\end{aligned}\tag{9.38}$$

where $\rho_{ij}(T_0, 0)$ and all tensor coefficients (in parentheses) are evaluated at temperature T_0 and zero stress. Notice that the second-order effects, $\partial^2\rho_{ij}/\partial T\partial\sigma_{kl}$ and $\partial^2\rho_{ij}/\partial\sigma_{kl}\partial\sigma_{op}$, represent the piezothermoresistive and quadratic piezoresistive effects, respectively. There will be no further discussion of the second-order effects, the remainder of which are self-explanatory.

Assuming that all measurements are to be conducted at a reference temperature of $T = T_0$ and that all second- and higher-order terms in stress can be neglected, Eq. (9.38) becomes

$$\Delta\rho_{ij} = \rho_{ij}(T_0,\sigma_{kl}) - \rho_{ij}(T_0,0) = \left(\frac{\partial\rho_{ij}}{\partial\sigma_{kl}}\right)_{(T_0,0)}\sigma_{kl} = P_{ijkl}\,\sigma_{kl}, \tag{9.39}$$

where P_{ijkl} is a fourth-rank polar tensor called the *piezoresistance tensor*. Because both ρ_{ij} and σ_{kl} are symmetrical second-rank tensors, we can write

$$\Delta\rho_i = P_{ij}\sigma_j \quad (i = 1-6;\ j = 1-6), \tag{9.40}$$

where it is understood that $P_{ij} \neq P_{ji}$. Thus, the piezoresistance tensor transforms the same as the linear piezo-optical coefficients given by Eq. (7.51) and is affected by crystal symmetry the same as presented in Table 7.1.

9.6 ELECTRODIFFUSIVE AND THERMODIFFUSIVE EFFECTS

There are two other two-flow processes that derive from Eqs. (8.20) and that are worthwhile mentioning, the electrodiffusive and thermodiffusive effects. These are represented as follows.

$$\left.\begin{aligned} -J^n &= L^{11}\nabla\left(\frac{\bar{\mu}}{T}\right)+L^{13}\nabla\left(\frac{\mu_c}{T}\right) \\ -J^m &= L^{31}\nabla\left(\frac{\bar{\mu}}{T}\right)+L^{33}\nabla\left(\frac{\mu_c}{T}\right)\end{aligned}\right. \quad \text{Electrodiffusive effects} \tag{9.41}$$

$$\left.\begin{aligned} J^q &= L^{22}\,\nabla\left(\frac{1}{T}\right)+L^{23}\,\nabla\left(\frac{\mu_c}{T}\right) \\ -J^m &= L^{32}\,\nabla\left(\frac{1}{T}\right)+L^{33}\,\nabla\left(\frac{\mu_c}{T}\right)\end{aligned}\right. \quad \text{Thermodiffusive effects} \tag{9.42}$$

The reader has already been introduced to the phenomenological developments of the thermoelectric effects in some detail including the application of Onsager's reciprocity principle as applied to the phenomenological coefficients given in Eqs. (8.20). The interaction effects in Eqs.(8.20) can be complex considering that charged matter (electrons, holes, ions) can carry charge, heat, and mass at the same time and that different species can influence other species. Although it is not our intention to explore the electrodiffusive and thermodiffusive effects in detail, a short discussion of the diffusive effects is necessary when dealing with the coupled effects in Eqs. (9.41) and (9.42).

9.6.1 Multiple Diffusing Species

In dealing with diffusion of matter, one must understand that several species could be diffusing simultaneous and that the different species may not all be independent. Thus, the flow of one species may influence the flow of another. The entropy density production associated only with the simultaneous diffusion of several species in the absence of an electrostatic field potential gradient ($\nabla\phi = 0$) and temperature gradient is from Eq. (8.19)

$$\dot{s} = -\sum_i J_i^m \nabla\left(\mu_i \middle/ T \right), \tag{9.43}$$

where J_i^m is the mass flux of the ith species and μ_i is the chemical potential for the ith species. From this we can generalize Fick's law in the modified form of Eq. (8.8) and under isothermal conditions as the sum of diffusing species given by

$$J_i^m = -\sum_j \frac{L^{ij}}{T}\nabla N_j = -\sum_j D_{ij}\nabla N_j\,(x). \tag{9.44}$$

Here, $N_j(x)$ is the concentration (mole number) of the jth component at any position in Cartesian space of the medium in which the diffusion is occurring. The problem now remains to relate the phenomenological coefficient L^{ij} with the physically measurable diffusion constant D_{ij}. This requires the use of Gibbs–Duhem relation, Eq. (4.4) under constant temperature, electric, magnetic, and stress fields together with the use of chemical thermodynamics as applied to the condensed state.

For example, at constant T, E, B, and σ, the Gibbs–Duhem relation for a non-independent, two-species system and for arbitrary dx, is expressed as

$$N_1\,\mathrm{d}\,\mu_1 + N_2\,\mathrm{d}\,\mu_2 = N_1\nabla\mu_1 + N_2\nabla\mu_2 = 0, \tag{9.45}$$

where N_1 is the mole number concentration of the (dilute) diffusing species and $N_2 \gg N_1$ is the mole number concentration of the host medium. Because diffusion flows do not produce a volume change, it follows that

$$\vec{J}_1 v_1 + \vec{J}_2 v_2 = 0, \tag{9.46}$$

where v_i is the partial molar volume of the species i. Now, by introducing Eqs. (9.45) and (9.46) into (9.43), the isothermal entropy density production for the two-component system becomes

$$\dot{s} = -\vec{J}_1 \cdot \frac{\nabla\mu_1}{T} - \vec{J}_2 \cdot \frac{\nabla\mu_2}{T} = -\left(\vec{J}_1 - \frac{N_1}{N_2}\vec{J}_2\right)\cdot\frac{\nabla\mu_1}{T} = -\left(1 + \frac{N_1 v_1}{N_2 v_2}\right)\vec{J}_1 \cdot \frac{\nabla\mu_1}{T} \tag{9.47}$$

in vector notation. With the information in Eq. (9.47), Eqs. (9.44) and (9.45) combine to give the linear force flux equation for the diffusing species as

$$\vec{J}_1 = -L^{11}\left(1 + \frac{N_1 v_1}{N_2 v_2}\right)\nabla\frac{\mu_1}{T} = -D_{11}\nabla N_1 . \tag{9.48}$$

But $\nabla\mu_1/\nabla N_1 = (\partial\mu_1 / \partial N_1)$, which allows

$$\vec{J}_1 = -L^{11}\frac{1}{T}\left(1 + \frac{N_1 v_1}{N_2 v_2}\right)\left(\frac{\partial\mu_1}{\partial N_1}\right)\nabla N_1 = -D_{11}\nabla N_1 , \tag{9.49}$$

resulting in

$$L^{11} = \frac{D_{11}T}{\left(1 + \frac{v_1 N_1}{v_2 N_2}\right)\left(\frac{\partial\mu_1}{\partial N_1}\right)} \cong \frac{D_{11}T}{\left(\frac{\partial\mu_1}{\partial N_1}\right)} \tag{9.50}$$

since $v_1 N_1 \ll v_2 N_2$ for a dilute condensed solution.

For an ideal dilute condensed solution, the chemical potential for a single diffusing species is

$$\mu_1 = \mu_0 + RTln(X_1), \tag{9.51}$$

where μ_0 is the chemical potential in the reference state (p, T) independent of μ_1, R is the familiar gas constant $R = 8.31$ J/mol K, and $X_1 = N_1 / (N_1 + N_2) \cong N_1 / N_2$ is the mole fraction noting that $N_1 \ll N_2$ for a dilute solution. Therefore, it follows that $\partial\mu_1 / \partial N_1 = RT / N_1$, giving the final result

$$L^{11} = \frac{N_1 D_{11}}{R}. \tag{9.52}$$

The addition of more diffusing species complicates the analyses significantly because the diffusion cross (interference) effects must be taken into account. In this case, at least three diffusing species are required to verify Onsager's reciprocal relations.

When dealing with electrodiffusive and thermodiffusive effects, it is clear that the diffusing species can carry charge and heat. Clearly, the phenomenological developments of these systems become excessively complex when multiple diffusing species are present in the system. The analysis of a simple two-species diffusion problem just discussed serves to illustrate this point.

• • • •

CHAPTER 10

Effect of Magnetic Field on the Transport Properties

Moving charges transport thermal energy as well as electrical charge and therefore interact with a magnetic field without regard to which quantity (heat or electric charge) is being transported. We are interested in the various direct and cross (transverse) effects due to an electrochemical potential gradient $\nabla\bar{\mu}$, a temperature gradient ∇T, and a magnetic field $\vec{H}$. Although Chapter 9 dealt with the thermoelectric effects in the absence of a magnetic field, we now must consider these effects as being a function of magnetic field and alter Onsager's reciprocal relations accordingly.

10.1 FIRST-ORDER THERMOMAGNETIC AND GALVANOMAGNETIC EFFECTS IN AN ISOTROPIC PLANE

To simplify what would be an unnecessarily complex development, we take the magnetic field as being directed perpendicular to the x, y plane assumed to be isotropic with respect to the various effects. Furthermore, we assume that the thermomagnetic and galvanomagnetic effects occur in a homogeneous medium so as to avoid the interference effects of diffusing species.

The total entropy density production for two-dimensional thermoelectric flows in the x, y plane then becomes

$$\dot{s} = -J_x^n \nabla_x \left(\frac{\bar{\mu}}{T}\right) - J_y^n \nabla_y \left(\frac{\bar{\mu}}{T}\right) + J_x^q \nabla_x \left(\frac{1}{T}\right) + J_y^q \nabla_y \left(\frac{1}{T}\right), \tag{10.1}$$

from which the phenomenological relations are found to be a truncated form of Eqs. (8.21) given by

$$\begin{bmatrix} -J_x^n \\ -J_y^n \\ J_x^q \\ J_y^q \end{bmatrix} = \begin{bmatrix} \left(L^{11*}\right) & L^{12*} & \left(L^{13*}\right) & L^{14*} \\ L^{21*} & \left(L^{22*}\right) & L^{23*} & \left(L^{24*}\right) \\ \left(L^{31*}\right) & L^{32*} & \left(L^{33*}\right) & L^{34*} \\ L^{41*} & \left(L^{42*}\right) & L^{43*} & \left(L^{44*}\right) \end{bmatrix} \begin{bmatrix} \nabla_x \left(\bar{\mu}/T\right) \\ \nabla_y \left(\bar{\mu}/T\right) \\ \nabla_x \left(1/T\right) \\ \nabla_y \left(1/T\right) \end{bmatrix}. \tag{10.2}$$

The coefficients ($L^{\alpha\beta^*}$) in parentheses are related to the conductivities and are independent of magnetic field. This is because in the isotropic *x*,*y* plane with the magnetic field vector $\vec{H}$ perpendicular to that plane, the conductivity tensors are symmetrical and do not need to be divided into symmetrical and antisymmetrical parts. (Note that the thermoelectric power is also related to the conductivities but is asymmetrical.) Therefore, the coefficients ($L^{\alpha\beta^*}$) are called *even functions* of $\vec{H}$, which means that $L^{\alpha\beta^*}(\vec{H}) = L^{\alpha\beta^*}(-\vec{H})$ for $\alpha = \beta$ or $\alpha \neq \beta$. The remainder of the coefficients are related to transverse effects (not related to the conductivities) and hence are odd functions of $\vec{H}$, meaning that $L^{\alpha\beta^*}(\vec{H}) = -L^{\alpha\beta^*}(-\vec{H})$ for $\alpha \neq \beta$. The asterisk (*) on the phenomenological coefficients allows a later change to a new set of coefficients without the asterisk.

Now consider applying the consequences of an isotropic *x*, *y* plane to the coefficients of even functions of $\vec{H}$. For this, the following relations apply by isotropy in the *x*, *y* plane and by Eqs. (10.2):

$$\left[\frac{J_x^n}{\nabla_x(\bar{\mu}/T)}\right]_{\nabla_y\bar{\mu}=\nabla_x T=\nabla_y T=0} = \left[\frac{J_y^n}{\nabla_y(\bar{\mu}/T)}\right]_{\nabla_x\bar{\mu}=\nabla_x T=\nabla_y T=0} \quad \text{or} \quad \sigma_{xx} = \sigma_{yy} \quad (\nabla\mu_c = 0)$$

$$\text{and} \quad \left[\frac{J_x^q}{\nabla_x(1/T)}\right]_{\nabla_x\bar{\mu}=\nabla_y\bar{\mu}=\nabla_y T=0} = \left[\frac{J_y^q}{\nabla_y(1/T)}\right]_{\nabla_x\bar{\mu}=\nabla_y\bar{\mu}=\nabla_x T=0} \quad \text{or} \quad k_{xx} = k_{yy}$$

together with

$$\left[\frac{J_x^n}{\nabla_x T}\right]_{\nabla_x\bar{\mu}=\nabla_y\bar{\mu}=\nabla_y T=0} = \left[\frac{J_y^n}{\nabla_y T}\right]_{\nabla_x\bar{\mu}=\nabla_y\bar{\mu}=\nabla_x T=0} \propto \left[(\sigma\Sigma)_{xx} = (\sigma\Sigma)_{yy}\right]_{\nabla\mu_c=0}$$

$$\text{and} \quad \left[\frac{J_x^q}{\nabla_x\bar{\mu}}\right]_{\nabla_y\bar{\mu}=\nabla_x T=\nabla_y T=0} = \left[\frac{J_y^q}{\nabla_y\bar{\mu}}\right]_{\nabla_x\bar{\mu}=\nabla_x T=\nabla_y T=0} \propto \left[(k/\Sigma)_{xx} = (k/\Sigma)_{yy}\right]_{\nabla\mu_c=0}, \qquad (10.3)$$

where it will be recalled that $\nabla(1/T) = -\nabla T/T^2$ and $\nabla(\bar{\mu}/T) = \nabla\bar{\mu}/T$.

As a result of the isotropy in the *x*,*y* plane, given by Eqs. (10.3) and the effect of Onsager's reciprocal relations, the relationships in Eqs. (10.2) between the phenomenological coefficients become, for the even functions of $\vec{H}$,

$$L^{11^*} = L^{22^*},\ L^{33^*} = L^{44^*},\ L^{24^*} = L^{42^*},\ \text{and}\ L^{13^*} = L^{24^*} = L^{31^*}. \qquad (10.4)$$

Then by applying the effect of Onsager's reciprocal relations (for two-dimensional thermoelectric flows) to the coefficients that are odd functions of $\vec{H}$, we conclude that

$$L^{12^*} = -L^{21^*},\ L^{14^*} = -L^{41^*} = -L^{23^*} = L^{32^*},\ \text{and}\ L^{43^*} = -L^{34^*}. \qquad (10.5)$$

When these coefficient relationships are introduced into Eqs. (10.2), there results only six independent phenomenological coefficients represented by the phenomenological relations given by

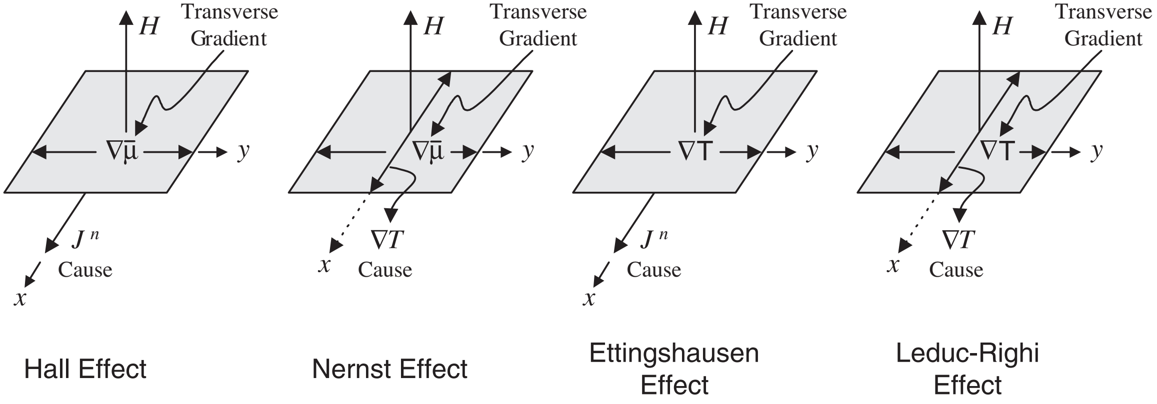
$$\begin{bmatrix} -J_x^n \\ -J_y^n \\ J_x^q \\ J_y^q \end{bmatrix} = \begin{bmatrix} L^{11^*} & L^{12^*} & L^{13^*} & L^{14^*} \\ -L^{12^*} & L^{11^*} & -L^{14^*} & L^{13^*} \\ L^{13^*} & L^{14^*} & L^{33^*} & L^{34^*} \\ -L^{14^*} & L^{13^*} & -L^{34^*} & L^{33^*} \end{bmatrix} \begin{bmatrix} \nabla_x \left(\bar{\mu} / T \right) \\ \nabla_y \left(\bar{\mu} / T \right) \\ \nabla_x \left(1 / T \right) \\ \nabla_y \left(1 / T \right) \end{bmatrix} \tag{10.6}$$

Mazur and Prigogine (see Endnotes) have shown that by partial inversion (using Legendre transforms) the algebra is greatly reduced when defining the various coefficients that have physical meaning (e.g., the Hall coefficient). The idea here is to place the electrical fluxes and temperature gradients, all of which are experimentally controllable, on the right side. When this is done, Eqs. (10.7) sresult, which allows simple relationships to occur between the physically significant coefficients. To accomplish this, we let $J^n \rightarrow eJ^n$, $\nabla\bar{\mu} \rightarrow \nabla\bar{\mu}\ /e$, and $\nabla(1/T) \rightarrow \nabla T$,such that the factors e, $1/e$, and $-1/T^2$ are absorbed in the new phenomenological coefficients $L^{\alpha\beta}$ with the asterisk (*) omitted. The phenomenological relations now become

$$\begin{bmatrix} -\frac{1}{e} \nabla_x \bar{\mu} \\ -\frac{1}{e} \nabla_y \bar{\mu} \\ J_x^q \\ J_y^q \end{bmatrix} = \begin{bmatrix} L^{11} & L^{12} & -L^{13} & -L^{14} \\ -L^{12} & L^{11} & L^{14} & -L^{13} \\ -TL^{13} & -TL^{14} & -L^{33} & -L^{34} \\ TL^{14} & -TL^{13} & L^{34} & -L^{33} \end{bmatrix} \begin{bmatrix} eJ_x^n \\ eJ_y^n \\ \nabla_x T \\ \nabla_y T \end{bmatrix}. \tag{10.7}$$

The symmetry of the $L^{\alpha\beta}$ coefficients in Eqs. (10.7) is implied by the $L^{\alpha\beta^*}$ in Eqs. (10.2), but the $L^{\alpha\beta}$ are fairly complicated functions of the $L^{\alpha\beta^*}$ coefficients. Note that the sign differences and the appearance of the $TL^{\alpha\beta}$ coefficients are a result of the partial inversion of Eqs. (10.2) and the fact that the new coefficients have absorbed the factors e, $1/e$, and $-1/T^2$.

We now define the direct and transverse thermomagnetic and galvanomagnetic effects in a homogeneous media (for which all $\nabla\mu_c = 0$) as they apply to the homogeneous isotropic x, y plane where the magnetic field $\vec{H}$ is directed perpendicular to that plane. The four transverse effects are the *Hall effect*, the *Nernst effect*, the *Ettingshausen effect*, and the *Leduc–Righi effect*, all depicted in Figure 10.1. The two electron flux parameters J^n, named as cause parameters, are produced by the gradient $\nabla\bar{\mu} = e\nabla\phi$, where $-\nabla\phi$ is the common electrostatic potential gradient (electric field strength, E). Conversely, the two temperature gradients, named as cause parameters, each produce



Hall Effect (a)

Nernst Effect (b)

Ettingshausen Effect (c)

Leduc-Righi Effect (d)

FIGURE 10.1: The four transverse thermomagnetic and galvanomagnetic effects as they occur in the *x*,*y* isotropic plane with the magnetic field *H* applied normal to that plane.

a heat flux that is responsible for the transverse effect indicated. In dealing with the definitions of these thermomagnetic effects that follow, this information must be kept in mind.

10.2 DEFINITIONS OF THE THERMOMAGNETIC AND GALVANOMAGNETIC EFFECTS IN AN ISOTROPIC *X*,*Y* PLANE

1. Absolute thermoelectric power

$$\Sigma \equiv \left[\frac{1}{e}\frac{\nabla_x\bar{\mu}}{\nabla_x T}\right]_{J_x^n = J_y^n = \nabla_y T = 0} = \left[\frac{1}{e}\frac{\nabla_y\bar{\mu}}{\nabla_y T}\right]_{J_x^n = J_y^n = \nabla_x T = 0} \qquad \Sigma = L^{13} = L^{24}, \tag{10.8}$$

which follows from the definition of $\Sigma \equiv \nabla\phi / \nabla T$, with $\nabla\mu_c = 0$ in Eqs. (8.14) and (9.2).

2. Isothermal electrical conductivity

$$\sigma^{\mathrm{I}} \equiv -\left[\frac{eJ_x^n}{(1/e)\nabla_x\bar{\mu}}\right]_{\nabla_x T = \nabla_y T = J_y^n = 0} = -\left[\frac{eJ_y^n}{(1/e)\nabla_y\bar{\mu}}\right]_{\nabla_x T = \nabla_y T = J_x^n = 0}$$

$$\sigma^{\mathrm{I}} = \left(L^{11}\right)^{-1} = \left(L^{22}\right)^{-1} \tag{10.9}$$

3. Adiabatic electrical conductivity

$$\sigma^{A} \equiv -\left[\frac{eJ_x^n}{(1/e)\nabla_x \bar{\mu}}\right]_{\nabla_x T = J_y^n = J_y^q = 0} = -\left[\frac{eJ_y^n}{(1/e)\nabla_y \bar{\mu}}\right]_{\nabla_y T = J_x^n = J_x^q = 0}$$

$$\sigma^{A} = \left[L^{11} - T(L^{14})^2 / L^{33}\right]^{-1} \tag{10.10}$$

4. Isothermal thermal conductivity

$$k^{I} \equiv -\left[\frac{J_x^q}{\nabla_x T}\right]_{J_x^n = J_y^n = \nabla_y T = 0} = -\left[\frac{J_y^q}{\nabla_y T}\right]_{J_x^n = J_y^n = \nabla_x T = 0} \qquad k^{I} = L^{33} = L^{44} \tag{10.11}$$

5. Adiabatic thermal conductivity

$$k^{A} \equiv -\left[\frac{J_x^q}{\nabla_x T}\right]_{J_x^n = J_y^n = J_y^q = 0} = -\left[\frac{J_y^q}{\nabla_y T}\right]_{J_x^n = J_y^n = J_x^q = 0} \qquad k^{A} = L^{33} + (L^{33})^{-1}(L^{34})^2 \tag{10.12}$$

6. Isothermal Hall coefficient

$$R^{I} \equiv \left[\frac{1}{e}\frac{\nabla_y \bar{\mu}}{HeJ_x^n}\right]_{\nabla_x T = \nabla_y T = J_y^n = 0} = -\left[\frac{1}{e}\frac{\nabla_x \bar{\mu}}{HeJ_y^n}\right]_{\nabla_x T = \nabla_y T = J_x^n = 0} \qquad R^{I} = L^{12}/H \tag{10.13}$$

7. Adiabatic Hall coefficient

$$R^{A} \equiv \left[\frac{1}{e}\frac{\nabla_y \bar{\mu}}{HeJ_x^n}\right]_{J_y^q = J_y^n = \nabla_x T = 0} = -\left[\frac{1}{e}\frac{\nabla_x \bar{\mu}}{HeJ_y^n}\right]_{J_x^q = J_x^n = \nabla_y T = 0}$$

$$R^{A} = (L^{12} + TL^{13}L^{14}/L^{33})/H \tag{10.14}$$

8. Isothermal Nernst coefficient

$$\eta^{I} \equiv -\left[\frac{1}{e}\frac{\nabla_y \bar{\mu}}{H\nabla_x T}\right]_{J_x^n = J_y^n = \nabla_y T = 0} = \left[\frac{1}{e}\frac{\nabla_x \bar{\mu}}{H\nabla_y T}\right]_{J_x^n = J_y^n = \nabla_x T = 0} \qquad \eta^{I} = L^{14}/H \tag{10.15}$$

9. Adiabatic Nernst coefficient

$$\eta^{A} \equiv -\left[\frac{1}{e}\frac{\nabla_y \bar{\mu}}{H\nabla_x T}\right]_{J_x^n = J_y^n = J_y^q = 0} = \left[\frac{1}{e}\frac{\nabla_x \bar{\mu}}{H\nabla_y T}\right]_{J_x^n = J_y^n = J_x^q = 0}$$

$$\eta^{A} = (L^{14} - L^{13}L^{34}/L^{33})/H \tag{10.16}$$

10. Ettingshausen coefficient

$$\varepsilon \equiv \left[\frac{\nabla_y T}{HeJ_x^n}\right]_{J_y^n = J_y^q = \nabla_x T = 0} \qquad = -\left[\frac{\nabla_x T}{HeJ_y^n}\right]_{J_x^n = J_x^q = \nabla_y T = 0} \qquad \varepsilon = TL^{14} / HL^{33} \tag{10.17}$$

11. Leduc–Righi coefficient

$$\zeta \equiv \left[\frac{\nabla_y T}{H\nabla_x T}\right]_{J_x^n = J_y^n = J_y^q = 0} \qquad = -\left[\frac{\nabla_x T}{H\nabla_y T}\right]_{J_x^n = J_y^n = J_x^q = 0} \qquad \zeta = L^{34} / HL^{33} \tag{10.18}$$

Notice that the transverse effects defined in Eqs. (10.13) to (10.18) are odd functions of the magnetic field strength *H* and require a sign reversal to accompany the coefficient definitions when the *x*,*y* axes are reversed. This is a consequent of “time-inversion” operator discussed in Appendix A. For the even functions of *H* (i.e., no function of *H* in these cases), there is no sign reversal accompanying a reversal of axes.

With the definitions given in Eqs. (10.8) to (10.18) for the six isothermal coefficients, the phenomenological relations in Eq. (10.7) can now be written as

$$\begin{bmatrix} -{}^{1}\!/_{e}\,\nabla_x \overline{\mu} \\ -{}^{1}\!/_{e}\,\nabla_y \overline{\mu} \\ J_x^q \\ J_y^q \end{bmatrix} = \begin{bmatrix} (\sigma^I)^{-1} & HR^{\mathrm{I}} & -\Sigma & -H\eta^{\mathrm{I}} \\ -HR^{\mathrm{I}} & (\sigma^I)^{-1} & H\eta^{\mathrm{I}} & -\Sigma \\ -T\Sigma & -TH\eta^{\mathrm{I}} & -k^{\mathrm{I}} & -Hk^{\mathrm{I}}\zeta \\ TH\eta^{\mathrm{I}} & -T\Sigma & Hk^{\mathrm{I}}\zeta & -k^{\mathrm{I}} \end{bmatrix} \begin{bmatrix} eJ_x^n \\ eJ_y^n \\ \nabla_x T \\ \nabla_y T \end{bmatrix} \tag{10.19}$$

There are certain relations inherent in Eqs. (10.19). These relations are as follows:

$$k^{\mathrm{I}}\varepsilon = T\eta^{\mathrm{I}} \text{ (Bridgman relation),} \tag{10.20}$$

$$k^{\mathrm{A}} - k^{\mathrm{I}} = k^{\mathrm{I}}(H\zeta)^2, \tag{10.21}$$

$$(\sigma^{\mathrm{I}})^{-1} - (\sigma^{\mathrm{A}})^{-1} = H^2\eta^{\mathrm{I}}\varepsilon, \tag{10.22}$$

$$R^{\mathrm{A}} - R^{\mathrm{I}} = \Sigma\varepsilon, \tag{10.23}$$

$$\eta^{\mathrm{I}} - \eta^{\mathrm{A}} = \Sigma\zeta. \tag{10.24}$$

That these expressions correctly express the simple relationships between direct and transverse effects is easily demonstrated. From the definition of the Ettingshausen coefficient, we can derive Eq. (10.20) by using Eq. (10.17) with Eqs. (10.7) or Eqs. (10.19) as follows:

$$\varepsilon \equiv \left.\frac{\nabla_y T}{HeJ_x^n}\right]_{J_y^n = J_y^q = \nabla_x T = 0} \quad \text{and} \quad \nabla_y \bar{\mu} = J_y^n = 0.$$

Thus, $J_y^q = 0 = TL^{14}eJ_x^n - L^{33}\nabla_y T$ or $J_y^q = 0 = TL\eta^1 eJ_x^n - k^{\mathrm{I}}\nabla_y T$. The result proves Eq. (10.20):

$$\varepsilon = TL^{14} / HL^{33} = T\eta^{\mathrm{I}} / k^{\mathrm{I}}. \tag{10.25}$$

In a somewhat similar fashion, we can derive Eq. (10.24) from Eqs. (10.15) and (10.16) by using Eqs. (10.7) and (10.19). We must first find η^{I} and then η^{A}:

$$\eta^{\mathrm{I}} \equiv -\frac{1}{e}\left.\frac{\nabla_y \bar{\mu}}{H\nabla_x T}\right]_{J_x^n = J_y^n = \nabla_y T = 0}.$$

Therefore, $-(1/e)\nabla_y \bar{\mu} = L^{14}\nabla_x T$, which yields $\eta^1 = L^{14} / H$. Next, from Eq. (10.16), we have

$$\eta^{\mathrm{A}} \equiv -\frac{1}{e}\left.\frac{\nabla_y \bar{\mu}}{H\nabla_x T}\right]_{J_x^n = J_y^n = J_y^q = 0}.$$

Thus, $-(1/e)\nabla_y \bar{\mu} = L^{14}\nabla_x T - L^{13}\nabla_y T$. But $J_y^q = 0 = L^{34}\nabla_x T - L^{33}\nabla_y T$. Then solving for $\nabla_y T$ gives $\nabla_y T = L^{34}\nabla_x T / L^{33}$, which, when substituted into the first expression, yields

$$-(1/e)\nabla_y \bar{\mu} = [L^{14} - L^{13}(L^{34} / L^{33})]T. \tag{10.26}$$

From this, we have $\eta^{\mathrm{A}} = [L^{14} - L^{13}(L^{34} / L^{33})] / H$. Now taking the difference between η^{I} and η^{A} proves Eq. (8.102):

$$\eta^{\mathrm{I}} - \eta^{\mathrm{A}} = L^{14} - L^{14} + L^{13}L^{34} / (L^{33} / H) = L^{13}(L^{34} / HL^{33}) = \Sigma\zeta. \tag{10.27}$$

Proof of the remaining three expressions, (10.21)–(10.23), will be left as exercises for the reader.

10.3 SECOND-ORDER EFFECTS IN A MAGNETIC FIELD—THE HALL AND MAGNETORESISTANCE TENSORS

In a conductor subjected to a magnetic field and in the absence of heat and matter currents (no chemical potential gradients), the components of conductivity and resistivity tensors become functions of the magnetic field strength (H). Thus, Eq. (8.5) can be extended to give the tensor equation representing electrical resistivity in a magnetic field expressed as

$$-\nabla_i\phi = \rho_{ij}(\vec{H})J_j^n, \tag{10.28}$$

where it follows that, for example, the resistivity tensor is no longer symmetrical (i.e., $\rho_{ij}(\vec{H}) \neq \rho_{ji}(\vec{H})$) and that the Hall and magnetoresistance tensor properties must be dealt with accordingly.

As with any second-rank tensor, the resistivity tensor can be divided into symmetrical and antisymmetrical parts, ρ_{ij}^{S} and ρ_{ij}^{A}, as in Eqs. (2.16), (2.17), and (2.18), respectively. Thus,

$$\rho_{ij} = \rho_{ij}^{\mathrm{S}} + \rho_{ij}^{\mathrm{A}}. \tag{10.29}$$

This requires that

$$\rho_{ij}^{\mathrm{S}}(H) = \rho_{ji}^{\mathrm{S}}(H) = \rho_{ji}^{\mathrm{S}}(-H) = \rho_{ij}^{\mathrm{S}}(-H) \tag{10.30}$$

and

$$\rho_{ij}^{\mathrm{A}}(H) = -\rho_{ji}^{\mathrm{A}}(H) = \rho_{ji}^{\mathrm{A}}(-H) = -\rho_{ij}^{\mathrm{A}}(-H). \tag{10.31}$$

By definition, $\rho_{ij}^{\mathrm{S}}(H)$ is an even function of the magnetic field strength H, whereas $\rho_{ij}^{\mathrm{A}}(H)$ is an odd function of H.

We now expand $\rho_{ij}^{\mathrm{S}}(H)$ in a Taylor's series as an *even function* of the magnetic field strength H about the state of a reference temperature T^0 (not shown) and in the absence of heat and matter currents. Thus, the expansion yields coefficients for $n = 0, 2, 4, \ldots$ in Eq. (2.52), with the result,

$$\begin{aligned} \rho_{ij}^{\mathrm{S}}(H) &= \rho_{ij}(0) + \left(\frac{\partial^2 \rho_{ij}}{\partial H_k \partial H_l}\right)_{(0,0)} H_k H_l + \cdots \\ &= \rho_{ij}(0) + \rho_{ijkl} H_k H_l + \cdots, \end{aligned} \tag{10.32}$$

where each term is evaluated at zero or near zero magnetic field. Introducing Eq. (10.32) into Eq. (10.28) gives

$$-\nabla_i\phi = \left\{\rho_{ij}(0) + \rho_{ijkl}H_kH_l + \cdots\right\}J_j^n. \tag{10.33}$$

The first term on the right side of Eq. (10.33) gives the generalized Ohm's law for which $\rho_{ij} = \rho_{ji}$ in the absence of a magnetic field. The second term in Eq. (10.33) represents the magnetoresistance effect. The fourth-rank polar, nonmagnetic tensor ρ_{ijkl} is called the magnetoresistance tensor, which has partial symmetry in $i, j = m$, and $k, l = n$ expressed as

$$\rho_{mn} \neq \rho_{nm} \quad (m, n = 1-6). \tag{10.34}$$

Thus, ρ_{mn} transforms as $\rho' = \alpha\rho\alpha^{-1}$, the same as Eq. (7.51), and is affected by crystal symmetry the same as the piezo-optical coefficients π_{mn} given in Table 7.1.

Expansion of $\rho_{ij}^{\mathrm{A}}(H)$ in a Taylor series as an *odd function* of the magnetic field strength coefficients for $n = 1, 3, \ldots$ in Eq. (2.52) gives

$$\rho_{ij}^{\mathrm{A}}(H) = \left(\frac{\partial \rho_{ij}}{\partial H_k}\right)_{(0)} H_k + \cdots = \rho_{ijk} H_k + \cdots, \tag{10.35}$$

where each term is evaluated at weak (near-zero) magnetic field. Introducing Eq. (10.35) into Eq. (10.28) gives the result

$$-\nabla_i \phi = (\rho_{ijk} H_k + \cdots)\, J_j^n \;.. \tag{10.36}$$

The third-rank tensor $R_{ijk} = \rho_{ijk} = \partial\rho_{ij} / \partial H_k$ is called the *Hall tensor*, and from Eq. (10.36), the *Hall field* is given by

$$-\nabla_i \phi^H = \rho_{ijk} H_k J_j^n \; = R_{ijk} H_k J_j^n \; . \tag{10.37}$$

Here, Eq. (10.37) agrees with the definitions in Eqs. (10.13) and (10.14) when we set $\nabla\bar{\mu} = e\nabla\phi$ (chemical potential gradient is zero) and $J^n = -J^e / e$ as given in Section 8.5.

Because the magnetic field H is an axial first-rank tensor, then the Hall tensor R_{ijk} is a third-rank, axial–magnetic, antisymmetrical tensor (in indices i, k). However, any axial, antisymmetrical, third-rank tensor corresponds to a polar, second-rank tensor according to the single and double contraction products given by Eqs. (2.65) and (2.69), respectively, and expressed here as

$$R_{ijkl} = e_{ijk} r_{kl} \tag{10.38}$$

and

$$r_{kl} = e_{ijk} R_{ijl}, \tag{10.39}$$

where it is understood that $r_{kl} \neq r_{lk}$. Thus, r transforms as in Eq. (2.13), and it is affected by crystal symmetry the same as the thermoelectric power $\Sigma_{ij} \neq \Sigma_{ji}$ components given in Table 9.1. Therefore, the components of the Hall tensor R_{ijl} can be obtained from the polar second-rank tensor r_{kl} or vice versa as provided in Eqs. (10.38) and (10.39) and by Table 9.1, assuming that data are available for a given crystal system. Actually, magnetic field strength H is an axial–magnetic vector that makes R_{ijk} an axial–magnetic, antisymmetrical tensor, and r_{kl} a polar–magnetic tensor. But the designation "magnetic" requires additional discussion, which is covered in Appendix A.

Both Ohm's law and the magnetoresistive effect contribute to Joule heating, but the Hall effect does not. The Hall effect is by Figure 10.1(a), and Eqs. (10.13) and (10.14), a transverse effect—the Hall field is always perpendicular to the electric current and cannot contribute to any Joule heat dissipation. Thus, any Joule heating is caused only by the symmetrical part of the resistivity (or conductivity) tensor, as expressed in tensor form by Eq. (10.33) after multiplying both sides by J_i^n.

10.4 FIRST-ORDER THERMOGALVANOMAGNETIC EFFECTS IN ISOTROPIC CONDUCTIVE MEDIA

Consider now the effects that occur when an electric current flows in the simultaneous presence of an electric field, weak magnetic field, and a temperature gradient but in the absence of mechanical stress and chemical potential gradients. To make this a manageable development, we will confine our attention to the first-order thermomagnetic and galvanomagnetic effects, as they are manifest in a homogeneous, isotropic conductive medium. Let us expand each of the dependent parameters, $-\nabla\phi = E$ and J^q, similar to those in Eq. (10.19), in a Taylor series as a function of electric flux J^n, temperature gradient ∇T, and weak magnetic field strength H about the state of zero stress and zero chemical potential. Because we will be dealing with transverse effects, vector cross products $\vec{H}\times\vec{J}^n$ and $\vec{H}\times\nabla T$ together with the "right-hand rule" are used. Furthermore, the following expansions must be consistent with Eq. (10.19), Figure 10.1, and the definitions in Section 10.2 but applicable to a homogeneous isotropic conductive medium without reference to coordinate axes. Carrying out the Taylor series expansions and retaining only the first-order terms, we obtain

$$\vec{E} = -\nabla\phi = -R(\vec{H}\times e\vec{J}^n) + \rho e\vec{J}^n + \eta(\vec{H}\times\nabla T) - \Sigma\nabla T \tag{10.40}$$

and

$$\vec{J}^q = k\varepsilon(\vec{H}\times e\vec{J}^n) - T\Sigma e\vec{J}^n + k\zeta(\vec{H}\times\nabla T) - k\nabla T. \tag{10.41}$$

In Eq. (10.41), we have used the Bridgman relation $k\varepsilon = T\eta$ given by Eq. (10.20). Notice that each term in Eq. (10.40) represents an electrostatic potential and that each term in Eq. (10.41) represents a heat flux density as, for example, in Eq. (9.11). Also, ρ and k are the electrical resistivity and thermal conductivity, respectively, and Σ is the thermoelectric power coefficient, all taken as constants in the isotropic solid. Note that, for self-consistency, the terms in Eqs. (10.40) and (10.41) are taken from the equations for $-(1/e)\nabla_y\bar{\mu} = -\nabla\phi = \vec{E}$ and $J_y^q = J^q$ in Eq. (10.19). The resulting transverse fields are consistent with Figure 10.1 and are defined as follows:

$$R(\vec{H} \times e\vec{J}^{\,n}) \equiv \text{Hall electrostatic potential gradient} \tag{10.42}$$

$$\eta(\vec{H} \times \nabla T) \equiv \text{Nernst electrostatic potential gradient} \tag{10.43}$$

$$\varepsilon(\vec{H} \times e\vec{J}^{\,n}) \equiv \text{Ettingshausen temperature gradient} \tag{10.44}$$

$$\zeta(\vec{H} \times \nabla T) \equiv \text{Leduc–Righi temperature gradient.} \tag{10.45}$$

Here, the coefficients R, η, ε, and ζ are all taken as constants for the isotropic solid. Implicit in these definitions is the equality $\nabla\bar{\mu} = e\nabla\varphi$ in the absence of chemical potential gradients, $\nabla\mu_c = 0$, and $eJ^n = -J^e$ as given in Section 8.5. All thermomagnetic and galvanomagnetic field gradients are assumed to be positive in a direction corresponding to the right-hand rule for the vector cross products. Thus, these four transverse fields are always perpendicular to the causal vectors J^n and ∇T.

In tensor notation, the Hall, Nernst, Ettingshausen, and Leduc–Righi field gradients must be dealt with somewhat differently because they do not necessarily represent a transverse field. To begin with, these thermomagnetic and galvanomagnetic properties are all third-rank tensors. The Hall field, previously given by Eq. (10.37), was obtained by expanding the electrical resistivity in a power series. Similarly, we can obtain Nernst, Ettingshausen, and Leduc–Righi fields by expanding the thermoelectric power, Peltier coefficient, and the thermal conductivity in their respective power series. Or alternatively, we can deduce them from Eq. (10.19) and Figure 10.1. When this is done, the results in tensor notation are given as follows:

$$-\nabla_i\phi^{\mathrm{H}} = R_{ijk}H_k eJ_j^n \tag{10.46}$$

$$-\nabla_i\phi^{\mathrm{N}} = \eta_{ijk}H_k\nabla_j T \tag{10.47}$$

$$-\nabla_i T^{\mathrm{E}} = \varepsilon_{ijk}H_k eJ_j^n \tag{10.48}$$

$$-\nabla_i T^{\mathrm{L}} = \zeta_{ijk}H_k\nabla_j T. \tag{10.49}$$

Here, each of the four thermomagnetic and galvanomagnetic properties are intrinsically related to their respective asymmetrical, second-rank tensors via Eq. (2.69) but are also magnetic in nature. Thus, any axial, antisymmetrical third-rank magnetic tensor property has intrinsic symmetry equivalent to that of an asymmetrical, polar, second-rank magnetic tensor property. The subject of magnetic tensor properties and the subject of time reversal have purposely been left to Appendix A, where they will be discussed in some detail.

10.5 OTHER HIGHER-ORDER MAGNETOTRANSPORT TENSOR PROPERTIES IN ANISOTROPIC MEDIA

One can expand the electrical and thermal conductivities (or their inverse resistivities) and the thermoelectric effects (mainly the thermoelectric power) in Taylor series as functions of magnetic field and/or stress at a reference temperature T^0, with the appropriate independent variables held constant. To do this would yield tensor properties of rank 4, 5, and higher, many of which are known to be unimportant or to not have been studied to any significant extent. Recall that we have already discussed the magnetoresistance effect in Section 10.3—a tensor property of the fourth rank. In this section for completeness, we simply enumerate a few of the other higher-order magnetotransport effects but by no means an exhaustive coverage. Property symbols will not be given because, in many cases, they have not yet been established.

Fourth-Rank Tensor Properties

Second-order (in H) magnetothermal conductivity (or resistivity) tensors
Second-order (in H) magnetothermoelectric power (Peltier or Thomson heat) tensors

Fifth-Rank Tensor Properties

First-order (in H) piezomagnetothermal conductivity (resistance) tensor
First-order (in H) piezomagnetothermoelectric power (Peltier or Thomson heat) tensor
Second-order (in H) thermomagnetic Nernst and Leduc–Righi tensors
Second-order (in H) galvanomagnetic Hall and Ettingshausen tensors
Third-order (in H) magnetothermal conductivity (or resistivity) tensor
Third-order (in H) magnetothermoelectric power (Peltier or Thomson heat) tensor
⋮

Sixth-Rank Tensor Properties

Second-order (in H) piezomagnetothermal conductivity (or resistance) tensor
Second-order (in H) piezomagnetothermoelectric power (Peltier or Thomson heat) tensor
First-order (in H) piezothermomagnetic Nernst and Leduc–Righi tensors
First-order (in H) piezogalvanomagnetic Hall and Ettingshausen tensors
Third-order (in H) thermomagnetic Nernst and Leduc–Righi tensors
Third-order (in H) galvanomagnetic Hall and Ettingshausen tensors
⋮

Clearly, the number of higher-order magnetotransport effects greatly increases with property tensor rank. This is easily understood when one considers that the three conductivities, for example, can be expanded in power series as a functions of weak magnetic field together with temperature, electric field, and stress. Add to these the thermomagnetic and galvanomagnetic effects also expanded with these intensive fields and we have a very large number of very complex effects to consider, many of which would involve property tensors of rank 7 and above. We will not continue consideration of tensor properties higher than rank 6.

Much can be said about the partial intrinsic symmetry possessed by these higher-order magnetotransport properties, and it is not difficult. For example, by expanding the thermoelectric power in a Taylor's series as a function of stress and magnetic field, the second-order (in H) piezomagnetothermoelectric power tensor would be represented as

$$\frac{\partial^3 \Sigma_{ij}}{\partial H_k \partial H_l \partial \sigma_{mn}} = \Gamma_{ijklmn}. \tag{10.50}$$

Here, Γ_{ijklmn} is a partially symmetrical sixth-rank tensor with symmetry in $kl = o$ and in $mn = p$ but not in ij. Because Σ_{ij}, σ_{mn}, and the dyadic $H_k H_l$ are all polar second-rank tensors, then Γ_{ijklmn} must be a polar sixth-rank tensor. Therefore, this piezomagnetothermoelectric power tensor can be represented as Γ_{ijop} with no further symmetry possible. Thus, it follows that

$$\Gamma_{ijop} \neq \Gamma_{ijpo} \text{ and } \Gamma_{ijop} \neq \Gamma_{jiop} \neq \Gamma_{jipo} \quad (i, j = 1-3;\ o, p = 1-6).$$

As a second example, consider the first-order (in H) piezogalvanomagnetic Leduc–Righi tensor obtained by expanding the thermal conductivity in a Taylor series as a function of stress and magnetic field. When this is done, the results for this sixth-rank tensor property are expressed as

$$\frac{\partial^2 \zeta_{ijk}}{\partial H_l \partial \sigma_{mn}} = \Psi_{ijklmn} \quad \text{or} \quad \frac{\partial^2 L_{lk}}{\partial H_m \partial \sigma_n} = \Psi_{klmn}. \tag{10.51}$$

Now recall that magnetic field strength H is an axial–magnetic vector and that any property that is a function of an odd powers of H must also be magnetic in nature. Because the Leduc–Righi tensor ζ_{ijk} is an axial–magnetic, antisymmetrical, third-rank tensor (see Eq. (10.49)), H_l is an axial–magnetic vector and stress σ_{mn} is a polar second-rank tensor, then ψ_{ijklmn} must be an antisymmetrical nonmagnetic six-rank tensor. Or by Eq. (2.69), $L_{lk} = e_{ijl}\zeta_{ijk}$ is a magnetic, asymmetrical second-rank tensor representing the third-rank Leduc–Righi tensor. Thus, Ψ_{klmn} must be an axial fourth-rank tensor with partial symmetry existing only in the stress tensor. The designation "magnetic" has significance only when spatial and spin–magnetic domain symmetries must be analyzed in certain magnetic crystals. Appendix A is devoted to a discussion of this subject.

The effect of crystal symmetry on these magnetotransport properties must be determined from the transformation laws together with the generating matrices in Table 3.6 and the 90 magnetic points groups. For zero (in H) or second order (in Hs), the properties are nonmagnetic, and the effect of crystal symmetry can be analyzed by using only the conventional 32 point groups, exclusive of the 90 magnetic point groups. This is a big advantage. For example, the second-order (in H) magnetothermal conductivity (or resistivity) tensors are nonmagnetic and are affected by crystal symmetry the same as the piezoresistance tensor with coefficient arrays obtained from Figure 7.1. Remember that the dyadic product H^2 is both polar and symmetrical. This makes possible the determination of crystal symmetry effects for an unknown tensor property from those of a property that has been studied previously. For example, the second-order (in H) magnetothermoelectric power (or Peltier) tensors transform as in Eq. (9.30), where the anisotropy of the magnetothermoelectric coefficients can be obtained from those of the piezothermoelectric arrays provided by Tinder (see Endnotes).

Characteristics-of-a-Kind

The reader will learn that to determine the character of a given tensor property, one needs to only add up the characteristics "of a kind"—an odd number of characteristics-of-a-kind produces that character, whereas an even number of characteristics-of-a-kind does not. The major characteristics-of-a kind include axial, antisymmetrical, and magnetic. The "polar" tensor character is the norm that can be overridden by any combination of the three characteristics-of-a-kind. The inherent symmetry designations, which include symmetrical, asymmetrical, and partial symmetrical, are also needed to establish the transformation law for a given tensor. When all of the above have been considered, there remains only the effect of crystal symmetry to completely identify the surviving components of a given tensor property.

• • • •

APPENDIX A

Magnetic Tensor Properties, Magnetic Crystals, and the Combined Space-Time Transformations

Up to this point, we have dealt with the 32 conventional point groups that are used to determine the effect of crystal symmetry on polar tensor property components. Chapter 3 was devoted entirely to this cause, and in subsequent chapters, only token mention was given to magnet tensor properties and the magnetocrystalline classes that add new variants to those invoked by the conventional crystal classes. Now it is necessary to delve further into the subject matter of this Appendix.

A.1 CONDITIONS FOR MAGNETOCRYSTALLINE CLASS APPLICATION

There are 90 magnetocrystalline classes (point groups), of which there are 58 distinct magnetic variants that result from the 32 conventional point groups. Complete lists of the 90 magnetocrystalline classes can be found in numerous texts (see Endnotes, Section VI). The important question is when to apply them and when not to apply them. The 90 magnetocrystalline classes apply under the following conditions:

Condition 1. The tensor property must be magnetic. That is, the property must be a function of odd powers of the vectors $\vec{B}, \vec{H}$ taken separately or in any combination to produce the magnetic characteristic-of-a-kind. These vectors are also axial in character and hence are classified as axial–magnetic vectors. Examples of first-, second-, and third-rank axial–magnetic tensor properties are the pyromagnetic effect (Eq. (4.53)), magnetoelectric susceptibility (Eq. (4.57)), and the piezomagnetic effect (Eq. (4.63)), respectively. Lacking the magnetic characteristic-of-a-kind requirement means that the property must be regarded as polar, for which the 32 conventional point groups are applied together with Neumann's principle (as in Section 3.5) to determine the effect of crystal symmetry on a given property. There are many examples of nonmagnetic (polar) tensor properties defined in Sections 4.5, 5.1, and 7.3, their identifications being left to the reader. Magnetic tensor properties can be classified as magnetic, axial–magnetic, or polar–magnetic, but the axial–magnetic tensors are by far the most common.

Condition 2. All materials are affected by magnetic fields to some degree or another. But some materials are affected much more strongly by the presence of a magnetic field than others and may demonstrate a highly nonlinear $B - H$ behavior. Some materials possess atomic spin–magnetic moment alignments that are repeated periodically over the space lattice of the crystal and may possess a remnant magnetism in the absence of a magnetic field. Such materials (crystals) are classified as *magnetic materials*. If the spin–magnetic dipole moment alignments in these materials are altered by a magnetic field, a purely spatial transformation, or both, then a special transformation is needed to restore the material's dipole moments back to their original alignments. The characteristics just mentioned apply to the magnetic materials classified as *ferromagnetic*, *ferrimagnetic*, or *antiferromagnetic* (defined in the Glossary). In contrast, there are the so-called nonmagnetic materials, called *paramagnetic* and *diamagnetic* (also defined in the Glossary), that show little and no significant change, respectively, in their magnetic dipole moment alignments due either to the presence of a magnetic field or to spatial transformations. So, as a rule, for application of the 90 magnetocrystalline point groups, the material in which the magnetic tensor property is manifest must be magnetic in nature and the domain alignment configuration must be known. Clearly, for nonmagnetic crystals or for magnetic crystals at temperatures above the Curie (Néel) point, there would be no need to apply the 90 magnetocrystalline point groups to a magnetic tensor property because the conventional 32 point groups would suffice for symmetry purposes. Exceptions to this rule appear in some paramagnetic subgroups. Therefore, assuming that conditions 1 and 2 are satisfied, knowledge of the nature of the spin–magnetic domain structure will be necessary before the magnetocrystalline point groups can be applied properly. Of course, if the spin–magnetic domain structure is unknown or assumed (without experimental proof) for a given magnetic tensor property, there is nothing preventing a complete analysis of the component arrays. However, carrying out such an analysis may or may not be an exercise in futility.

A.2 COMBINED SPACE-TIME TRANSFORMATIONS

To deal with the effect crystal symmetry on magnetic properties manifest in magnetic materials, a *time-inversion operator* must be included in the tensor transformation forms. This time-inversion operator, designated by the symbol, $\Re$, is necessary to restore the magnetic dipole moments back to their original alignments after having been altered by a conventional (spatial) transformation or by a magnetic field or both. Recall that for an axial (pseudo) tensor an operator $|a| = \pm$ is attached to the tensor transformation form to counter a handedness change as in Eq. (2.51). However, the operators $\Re$ and $|a|$ may be thought of as complementary operators on tensor transformation forms and will often appear as composite and commutative space–time operators $\Re|a| = |a|\Re$, which must be added to the transformation form for certain tensor properties. For example, for tensors of arbitrary rank we site the following four possible transformation forms:

$$T_{ijk\cdots} = \Re a_{il}\, a_{jm}\, a_{kn} \cdots T_{lmn\cdots} \qquad \text{Polar magnetic tensor} \tag{A.1}$$

$$T_{ijk\cdots} = \Re\,|\,a\,|\, a_{il}\, a_{jm}\, a_{kn} \cdots T_{lmn\cdots} \qquad \text{Axial magnetic tensor} \tag{A.2}$$

$$T_{ijk\cdots} = a_{il}\, a_{jm}\, a_{kn} \cdots T_{lmn\cdots} \qquad \text{Polar nonmagnetic tensor} \tag{A.3}$$

$$T_{ijk\cdots} = |\,a\,|\, a_{il}\, a_{jm}\, a_{kn} \cdots T_{lmn\cdots} \qquad \text{Axial nonmagnetic tensor,} \tag{A.4}$$

where $|a|$ is replaced by $|s|$ as discussed in Section 3.5. For polar magnetic tensors, $\Re = -1$, and for all other polar nonmagnetic tensors, $\Re = +1$ and is usually not included in polar tensor transformation forms. Keep in mind that $\Re$ and $|a|$ taken separately do not constitute a symmetry transformation. But for axial–magnetic properties, their combination $\Re|a| = |a|\Re$ is complementary and must be administered with great care. Also, it is customary to view ferromagnetic, ferrimagnetic, and some antiferromagnetic solids as magnetic for which either Eq. (A.1) or Eq. (A.2) must be applied to magnetic tensor properties. Diamagnetic solids and most of the paramagnetic solids and their subgroups are generally regarded as nonmagnetic for which Eqs. (A.3) and (A.4) apply. However, there are exceptions to these rules. For further reading on this subject, see Endnotes, Section VI.

To illustrate, let us consider a few examples. The magnetic field strength vector H_i is both axial and magnetic, and its transformation law is represented as

$$H_i' = \Re\,|\,a\,|\, a_{ij} H_j = -\,|\,a\,|\, a_{ij} H_j. \tag{A.5}$$

In contrast, the magnetic susceptibility given in Eq. (4.46) is a principal effect and expressed as

$$\psi_{ik} = \mu_0 \frac{\partial M_i}{\partial B_k}. \tag{A.6}$$

Consequently, Ψ_{ik} is a polar, symmetrical, second-rank tensor property because M and B are both axial–magnetic in character. Thus, Ψ_{ik} transforms as in Eqs. (2.13), (2.14), or (2.22).

Now consider the magnetoelectric susceptibility defined by Eqs. (4.57) and (4.58) and expressed as

$$\lambda_{ij} = \frac{\partial M_i}{\partial E_j}. \tag{A.7}$$

The magnetoelectric susceptibility is an asymmetrical second-rank tensor that is both axial and magnetic in character. Accordingly, if manifest in a magnetic material, it must transform as

$$\lambda_{ij} = \Re\,|\,a\,|\, a_{ik} a_{kl} \lambda_{kl} \qquad \text{or} \qquad \lambda' = \Re\,|\,a\,|\, a\lambda\tilde{a} = \Re\,|\,a\,|\,\beta\lambda, \tag{A.8}$$

where the latter two equations are given in matrix notation, with β representing the quadratic transformation matrix for asymmetrical second-rank tensors given by Eq. (9.31).

The Hall tensor R_{ijk} given by Eq. (10.35) is an axial–magnetic third-rank tensor property expressed as

$$R_{ijk} = \frac{\partial \rho_{ij}}{\partial H_k}, \tag{A.9}$$

which is also antisymmetrical. Accordingly, if manifest in a magnetic material, it must transform according to Eq. (A.2) or in conformable matrix notation as

$$\tilde{R}' = \Re \,|\, a \,|\, \alpha \tilde{R} \tilde{a}, \tag{A.10}$$

with the understanding that R is also antisymmetrical. The form of Eq. (A.10) is easily deduced as follows: $\rho = \tilde{R}H$ relative to the old axes $0x_i$ and $\rho' = \tilde{R}'H'$ relative to the new axes $0x_i'$. Disregarding operators $\Re\,|a|$ for the moment, H transforms as $H' = aH$ or $H = a^{-1}H' = \tilde{a}H'$. Now, using Eq. (2.22), we have the result

$$\rho' = \alpha\rho = \alpha\tilde{R}H = \alpha\tilde{R}\tilde{a}H' = \tilde{R}'H',$$

which yields Eq. (A.10) after the operators $\Re\,|a|$ are added. To avoid dealing with an antisymmetrical third-rank tensor, we can use the permutation tensor as in Eq. (10.39) to produce the dual of R given by

$$r_{kl} = e_{ijk} R_{ijl} \qquad \text{or} \qquad r = e\tilde{R}. \tag{A.11}$$

Because R is an axial–magnetic antisymmetrical tensor and e_{ijk} is an axial antisymmetrical tensor, it follows that r_{kl} must be an asymmetrical, polar–magnetic, second-rank tensor that transforms according to Eqs. (A.1) and (2.23), that is,

$$r' = \Re\beta r. \tag{A.12}$$

Now it is possible to use Eqs. (A.11) and the components found for r_{kl}' to determine those for R_{ijl}.

A.3 APPLICATION OF NEUMANN'S PRINCIPLE TO MAGNETOCRYSTALLINE TRANSFORMATIONS

Once the transformation form for a given tensor property has been established from those in Eqs. (A.1) to (A.4) together with the conditions 1 and 2 set forth earlier, all that remains is to determine how to apply Neumann's principle. Chapter 3 dealt exclusively for the case of polar nonmagnetic tensor properties. There we learned that to apply Neumann's principle, we substituted s for a and σ for α in the transformation forms so as to make use of Tables 3.5 and 3.6. We also found it useful to apply the method of direct inspection to all crystal classes (except for $s^{(7)}$ in the trigonal and hexagonal classes) to reduce the calculation effort. Now, in dealing with the 90 magnetocrystalline classes, we add another layer of complexity but normally only if conditions 1 and 2 are met. For axial and polar tensor properties, we restate the Neumann's principles from Eq. (3.22) as follows:

$$T' = -T = 0 \Rightarrow \left\{ \begin{array}{l} \text{for polar tensors of odd rank} \\ \text{for axial tensors of even rank} \end{array} \right\}. \tag{A.13}$$

This means that all 11 centrosymmetrical crystal classes will be lacking in odd-rank polar tensor property components and even-rank axial tensor property components. These statements will always be true, but the addition of the magnetic characteristic-of-a-kind adds new variants to the crystal symmetry problem.

The reversal of the atomic spin–magnetic moments can be accomplished by the time-inversion operator $\Re t = -t$. This reversal of spins by means of the operator $\Re$ (creating time inversion) is actually a quantum mechanical quantity whereby spin reversal and current reversal correspond to time inversion $t \to -t$. To deal with this concept, crystallographers modify the conventional notation for rotation, reflection, and inversion given by n, m, and $\overline{n}$ by adding the symbols $\underline{n}$, $\underline{m}$, and $\underline{\overline{n}}$, respectively. Thus, underlining the symbol indicates the use of the time-inversion operator $\Re$.

As an example, consider the pyromagnetic effect defined in Eq. (4.53) and expressed as

$$q_i = \frac{\partial M_i}{\partial T}, \tag{A.14}$$

where the pyromagnetic modulus q_i is an axial–magnetic first-rank tensor (vector) that transforms as

$$q' = \Re\,|\,a\,|\,aq \qquad \text{or} \qquad q' = \Re\,|\,s\,|\,sq \tag{A.15}$$

when the generating matrices given in Table 3.5 are used. Thus, all centrosymmetrical crystal classes are potentially able to support pyromagnetic moduli according to Eq. (A.13). In general, we can say that the pyromagnetic moduli will be absent in all classes for which $\Re\,|\,s\,|\,sq = -1$. It is found that 31 of the 90 magnetocrystalline classes are potentially capable of exhibiting the pyromagnetic effect. As an example, ferromagnetic cobalt (Co) has a hexagonal close-packed crystalline structure with magnetic spin alignments parallel to the optic axis [0001] = z. The magnetic point group required for Co is $6/m\underline{m}\,\underline{m}$, with generating matrices from Table A.1 given by $\underline{s}^{(4)} = (\underline{m} \perp x)$, $\underline{s}^{(6)} = (\underline{m} \perp z)$, and $\underline{s}^{(14)} = (6z)$ given in Table A.2. From Table 3.5 and Eq. (A.15) for $\underline{s}^{(4)} = (\underline{m} \perp x)$ with $\Re = -1$ and $|a| = -1$, there results

$$\begin{bmatrix} q_1' \\ q_2' \\ q_3' \end{bmatrix} = \Re \mid s \mid sq = (-1)(-1)\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} q_1 \\ q_2 \\ q_3 \end{bmatrix} = \begin{bmatrix} -q_1 \\ q_2 \\ q_3 \end{bmatrix}, \tag{A.16}$$

which by Neumann's principle requires that $q_1 = 0$. Now, applying $\underline{s}^{(6)} = (\underline{m} \perp z)$, Eq. (A.15) becomes

$$\begin{bmatrix} q_1' \\ q_2' \\ q_3' \end{bmatrix} = \Re \mid s \mid sq = (+1)(-1)\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} 0 \\ q_2 \\ q_3 \end{bmatrix} = \begin{bmatrix} 0 \\ -q_2 \\ q_3 \end{bmatrix}. \tag{A.17}$$

Equation (A.17) requires that $q_2 = 0$, leaving only q_3 as the surviving nonzero component for Co. Application of the operator $s^{(14)} = (6z)$ does not change this result.

It is necessary to explain the results given in Eqs. (A.16) and (A.17). Application of $\underline{s}^{(4)} = (\underline{m} \perp x)$ changes both the handedness of the coordinate axes and the spin–magnetic moment alignments for which, in this case, the two operators are independent. Hence, $\Re|s| = (-1)(-1) = +1$. Application of $\underline{s}^{(6)} = (\underline{m} \perp x)$ also changes both handedness of the coordinate axes and the spin–magnetic moment alignments, but now $|a| = -1$ is a sufficient symmetry operation to restore complete space–time congruency to the crystal structure. Hence, $\Re|s| = (+1)(-1) = -1$. It must be remembered that $\Re$ and $|s|$ are complimentary operators allowing $|s|$ to act on behalf of both space and time transformations for some generating matrices. Thus, the reader is admonished to exercise great care in the use of Eq. (A.2), the most common transformation form for magnetic properties. For example, in ferromagnetic and ferrimagnetic crystals, it is necessary to know the orientation of the spin–magnetic domain alignments so as to properly apply Eq. (A.2).

As a second example, consider the magnetoelectric susceptibility tensor defined by Eq. (A.7), which is an asymmetrical, axial–magnetic, second-rank tensor property. To begin with, its property coefficients will be absent in all conventional centrosymmetrical groups. The effect can exist in groups with both space and time inversion and in some noncentrosymmetrical groups. For example, the magnetic point group $\bar{3}\underline{m}$ applies to the ferromagnetoelectric crystal Cr_2O_3 below the Curie (Néel) point. From Table A.1, $\bar{3}\underline{m}$ has generating matrices $\underline{s}^{(4)} = (\underline{m} \perp x)$ and $\underline{s}^{(13)} = (\bar{3}z)$ given in Table A.2. Applying $(\underline{m} \perp x)$ first to Eq. (A.8) gives the result

$$\lambda' = \mathfrak{R}\,|\,s\,|\,s\lambda\tilde{s} = (-1)(-1)\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{21} & \lambda_{22} & \lambda_{23} \\ \lambda_{31} & \lambda_{32} & \lambda_{33} \end{bmatrix}\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$= \begin{bmatrix} \lambda_{11} & -\lambda_{12} & -\lambda_{13} \\ -\lambda_{21} & \lambda_{22} & \lambda_{23} \\ -\lambda_{31} & \lambda_{32} & \lambda_{33} \end{bmatrix}, \qquad (A.18)$$

Therefore, $\lambda_{12} = \lambda_{13} = \lambda_{21} = \lambda_{31} = 0$ by Neumann's principle. Next, applying $(\underline{\bar{3}}\,z) = [s^{(1)}\cdot\underline{s}^{(7)}]$ yields

$$\lambda' = \mathfrak{R}\,|\,s\,|\,s\lambda\tilde{s} = (-1)(-1)\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} \lambda_{11} & 0 & 0 \\ 0 & \lambda_{22} & \lambda_{23} \\ 0 & \lambda_{32} & \lambda_{33} \end{bmatrix}\begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$= \begin{bmatrix} \left(\frac{1}{4}\lambda_{11} + \frac{3}{4}\lambda_{22}\right) & \left(\frac{\sqrt{3}}{4}\lambda_{11} - \frac{\sqrt{3}}{4}\lambda_{22}\right) & \left(\frac{\sqrt{3}}{2}\lambda_{23}\right) \\ \left(\frac{\sqrt{3}}{4}\lambda_{11} - \frac{\sqrt{3}}{4}\lambda_{22}\right) & \left(\frac{3}{4}\lambda_{11} + \frac{1}{4}\lambda_{22}\right) & \left(-\frac{1}{2}\lambda_{23}\right) \\ \left(\frac{\sqrt{3}}{2}\lambda_{32}\right) & \left(-\frac{1}{2}\lambda_{32}\right) & -\lambda_{33} \end{bmatrix} \qquad (A.19)$$

$$= \begin{bmatrix} \lambda_{11} & 0 & 0 \\ 0 & \lambda_{22} & \lambda_{23} \\ 0 & \lambda_{32} & \lambda_{33} \end{bmatrix}. \qquad (A.20)$$

But by Neumann's principle, the equality of Eqs. (A.19) and (A.20) can be justified only if $\lambda_{11} = \lambda_{22}$ and $\lambda_{23} = \lambda_{32} = 0$. Therefore, the magnetoelectric susceptibility array for point group $\underline{\bar{3}}\,\underline{m}$ must be

$$\lambda_{(\underline{\bar{3}}\,\underline{m})} = \begin{bmatrix} \lambda_{11} & 0 & 0 \\ 0 & \lambda_{11} & 0 \\ 0 & 0 & \lambda_{33} \end{bmatrix} = \begin{bmatrix} \lambda_{1} & 0 & 0 \\ 0 & \lambda_{1} & 0 \\ 0 & 0 & \lambda_{3} \end{bmatrix}. \qquad (A.21)$$

A.4 THE MAGNETIC POINT GROUPS

The 58 magnetic point groups are listed in Table A.1 together with their minimum generating matrices that are based on the 10 basic generating matrices given in Table 3.5. These are to be

TABLE A.1: Minimum generating matrices for the 58 magnetic point groups showing the 11 centrosymmetrical crystal classes designated by $\left\| X \right\|$

CRYSTAL SYSTEM	INTERNATIONAL SYMBOL (SHORT FORM)	MINIMUM GENERATING MATRICES
Triclinic	$\left\| \underline{\underline{\bar{1}}} \right\|$	$\underline{s}^{(1)}$
Monoclinic	$\underline{2}$	$\underline{s}^{(2)}$
	$\underline{m}$	$\underline{s}^{(5)}$
	$\left\| \underline{2} / m \right\|$	$\underline{s}^{(2)}, \underline{s}^{(5)}$
	$\left\| 2 / \underline{m} \right\|$	$\underline{s}^{(2)}, \underline{s}^{(5)}$
	$\left\| \underline{2} / \underline{m} \right\|$	$\underline{s}^{(2)}, \underline{s}^{(5)}$
Orthorhombic	$\underline{2}\,\underline{2}\,2$	$\underline{s}^{(2)}, s^{(3)}$
	$\underline{m}\,\underline{m}\,2$	$\underline{s}^{(3)}, s^{(5)}$
	$\underline{m}m\underline{2}$	$s^{(3)}, \underline{s}^{(5)}$
	$\underline{m}mm$	$\underline{s}^{(4)}, s^{(5)}, s^{(6)}$
	$\underline{m}\,\underline{m}m$	$\underline{s}^{(4)}, \underline{s}^{(5)}, s^{(6)}$
	$\underline{m}\,\underline{m}\,\underline{m}$	$\underline{s}^{(4)}, \underline{s}^{(5)}, \underline{s}^{(6)}$
Tetragonal	$\underline{4}$	$\underline{s}^{(9)}$
	$\underline{\bar{4}}$	$\underline{s}^{(11)}$
	$\underline{4} / m$	$s^{(6)}, \underline{s}^{(9)}$
	$4 / \underline{m}$	$\underline{s}^{(6)}, s^{(9)}$
	$\underline{4} / \underline{m}$	$\underline{s}^{(6)}, \underline{s}^{(9)}$
	$\underline{4}22$	$s^{(12)}, \underline{s}^{(9)}$
	$4\underline{2}\,\underline{2}$	$\underline{s}^{(12)}, s^{(9)}$

TABLE A.1: (Continued)

CRYSTAL SYSTEM	INTERNATIONAL SYMBOL (SHORT FORM)	MINIMUM GENERATING MATRICES
Tetragonal	$\underline{4}m\underline{m}$	$s^{(4)}, \underline{s}^{(9)}$
	$4\underline{m}\,\underline{m}$	$\underline{s}^{(4)}, s^{(9)}$
	$\underline{\bar{4}}\,2\underline{m}$	$s^{(12)}, \underline{s}^{(11)}$
	$\underline{\bar{4}}\,\underline{2}m$	$\underline{s}^{(12)}, \underline{s}^{(11)}$
	$\bar{4}\,\underline{2}\,\underline{m}$	$\underline{s}^{(12)}, s^{(11)}$
	$\underline{4}\,/\,mm\underline{m}$	$s^{(4)}, s^{(6)}, \underline{s}^{(9)}$
	$4\,/\,\underline{m}mm$	$s^{(4)}, \underline{s}^{(6)}, s^{(9)}$
	$4\,/\,m\underline{m}\,\underline{m}$	$\underline{s}^{(4)}, s^{(6)}, s^{(9)}$
	$\underline{4}\,/\,\underline{m}m\underline{m}$	$s^{(4)}, \underline{s}^{(6)}, \underline{s}^{(9)}$
	$4\,/\,\underline{m}\,\underline{m}\,\underline{m}$	$\underline{s}^{(4)}, \underline{s}^{(6)}, s^{(9)}$
Trigonal	$++$	$\underline{s}^{(13)}$
	$3\underline{2}$	$\underline{s}^{(12)}, \underline{s}^{(7)}$
	$3\underline{m}$	$\underline{s}^{(4)}, \underline{s}^{(7)}$
	$\|\underline{3}\,/\,\underline{m}\|$	$\underline{s}^{(4)}, \underline{s}^{(13)}$
	$\|\underline{\bar{3}}\;m\|$	$\underline{s}^{(4)}, \underline{s}^{(13)}$
	$\|\underline{\bar{3}}\;\underline{m}\|$	$\underline{s}^{(4)}, \underline{s}^{(13)}$
Hexagonal	$\underline{6}$	$\underline{s}^{(14)}$
	$\underline{\bar{6}}$	$\underline{s}^{(15)}$
	$\|6\,/\,\underline{m}\|$	$\underline{s}^{(6)}, s^{(14)}$
	$\|\underline{6}\,/\,m\|$	$s^{(6)}, \underline{s}^{(14)}$
	$\|\underline{6}\,/\,\underline{m}\|$	$\underline{s}^{(6)}, \underline{s}^{(14)}$

TABLE A.1: (Continued)

CRYSTAL SYSTEM	INTERNATIONAL SYMBOL (SHORT FORM)	MINIMUM GENERATING MATRICES
Hexagonal	$\underline{6}2\underline{2}$	$s^{(12)}, \underline{s}^{(14)}$
	$6\underline{2}\,\underline{2}$	$s^{(12)}, s^{(14)}$
	$\underline{6}m\,\underline{m}$	$s^{(4)}, \underline{s}^{(14)}$
	$6\underline{m}\,\underline{m}$	$\underline{s}^{(4)}, s^{(14)}$
	$\underline{\bar{6}}\,2\underline{m}$	$\underline{s}^{(4)}, \underline{s}^{(15)}$
	$\underline{\bar{6}}\,\underline{2}m$	$s^{(4)}, \underline{s}^{(15)}$
	$\bar{6}\,\underline{2}\,\underline{m}$	$\underline{s}^{(4)}, s^{(15)}$
	$\|6\,/m\,\underline{m}\,\underline{m}\|$	$s^{(4)}, s^{(6)}, s^{(14)}$
	$\|6\,/\,\underline{m}m\,m\,\|$	$s^{(4)}, \underline{s}^{(6)}, s^{(14)}$
	$\|6\,/\,\underline{m}\underline{m}\underline{m}\|$	$s^{(4)}, \underline{s}^{(6)}, s^{(14)}$
	$\|6\,/mm\underline{m}\|$	$\underline{s}^{(4)}, s^{(6)}, \underline{s}^{(14)}$
	$\|\underline{6}\,/\,\underline{m}m\,\underline{m}\|$	$s^{(4)}, s^{(6)}, \underline{s}^{(14)}$
Cubic	$\|\,\underline{m}3\|$	$\underline{s}^{(4)}, s^{(10)}$
	$\underline{4}32$	$\underline{s}^{(8)}, s^{(10)}$
	$\underline{\bar{4}}3\underline{m}$	$\underline{s}^{(16)}, s^{(10)}$
	$m3\underline{m}$	$\underline{s}^{(4)}, s^{(10)}, \underline{s}^{(17)}$
	$\underline{m}3m$	$\underline{s}^{(4)}, s^{(10)}, s^{(17)}$
	$\underline{m}3\underline{m}$	$\underline{s}^{(4)}, s^{(10)}, \underline{s}^{(17)}$

TABLE A.2: Combinations $s^{(11)}$ - $s^{(17)}$ of the 10 basic generating matrix operators used in Table A.1 and in Table 3.6

$$(\bar{4}\,z) = s^{(1)} \cdot s^{(9)} = s^{(11)}, \quad (2\,x) = s^{(1)} \cdot s^{(4)} = s^{(12)}, \quad (\bar{3}\,z) = s^{(1)} \cdot s^{(7)} = s^{(13)}, \quad (6\,z) = s^{(3)} \cdot s^{(7)} = s^{(14)}$$

$$(\bar{6}\,z) = s^{(1)} \cdot s^{(14)} = s^{(15)}, \quad (\bar{4}\,x) = s^{(1)} \cdot s^{(8)} = s^{(16)}, \quad m \perp (110) = s^{(4)} \cdot s^{(9)} = s^{(17)},$$

used in connection with those for the 32 conventional point groups given in Table 3.6. Together, these two sets of point groups make up a total of 90 point groups that are commonly referred to as magnetic point groups. Strictly speaking, of course, only the 58 point groups involve time inversion.

Proper use of Table A.1 requires some explanation. Time inversion is represented by the symbols $\underline{n}$, $\underline{m}$, and $\underline{\bar{n}}$, denoting rotation, reflection, and inversion, respectively. Combinations of the 10 basic generating operators used in Table A.1 are given in Table A.2. The rule to follow is that the time–space operators $\mathfrak{R}|s|$ must be applied to the appropriate transformation form and then only with use of the generation matrix required by the point group. Given change in the handedness of the coordinate axes for a given generation matrix operation $(|s| = 1,)$ the tricky part is to know how to apply the time-inversion operator $\mathfrak{R}$. The examples in Eqs. (A.16) and (A.17) are typical. In Eq. (A.16), the operation $\underline{s}^{(4)} = (\underline{m} \perp x)$ changes both the handedness and magnetic domain alignments, but independently, requiring that $\mathfrak{R}|a| = (-1)(-1)$. However, application of $\underline{s}^{(6)} = (\underline{m} \perp z)$ again changes both, but dependently, thereby requiring $\mathfrak{R}|a| = (+1)(-1)$.

To apply the combinations in Table A.2 to the magnetic point groups in Table A.1, it is necessary to know how to use time inversion. The rule is straightforward. Time inversion for operator combinations must be applied to the resultant matrix operator. Typical examples are $\underline{s}^{(13)} = \underline{s^{(1)} \cdot s^{(7)}} = (\underline{\bar{3}}\, z)$, $\underline{s}^{(14)} = \underline{s^{(3)} \cdot s^{(7)}} = (\underline{6} z)$, and $\underline{s}^{(15)} = \underline{s^{(1)} \cdot s^{(14)}} = (\underline{\bar{6}} z)$. Thus, the matrix multiplication indicated must be carried out before applying time inversion. Other examples that are not combinations include $\underline{s}^{(2)} = (\underline{2} y)$, $\underline{s}^{(7)} = (\underline{3} z)$, and $\underline{s}^{(8)} = (\underline{4} x)$. The reader should refer to Tables 3.5 and 3.6 as needed.

Remember that the symbols $\underline{n}$, $\underline{m}$, and $\underline{\bar{n}}$ require the use of the time-inversion operator $\mathfrak{R}$, which is used only to establish congruency of the spin–magnetic domain alignments after a transformation of axes. However, because the operator combination $\mathfrak{R}|s|$ is complementary, care must be taken to know whether the congruency of the alignments is established by $|s|$, as in the case of Eq. (A.17). Thus, if a given group transformation changes the handedness of the coordinate axes for an axial–magnetic crystal, it is necessary to know what effect the axial operator $|s| = -1$ has on the spin–magnetic domain alignments. Only then can the time-inversion operator $\mathfrak{R}$ be applied appropriately. This, of course, is the reason why it is necessary to know the magnetic domain structure before any symmetry group transformation. If, as for the nonmagnetic materials, the magnetic domain structure is of no consequence, then $\mathfrak{R} = +1$ and only $|s|$ must be considered for an axial–magnetic tensor property.

For further reading regarding subject matter presented in Sections A.3 and A.4, see Newnham, Billings, and Birss in Endnotes, Section VI. The examples given in Section A.3 follow closely those presented by Newnham.

Endnotes

An exhaustive bibliography for the subjects covered in this text would be enormous and would not serve the reader well. Consequently, we carefully select those references that provide support for material covered in this text and further reading for those needing additional information. It will be noticed that many of the references that follow date back 40 years or older. This is expected because it was in that era that most of the important fundamental work was established in tensor properties of solids. It is for this reason that these references are frequently cited by current authors.

I. GENERAL TEXTS ON THE PHYSICAL (TENSOR) PROPERTIES OF SOLIDS

The work of Nye is a classic text that provides essential background materials, including the treatment of equilibrium and nonequilibrium thermodynamics of the physical properties in anisotropic and isotropic solid state media. Other recommended sources of information in this category that complement Nye are the texts by Billings, Lovett, Newnham, and Bhagavantam, all providing a somewhat different approach to the subject matter at varying technical levels of treatment. Billings' treatment is quite succinct but covers the equilibrium tensor properties, time inversion, and the transport properties in sufficient detail. From a physics point of view, the text by Lovett supplements quite well the other texts cited in this section. Newnham provides a recent, more detailed, and lucid coverage of tensor properties of solids and supports this coverage with pertinent data presented in graphic form. This author also provides an extensive list of references for further reading. Bhagavantam is strong on crystal symmetry and crystal groups and covers elasticity, magnetic properties, and transport phenomena rather well. The work of Callen is a classic text in thermodynamics that provided useful supporting material in thermodynamics for this book. The text by Masson is also a worthwhile read and is especially strong on piezoelectric effects. For the treatment of stereograms, the reader will find the texts of Nge, Billings and Newnham more than adequate.

J. F. Nye, *Physical Properties of Crystals*, Oxford University Press, Oxford, 1957.

A. R. Billings, *Tensor Properties of Materials—Generalized Compliance and Conductivity*, Wiley-Interscience, John Wiley & Sons Ltd., New York, 1969.

D. R. Lovett, *Tensor Properties of Crystals*, Institute of Physics Publishing, Bristol, 1999.

R. E. Newnham, *Properties of Materials, Anisotropy, Symmetry, Structure*, Oxford University Press, Oxford, 2005.

S. Bhagavantam, *Crystal Symmetry and Physical Properties*, Academic Press, New York, 1966.
H. B. Callen, *Thermodynamics—An Introduction to the Physical Theories of Equilibrium Thermostatics and Irreversible Thermodynamics*, John Wiley & Sons, New York, 1960.
W. P. Masson, *Crystal Physics of Interaction Processes*, Academic Press, New York, 1966.

II. IRREVERSIBLE THERMODYNAMICS AND THE TRANSPORT PROPERTIES OF SOLIDS

Without question, the subject of nonequilibrium (irreversible) thermodynamics is more complicated than equilibrium thermodynamics (thermostatics). This is mainly because irreversible thermodynamics has its foundation in fluctuation theory, and the principle of detailed balance of microscopic reversibility is accredited to Lars Onsager (1903–1976). The texts by Nye, Billings, Newnham, Bhagavantam, and Callen, previously cited above, touch on this subject to one degree or another. However, for a rigorous treatment of irreversible thermodynamics, the reader can find no better sources than in the texts by Prigogine, De Groot, and De Groot and Mazur. However, the reader must be warned that these three texts are at an advanced level in theoretical physics and will require significant background preparation to comprehend their contents. The text by Kondepudi and Prigogine is very well written and provides a more general treatment of thermodynamics "from heat engines to dissipative structures" but leans somewhat toward chemical thermodynamics.

I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, John Wiley & Sons, New York, 1967.
S. R. De Groot, *Thermodynamics of Irreversible Processes*, North-Holland, Amsterdam, 1963.
S. R. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, Amsterdam, 1962.
D. Kondepudi and I. Prigogine, *Modern Thermodynamics*, John Wiley & Sons, New York, 1998.

III. GENERAL TEXTS FROM A THEORETICAL PHYSICS POINT OF VIEW

The works of Landau and Lifshitz and by Smith, Janak, and Adler are classic texts in their own right but have limited contributions to the subject matter of this book. Although both texts may be classified as theoretical physics, the work of Landau and Lifshitz is the most useful, particularly in areas of thermoelectric and magneto-optical effects. Again, the reader is warned that substantial background knowledge is most likely needed to assimilate this material.

L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Pergamon Press, Oxford, 1960.
A. C. Smith, J. F. Janak, and R. B. Adler, *Electronic Conduction in Solids*, McGraw-Hill, New York, 1967.

IV. MATHEMATICS AND THE PHYSICAL PROPERTIES OF CRYSTALS

Adding to the mathematical treatment provided by the texts in Part I above is the well-known article by Bond and the book by Prince. Both are useful references to complement the material presented in the author's text.

W. L. Bond, "The mathematics of the physical properties of crystals," *Bell Systems Tech. J.* **22**, 1–72, 1943.
E. Prince, *Mathematical Techniques in Crystallography and Material Science*, Springer-Verlag, Berlin, 1994.

V. VECTOR AND TENSOR ANALYSIS

There is a plethora of texts on vector and tensor analyses that can be listed here. Two such texts that provide the necessary information for the author's text are those of Bourne and Kendall, and Young. Most readers with some mathematical background will find these two texts quite manageable and useful.

D. E. Bourne and P. C. Kendall, *Vector Analysis and Cartesian Tensors*, 3rd ed., Chapman & Hall, London, 1992.
E. C. Young, *Vector and Tensor Analysis*, Marcel Dekker, New York, 1993.

VI. MAGNETIC PROPERTIES AND SYMMETRY CONSIDERATIONS

Because of the complex nature of the subject matter in this section, we must carefully pick and choose certain references that provide the necessary background but that also provide supplementary material for further reading. The texts by Billings, Newnham, and Bhagavantam, previously cited, provide an excellent beginning. As a second-level read, the text by Landau and Lifshitz, also previously cited, is recommended. For further more specialized reading, we recommend the text by O'Dell and the contributions by Birss and Dillon. As a supplementary source of information on magnetic properties, the text by Newnham is highly recommended. The subjects of time reversal (inversion) and the 90 magnetocrystalline classes, as associated with the spin magnetic moments and their reversal, are an inherent part of these and previously cited references.

R. E. Newnham, *Properties of Materials, Anisotropy, Symmetry, Structure*, Oxford University Press, 2005.
A. R. Billings, *Tensor Properties of Materials—Generalized Compliance and Conductivity*, Wiley-Interscience, John Wiley & Sons Ltd., New York, 1969.

T. H. O'Dell, *The Electrodynamics of Magneto-Electric Media*, North-Holland, Amsterdam, 1970.
R. R. Birss, *Symmetry and Magnetism, Vol. III. Selected Topics in Solid State Physics*, North Holland, Amsterdam, 1964.
J. F. Dillon, "Magneto-optical properties of magnetic crystals," in *Magnetic Properties of Materials*, McGraw-Hill, New York, pp. 149–204, 1967.

VII. SPECIALIZED ARTICLES REFERENCED IN THE AUTHOR'S TEXT

The article by Mazur and Prigogine demonstrates how Legendre transforms can be used to partially invert the matrix of phenomenological coefficients for the thermomagnetic and galvanomagnetic effects in an isotropic crystal plane. The article by Tinder provides a detailed development of the piezothermoelectric and elastothermoelectric tensor properties in anisotropic media together with the aelotropism for these effects.

P. Mazur and I. Prigogine, "Galvanomagnetic and Thermomagnetic Effects," *J. Phys. Radium* **12,** 616, 1951.
R. F. Tinder, "Piezothermoelectric effects in anisotropic media," *J. Appl. Phys.*, **43**(6), 2522–2529, June 1972.

VIII. MEASUREMENT TECHNIQUES AND DATA OF TENSOR PROPERTIES OF SOLIDS

A good place to begin search for experimental data of the tensor properties of solids is the *Electrical Engineering Handbook*. Other sources include the recent text by Newnham (previously cited in Section I), who has also contributed to the *Electrical Engineering Handbook*, and the text by Masson (also previously cited in Section I). Still other sources of such information include the "Standards on Piezoelectric Crystals" and, for measurements techniques, the text by Newnham and an older book by Bond. The text by Newnham contains a variety of references from which measurement data on both equilibrium and transport properties can be obtained. The text by Kondepudi and Prigogine (previously cited in Section II) also yields some useful data on these properties.

Richard C. Dorf, editor in chief, *The Electrical Engineering Handbook*, 2nd ed., CRC Press and IEEE Press, Boca Raton, FL, 1997.
R. E. Newnham, *Properties of Materials, Anisotropy, Symmetry, Structure*, Oxford University Press, Oxford, 2005.
"Standards on piezoelectric crystals," *Proc. IRE.* **37**, 1378–1385, 1949.
W. L. Bond, *Crystal Technology*, John Wiley & Sons, New York, 1976.

Glossary of Terms and Expressions

Adiabatic process. Any thermodynamic process, reversible or irreversible, that takes place in a system without an interchange of heat with the surroundings. When the process is also reversible, it is called *isentropic* because the entropy of the system remains constant at each step in the process.

Aelotropic solid. An anisotropic solid.

Affinity. The driving force in an irreversible process.

Alternating (permutation) tensor. An axial, antisymmetrical third-rank tensor that is 1 for an even permutation of 123 is –1 for an odd permutation of 123 and is 0 if any two of its subscripts are the same.

Antiferromagnetic solid. A solid that has alternating alignment of atomic magnetic dipole moments that produce a zero net magnetic moment (zero magnetization) in the absence of an applied magnetic field.

Anisotropic solid. Any solid in which a property varies with direction—a solid that is not isotropic.

Antisymmetric tensor. A tensor of second or higher rank is antisymmetric if any two suffixes are interchanged such that $T_{\ldots ijk\ldots} = -T_{\ldots jik\ldots}$ For example, a second-rank tensor is antisymmetric if $T_{ij} = -T_{ji}$ resulting in $T_{ii} = 0$.

Asymmetrical tensor. A tensor lacking symmetry in any pair of its subscripts.

Axial–magnetic tensor. A tensor that requires both space and time inversion operators for its transformation.

Axial tensor. A tensor whose components change sign when the handedness of the coordinate axes is changed by a transformation involving a mirror plane or an inversion of axes—also a pseudotensor.

Biaxial crystal. A crystal that has two distinct optic axes.

Birefringence (double refraction). An optical condition in which two different refracted light waves are formed that do not, in general, lie in the plane of incidence.

Bridgman heat. A heat that is generated in an anisotropic crystal resulting from the nonuniformity in the distribution of electric current as, for example, in an L-shaped crystal in which the current flux changes direction.

Brute-force method. A coined expression referring to the case where the effect of crystal symmetry on a given property cannot be determined by the method of direct inspection but instead must be obtained by the all-embracing expansion of the corresponding transformation equation.

Cartesian tensor. A tensor that is completely specified by orthogonal Euclidean coordinates.

Cause parameter. Usually, an intensive parameter that, when related to an extensive (effect) parameter, defines a tensor property.

CCW. Counterclockwise (positive rotation).

Center of symmetry. A fundamental macroscopic operation involving an inversion of Cartesian axes through the origin of coordinates.

Centrosymmetrical crystal class. A point group that contains a center of symmetry.

Characteristics-of-a-kind. As used in this book, tensor characteristics that include axial, magnetic, and antisymmetrical designations that can override the normal (polar) character of a tensor.

Chemical potential gradient. The chemical driving force responsible for the diffusion of chemical species in a given medium as, for example, in the application of a concentration gradient in Fick's law.

Clamped condition. A measurement condition that requires a given extensive parameter to remain constant.

Closed system. As used in this text, a system that can only exchange energy with its surroundings but not mass or charged mass.

Cofactor. The determinant minor of a square matrix obtained by crossing out the ith row and jth column and multiplied by $(-1)^{(i+j)}$.

Compliance matrix. A property matrix generated from the equations of state for which the extensive parameters are given as functions of the intensive parameters—the inverse of the rigidity matrix.

Concentration gradient. In most cases, the same as the chemical potential gradient.

Conformable matrices. If A is an m × n (rows × columns) matrix and B is an n × p (rows × columns) matrix, then A and B are conformable in the order AB. Hence, the number of columns in A must be equal to the number of rows in B.

Conjugate parameters. Parameters that are intrinsically (physically) related as, for example, stress and strain, temperature and entropy, and electric current flux and electrostatic potential gradient.

Conventional point group. One of 32 point groups into which all seven possible crystal systems can be classified as to their macroscopic symmetry elements.

Convergence of a tensor. The single contraction product of a field tensor with the vector operator that gives at each point on an element the net rate per unit volume at which a physical entity is incoming to that element (opposite of the divergence of a tensor).

Converse effect. An independent coupled effect derived from a Maxwell relation for the direct/converse effects expressing the rate of change of an extensive parameter with an intensive parameter.

Converse piezoelectric effect. The polar third-rank tensor property expressing the change in elastic strain as a function of the applied electric field.

Cotton–Mouton effect. The polar, nonmagnetic, fourth-rank tensor property representing the quadratic magneto-optical effect that is produced when a dielectric is placed in a magnetic field such as to produce a phase difference or retardation between the linearly polarized light wave in the direction of the magnetic field and a wave propagating in a plane perpendicular to the magnetic field.

Coupled effect. An interaction effect not relating conjugate parameters but which constitutes a Maxwell relation derived from a suitable thermodynamic potential such as the Gibbs free energy density.

Crystallographic direction. The direction in a crystalline lattice designated by Miller or Miller–Bravais indices that are determined by the lattice vector magnitudes along the crystallographic axes.

Crystallographic plane. The set of Miller or Miller-Bravais indices derived from the reciprocal of intercepts on the crystallographic axes that define a plane.

Crystal system. One of seven sets of unit cell axes and angles into which all crystals must belong.

Curie point. A second-order phase transition at a temperature for the ferromagnetic-paramagnetic change.

Current density. A flux representing the flow of charge, heat, or mass crossing a unit area per second.

Dependent coupled effect. An effect relating any two intensive parameters with the corresponding two extensive parameters that derive from the appropriate choice of thermodynamic potential together with the application of Green's theorem in a plane.

Dependent variable. The variable taken as the function of an independent variable in defining a given property.

Diad. In crystallography, a twofold (180°) rotation axis of symmetry.

Diamagnetic solid. A solid whose magnetic susceptibility is negative and that exhibits a zero net magnetic moment in the absence of an externally applied magnetic field but that produces a small net magnetic moment that opposes an applied magnetic field.

Diathermal system. Any system that permits the flow of heat with the surroundings—a perfect heat conductor.

Dielectric constant. The second-rank, polar tensor property equal to the relative permittivity tensor.

Dielectric impermeability. As used in this text, the symmetrical second-rank polar tensor whose components are used to phenomenologically develop the optical properties of crystals.

Dielectric susceptibility. The rate of change of polarization with electric field all multiplied by the reciprocal of the permittivity in a vacuum.

Diffusion. The movement of a matter species under the influence of a chemical potential (concentration) gradient.

Diffusivity. The second-rank tensor transport property relating the flux of matter to a chemical potential gradient.

Direct effect. An independent coupled effect derived from a Maxwell relation for the direct/converse effects expressing the rate of change of an extensive parameter with an intensive parameter.

Direct inspection method. A simple deductive means of applying Neumann's principle by using the minimum generating matrices applied to the crystal classes other than those containing a three or sixfold rotation axis of symmetry.

Divergence of a tensor. The single contraction product of a field tensor with the vector operator that gives at each point on an element the net rate per unit volume at which a physical entity is issuing from that element. (opposite of the convergence of a tensor).

Double refraction. A beam of light traversing an anisotropic medium, such that the beam is separated into two components, distinguished as the ordinary and extraordinary rays, that are polarized at right angles to each other, that have different velocities within the medium, and that propagate in different directions (same as birefringence).

Driving force. An affinity (potential gradient) that produces an irreversible process.

Dual of a tensor. A tensor or rank $(r + 1)$ resulting from the application of alternating (permutation) tensor on another tensor of rank r.

Dummy suffix. A repeating subscript.

Dyadic product. As used in this text, an outer product involving two first-order tensors (vectors) to form a second-rank tensor combination having nine components.

Effect parameter. Usually, an extensive parameter which when related to an intensive (cause) parameter defines a tensor property.

Einstein summation convention. The implied summation(s) over the dummy (repeating) suffix(s) or subscript(s) in a tensor equation.

Elastic strain. The extensive parameter that when related to a stress parameter defines an elastic compliance coefficient or elastic stiffness coefficient as in Hooke's law or its inverse.

Elasticity. The reversible process whereby the application of a stress to a solid produces a deformation (elastic strain) that is completely recoverable upon removal of the causal stress.

Elasto-. A prefix denoting the influence of elastic strain on a physical property.

Elasto-optical effect. The fourth-rank, partially symmetrical, polar tensor property that expresses the rate of change of the impermeability tensor with the strain tensor and that is also related to the piezo-optical effect via the elastic stiffness or elastic compliance moduli.

Elastothermoelectric power effect. The partially symmetrical fourth-rank, polar tensor property that expresses the rate of change of the thermoelectric power with strain.

Electric dipole moment. A vector formed by the combination of two equal but opposite charge distributions multiplied by the distance that separates the combination and directed from the negative to the positive charge distribution.

Electric field. The negative of the electrostatic potential gradient produced between opposite charge distributions that are separated by finite distance. A measure of the torque on a unit electric dipole.

Electrical conductivity. The second-rank, polar tensor property that relates an electric current density to an electrostatic potential gradient (electric field).

Electrical resistivity. The second-rank, polar tensor transport property (inverse of the electrical conductivity) that relates an electrostatic potential gradient (electric field) to an electric current density—generalized Ohm's law.

Electro-. A prefix denoting the influence of electric field strength on a physical property.

Electrocaloric effect. The polar vector property that gives the change in entropy with electric field strength and whose coefficients are the same as those for its corresponding pyroelectric effect.

Electrochemical potential. The total energy per particle equal to the sum of the chemical potential per particle and the electrostatic potential per particle. Also called the Fermi level in the equilibrium state.

Electrodiffusive effect. Any effect that results from the simultaneous flow of electricity and mass.

Electrostatic potential gradient. Minus the electric field strength produced between opposite charge distributions separated by finite distance.

Electrostriction. The elastic strain produced in a crystalline solid by the application of an electric field. The converse piezoelectric effect.

Energy density. The energy per unit volume as, for example, internal energy density.

Enthalpy. The Legendre transform of the Euler relation that replaces all extensive parameters (except entropy) by their conjugate intensive parameters as the independent variables and is the thermodynamic potential used to define the heat capacity of a solid at constant electric field, magnetic field, and stress.

Entropy. The negative change of Gibbs free energy with temperature at constant electric field, magnetic field, and stress.

Entropy production. The time variation of unrecoverable work per unit volume per unit temperature inside a closed system and which must be positive definite if an irreversible process is to occur.

Equation of state. A characteristic equation in thermodynamics, empirical or derived, expressing the functional relationship between an extensive parameter and all relevant intensive parameters and vice versa for an intensive parameter.

Equilibrium thermodynamics (thermostatics). The field of study for which all systems are required to be in thermodynamic equilibrium.

Ettingshausen effect. The generation of a transverse temperature gradient when a magnetic field is imposed in a direction perpendicular to an electric current flux.

Euler relation. A thermodynamic potential that combines the first and second laws of thermodynamics in terms of the product of conjugate parameters and is used in the creation of the 16 thermodynamic potentials from Legendre transforms.

Even function. A function that does not change sign when the dependent variable changes sign as in $f(x) = f(-x)$ (*see* **odd function**).

Exact differential. A differential that is path independent as, for example, the infinitesimal change in internal energy in the first law of thermodynamics.

Extensive parameter. Extensive parameters are those that depend on the amount of material of a solid phase system, hence volume or size dependent.

False effect. A false or secondary effect, usually of higher tensor order than the true (primary) effect, occurs by indirect means, and functions as a correction factor to the primary effect.

Faraday effect. When a transparent isotropic crystal is placed in a strong DC magnetic field and linear polarized light travels parallel or antiparallel to the magnetic field, the plane of polarized light is rotated through an angle.

Faraday rotation. The angle through which the plane of polarized light is rotated as a result of the action of the Faraday effect.

Faraday tensor. A polar nonmagnetic second-rank tensor that is related to the Faraday rotation angle.

Fermi energy. As used in this text, the same as the electrochemical potential of electrons assuming equilibrium conditions.

Ferrimagnetic solid. A solid that has spontaneous antiparallel alignment of the magnetic dipole moments but with incomplete cancellation, that shows hysteresis, and whose magnetism disappears at the Curie temperature.

Ferromagnetic solid. A solid that has spontaneous aligned atomic magnetic dipole moments (a remnant magnetization) in the absence of a magnetic field, that shows hysteresis, and whose spontaneous magnetism disappears at the Curie temperature.

Fick's law. An irreversible transport process in which the diffusing matter flux is proportional to a corresponding chemical potential (concentration) gradient.

Flux. The flow of electric current, heat, or mass across a unit area per second in a transport process.

Force. In an irreversible system, the driving force is a potential gradient responsible for producing a flux. In an equilibrium system, the force applied to a unit area of a solid defines a stress.

Fourier's law. An irreversible transfer process in which the diffusing heat flux is proportional to the temperature gradient.

Free condition. A measurement condition that requires a given intensive parameter to remain constant.

Galvanomagnetic effect. One of several effects that results from the application of an electrostatic potential gradient perpendicular to a magnetic field and producing either a transverse electrochemical potential gradient or a transverse temperature gradient. Examples are the Hall, magnetoresistance, and Ettingshausen effects.

Generating matrix. One of 10 symmetry operations used in the generation of the 32 point groups.

Generation operator. A minimum generating matrix used to determine the effect of crystal symmetry on the components of a property tensor.

Gibbs–Duhem equation. An expression showing that small increments in the intensive variables cannot all be independent.

Gibbs free energy. A Legendre transform of the Euler relation that replaces all extensive parameters by their conjugate intensive parameters as the independent variables.

Gradient of a scalar. *See* **scalar gradient**.

Gradient of a tensor. The outer product of a field tensor of rank r with a tensor operator of rank n resulting in a tensor of rank $r + n$.

Grüneisen tensor. In its general form, the Grüneisen tensor expresses the rate of change in stress with internal energy density and is proportional to the inverse of the isometric piezocaloric coefficient.

Hall effect. The generation of a transverse electrochemical potential gradient when a magnetic field is imposed in a direction perpendicular to an electric current flux.

Heat capacity. As used in this text, a scalar expressing the rate of change of entropy density with absolute temperature (at constant electric, magnetic, and stress fields), multiplied by the absolute temperature.

Helmholtz free energy. The Legendre transform of the Euler relation that replaces the entropy by temperature as the independent variable.

Hermann–Mauguin International Short System. The system of symbols used in this text to represent the symmetry elements characteristic of each of the 32 conventional crystal classes or point groups.

Hermitian tensor. As used in this text, a second-rank tensor property for which the optical absorption factor is zero.

Hexad. In crystallography, a sixfold (60°) rotation axis of symmetry.

Holohedral group. A point group that contains a center of symmetry. Same as a centrosymmetrical group.

Hooke's law. The proportionality of stress to strain as a suitable description of the behavior of solids in the elastic range.

Identity matrix. A square matrix for which the leading diagonal components are +1, all others being zero.

Independence of path principle. A principle given to a thermodynamic property whose changes depend only on its initial and final states as expressed mathematically by Green's theorem in a plane.

Independent variable. The variable whose change causes a corresponding change in the dependent variable via the system property that links the two variables.

Index of refraction. A measurable quantity equal to the ratio of the velocity of light in a vacuum to that in a given material; also, equal to the square root of the dielectric constant (relative permittivity) of a medium.

Indicatrix. An ellipsoid, whose major and minor axes are the principle axes of the dielectric constant tensor, which is descriptive of the passage of light through a crystal and must satisfy the symmetry of the crystal. A plane cutting the indicatrix ellipsoid and passing through its center will intersect the surface generally as an ellipse having a normal along the direction of light propagation. The light resolves into two components with wave fronts that lie along the semiaxes of the ellipse and having refractive indices that are proportional to the lengths of the semiaxes—the major axis represents the slower component, whereas the minor axis represents the faster component.

Inexact differential. Inexact differentials are path-dependent differentials called *Pfaffians*.

Inner product. The single contraction product of two tensors $A \cdot B$, which results in a tensor of rank 2 less than the sum of the ranks of the two product tensors, that is $r_A + r_B - 2$.

Intensive parameter. An intensive parameter is independent of the volume or size of a given system such that if subsystems are adjoined, the intensive parameter of the whole is the same as those of its parts.

Interaction diagram. As used in this text, a diagram consisting of intensive and extensive parameters representing the first-order properties given by the principle, coupled, and dependent-coupled effects.

Interaction effect. *See* **coupled effect**.

Inverse of a matrix. The inverse (reciprocal) of a matrix M is the transpose of the cofactor of each element of M divided by the determinant of M.

Irreversible process. Any nonreversible process for which the entropy production is positive definite.

Irreversible thermodynamics. The thermodynamics of transport (irreversible or Markoff) processes.

Isentropic process. Any thermodynamic process in which the entropy is maintained constant at each step in the process, hence also an adiabatic process that is reversible.

Iso-. A prefix denoting constancy or uniformity of a field tensor.

Isolated system. A system that does not exchange energy, mass, or charged mass with its surroundings.

Isometric. As used in this text, constant strain.

Isopiestic. As used in this text, constant stress.

Isothermal condition. Constant temperature condition.

Isotropic solid. Any solid in which a property is invariant with direction in the solid.

Joule heat. The heat generated by the passage of electric current in a conductor.

Kelvin relation. One of two relations used in the expression of the thermoelectric effects and that exist as a consequent of Onsager's reciprocal principle.

Kerr effect. A quadratic electro-optical effect that occurs when an isotropic solid becomes anisotropic in the presence of a magnetic field.

Kronecker delta. In Cartesian tensor analysis, the function δ_{ij} takes the value $\delta_{ij} = 1$ if $i = j$ or the value $\delta_{ij} = 0$ if $i \neq j$ and forms a unitary matrix.

Lattice parameter. A length representing the size of the unit cell in a crystalline lattice.

Leduc–Righi effect. The generation of a transverse temperature gradient when a magnetic field is imposed in a direction perpendicular to a heat flux.

Legendre transform. A transform that simultaneously replaces as the independent variable one or more of the extensive parameters by their conjugate intensive parameters.

Maclaurin series expansion. A special case of a Taylor's series expansion such that the expansion is taken about the state of zero reference values for all variables involved in the expansion.

Magnetic dipole moment. Per unit volume, the magnetic dipole moment is the magnetization.

Magnetic field strength. A derived axial magnetic vector H that is associated with the external magnetic flux density B and that is independent of the magnetic properties of the material in which it is manifest.

Magnetic flux density (magnetic induction). The observable (external) axial magnetic vector B associated with a magnetic field strength and equal to that magnetic field strength H times the permeability of the substance in which H is present.

Magnetic point group. One of 90 self-consistent magnetic symmetry operations (point groups) that introduce the time-reversal operator whose application together with the symmetry elements of a conventional point group bring the spatial and magnetic moment orientations of a crystal into self-congruence.

Magnetic solid. As used in this text, any crystalline solid that is ferromagnetic, ferromagnetic, or antiferromagnetic in nature and that possesses both conventional crystallographic symmetry and time-reversal symmetry elements.

Magnetic susceptibility. A second-rank tensor property that expresses the rate of change of magnetization with magnetic field strength.

Magnetic tensor. A tensor whose components transform as a polar tensor but that may also be affected by the time-reversal operator for certain crystals.

Magnetization. The magnetization (relative permeability) is the negative change in the Gibbs free energy density with magnetic flux density and is equal to the magnetic susceptibility per unit magnetic field strength applied. The total magnetic dipole moment per unit volume of solid.

Magneto-. A prefix denoting the influence of the magnetic field strength on a physical property.

Magnetocaloric effect. A first-order axial magnetic tensor property that produces a change in the entropy density of a crystal with magnetic flux density and whose components are the same as those of the pyromagnetic effect.

Magnetoelectric susceptibility effect. The independent coupled effect that expresses the rate of change of polarization with magnetic flux density or its converse effect expressing the rate of change of magnetization with electric field strength.

Magneto-optical effect. Any one of several linear or quadratic effects where the dielectric impermeability tensor is caused to change as a result of a changing magnetic flux density vector together with possible changes in temperature, electric field, and stress.

Magnetoresistance effect. The fourth-rank tensor property that expresses the effect of second-order magnetic field strength on the electrical resistivity.

Magnetothermoelectric power effect. The fourth-rank tensor property that expresses the effect of second-order magnetic field strength on the Seebeck or Peltier tensors.

Markoff process. As used in this text, transport processes for which the fluxes at any given instant depend only on the forces (affinities) in effect at that instant—a transport process that has no memory.

Matrix. A rectangular array of scalars or matrix elements that conforms to certain rules of combination with other matrices but whose elements can represent physically meaningful coefficients or moduli.

Matter tensor property. As used in this text, any tensor effect or property associated with a solid.

Maxwell relations. As distinguished from Maxwell equations in electromagnetic theory, Maxwell relations are used to equate the coefficients of the off-diagonal coupled effects as allowed by thermodynamic symmetry.

Method of direct inspection. A simple deductive means of applying Neumann's principle by using the minimum generating matrices applied to the crystal classes other than those containing a threefold or sixfold rotation axis of symmetry.

Microscopic reversibility, principle of. As used in this text, it states: "For a system in the thermodynamic equilibrium, every type of micromotion occurs just as often as its reverse."

Miller indices. A notation used to describe crystallographic planes and directions for the six crystal systems.

Miller–Bravais indices. A alternative notation used to describe crystallographic planes and directions for the trigonal and hexagonal crystal systems.

Mirror plane. A plane of reflection that is equivalent to a center of symmetry followed by a 180° rotation about the mirror plane normal.

Modulus of rigidity. *See* **shear modulus**.

Mole number. As used in this book, the actual number of a diffusing species divided by Avogadro's number.

Monad. A onefold (360°) rotation axis of symmetry.

Morphic effect. An effect that contributes higher-order coefficients to a first-order property whose coefficients vanishes for the 11 centrosymmetrical crystal classes.

Nernst effect. The generation of a transverse electrochemical potential gradient when a magnetic field is imposed in a direction perpendicular to a heat flux caused by a thermal gradient.

Neumann's principle. Requirement that the component of a tensor property must remain invariant under a transformation of coordinates governed by a symmetry operation valid for the point group of the crystal.

Nonequilibrium property. A property governed by an irreversible thermodynamic processes; a transport property.

Nonmagnetic solid. As used in this text, any crystalline solid that is either diamagnetic or paramagnetic in nature but which may possess both conventional crystallographic symmetry and time-reversal symmetry elements.

Odd function. A function that changes sign when the dependent variable changes sign as in $f(x) = -f(-x)$ (*see* **even function**).

Ohm's law. In its generalized form, a statement that the electric current flux is proportional to the electrostatic potential gradient.

Onsager's reciprocity principle. As used in this text, it states: "Provided a proper choice is made for the fluxes and driving forces (affinities), the matrix of phenomenological coefficients is symmetrical."

Open system. A system that can exchange heat as well as electric current and mass with the surroundings.

Optical absorption factor. The ratio of absorbed to unabsorbed light radiation in a dielectric medium.

Optically uniaxial crystal system. A member of the tetragonal, trigonal, and hexagonal crystal classes where the $x_3 = c$ axis is the principle or optical axis along which a wave normal can produce no double refraction.

Optic axis. In an anisotropic crystal, the direction along which double refraction does not occur.

Outer product. The product of two tensors AB that yields a resultant tensor of rank r_R equal to the sum of the tensor ranks of the two product tensors, $r_R = r_A + r_B$.

Paramagnetic solid. A solid whose atomic magnetic moments are randomly oriented but that exhibit a small, often negligible, magnetization in the presence of a magnetic field.

Partial symmetry. Refers to tensors for which there is partial symmetry in its subscripts such as $T_{ijk} = T_{jik}$ but $T_{mk} \neq T_{km}$.

Particle. As used in this text, a positive test charge equal to the absolute value of the charge on an electron.

Peltier effect. The evolution or absorption of heat accompanying the flow of electric current across and isothermal junction between two dissimilar conductors or semiconductors.

Permeability. A polar second-rank property tensor that is the ratio of the magnetic flux density vector to the magnetic field strength vector.

Permittivity. A polar second-rank property tensor that is proportional to the dielectric constant tensor.

Permutation tensor. An axial, antisymmetrical tensor of rank 3 that takes the value of +1 for an even permutation of 123, the value of –1 for an odd permutation of 123 (e.g., 132), and is zero if any two of the subscripts are the same—also called the alternating tensor.

Pfaffian. An inexact differential that is path dependent as, for example, the external work $đW$ done on a solid phase system—the external work depends on the path taken between initial and final states when integrating $đW$.

Phenomenological development. As used in this text, property developments based mainly on equilibrium and irreversible thermodynamics arguments.

Piezo-. A prefix denoting the influence of mechanical stress on a physical property.

Piezocaloric effect. A second-rank polar tensor property expressing the rate of change of entropy density with stress whose coefficients are the same as those for the thermal expansion effect.

Piezoelectric effect. A third-rank polar tensor property expressing the rate of change of polarization with stress whose coefficients are the same as the first-order electrostrictive effect.

Piezomagnetic effect. An axial–magnetic, third-rank tensor property expressing the rate of change of magnetization with stress whose coefficients are the same as the first-order magnetostrictive effect and with partial inherent symmetry due to their symmetrical stress and strain tensors, respectively.

Piezo-optical effect. A linear or quadratic effect that expresses the rate of change of the dielectric impermeability tensor with the stress tensor.

Piezothermoelectric power effect. The partially symmetrical, fourth-rank, polar tensor property that expresses the rate of change of the thermoelectric power tensor with the stress tensor and whose coefficients are not all equal to those of the elastothermoelectric power effect.

Plane of symmetry. *See* **mirror plane**.

Point group. One or a set of macroscopic symmetry elements that contain a center of symmetry, a mirror plane, a proper rotation axis of symmetry, or a combination of these that apply to one of the 32 crystal classes belonging to one of the seven crystal systems; a self-consistent set of macroscopic symmetry elements whose operations with respect to a given reference point restores that point to its original position with the same handedness.

Poisson's ratio. The ratio of lateral strain to longitudinal strain in simple tension or compression.

Polarization. The total electric dipole moment per unit volume induced by the separation of positive and negative electric charges produced by an external electric field.

Polar tensor. As used in this text, an ordinary Cartesian tensor whose components are neither changed by a handedness change of the coordinate axes nor by the presence of a magnetic field; also called a *true tensor*.

Positive current convention. The use of a positive test charge to determine the direction of electric current flux.

Positive test charge. The $+|e|$ charge equal in magnitude to the charge on an electron.

Power series. As used in this text, an infinite series that is used to express a given function of one or more variables, that is convergent within a finite interval, and for which all derivatives (or partial derivatives) of the function are convergent within that interval.

Primary effect. Usually a first-order (true) effect as opposed to a higher-order secondary (false) effect.

Principal effect. A first-order physical property or effect that relates conjugate parameters.

Proper choice of parameters. As used in this text, a requirement that all conjugate force–flux inner products have the same dimensions of entropy density production, $\dot{s}$.

Proper rotation axis of symmetry. A onefold, twofold, threefold, fourfold, or sixfold rotation axis.

Property. A physically measurable macroscopic characteristic of a thermodynamic system relating cause and effect parameters.

Property compliance. In equilibrium thermodynamics, a physical property expressing the rate of change of an extensive parameter with an intensive parameter.

Property rigidity. In equilibrium thermodynamics, a physical property expressing the rate of change of an intensive parameter with an extensive parameter.

Pseudo-tensor. An axial tensor.

Pyroelectric effect. An independent coupled effect expressing the rate of change of polarization components with temperature or the rate of change of entropy density with electric field strength, as required by a Maxwell relation.

Pyromagnetic effect. An independent coupled effect expressing the rate of change of magnetization components with temperature or the rate of change of entropy density with magnetic flux density, as required by a Maxwell relation.

Quadratic transformation form. A 6 × 6 or 9 × 9 transformation matrix derived from the transformation forms for a symmetrical or asymmetrical second-rank tensor, respectively.

Refractive index. *See* **index of refraction**.

Relative permittivity tensor. The ratio of the symmetrical polar second-rank permittivity tensor to the permittivity in a vacuum (*see* **dielectric constant**).

Reversible process. A process for which changes in the parameters that characterize the state of a system return to the initial values in the reverse order by passing through a succession of equilibrium states.

Rhombohedral axes. An alternative set of axes sometimes used for the trigonal and hexagonal crystal systems in place of the hexagonal axes used in this text.

Righi–Leduc effect. *See* **Leduc–Righi effect**.

Right-hand rule. The rule for the vector (cross) product $\vec{V} = \vec{A} \times \vec{B}$ is such that a right-handed rotation about $\vec{V}$ carries $\vec{A}$ into $\vec{B}$ through an angle ϕ that is not greater than 180°. As used in this text, the three vectors $\vec{A}$, $\vec{B}$, and $\vec{A} \times \vec{B}$ are mutually orthogonal where $\phi = 90°$.

Rigidity matrix. A property matrix generated from the equations of state for which the intensive parameters are given as functions of the extensive parameters—the inverse of the compliance matrix.

Rotoinversion axis. An operation in crystallography involving a permissible *n*-fold rotation followed by inversion through a center of coordinates.

Rule of subscript order. As used in this text, the rule by which the subscripts are read from top to bottom and from left to right (hence, reading order) in a tensor differentiation operation.

Scalar gradient. A vector denoting the maximum rate of change of a scalar field and directed along the direction of maximum change.

Scalar product. The limit of tensor contraction when the product between two tensors yields a tensor of rank 0.

Schoenflies symbols. A symbology used to represent the symmetry elements characteristic of each crystal class as an alternative to the Hermann–Mauguin International Short System used in this text.

Secondary (false) effect. Usually of higher order than its corresponding primary effect but may be caused by influences different from those causing the primary effect and that may serve as a correction term to the primary effect.

Seebeck effect. The production of an open-circuit voltage, or thermoelectric electromotive force, between two dissimilar conductors held at different temperatures under zero electric current conditions.

Self symmetry. The symmetry possessed by property coefficients that lie along the leading diagonal of a property matrix.

Shear modulus. In simple shear, the ratio of shear stress to shear strain; the same as the modulus of rigidity.

Skew-symmetrical tensor. *See* **antisymmetrical tensor**.

Space group. One of 230 self-consistent arrangements of symmetry elements, perhaps over and above those of a point group, that can bring a given crystal lattice into self-congruence.

Space lattice. The atomic arrangement in a crystal represented as a three-dimensional network of straight lines.

Specific heat. As used in this text, the heat capacity per unit volume.

State function. A thermodynamic property that depends on the state of the solid independent of the path taken to reach that state.

Stereogram. A two-dimensional depiction of a point group showing the relationship of all three crystallographic axes.

Strain. The deformation resulting from the application of a generalized stress on the surface of a solid such that the product of a generalized strain and stress results in the elastic strain energy of the solid.

Strain gage effect. The piezoresistance effect.

Stress. A quantitative expression of the external force applied to a unit area of a condensed medium but which can also arise from internal inequalities in temperature distributions or by an isometric temperature change.

Subscript order rule. *See* **rule of subscript order**.

Sum rule. A generalization of Cartesian tensor summation that is restricted to tensors of the same rank and tensor character.

Symmetric tensor. A tensor character expressed by the interchange of an even number of subscripts, used to represent tensor rank, without altering the values of the components.

Symmetry element. One of several symmetry operations that include a center of symmetry, a mirror plane, a proper rotation, or rotoinversion axis of symmetry that apply to one of the 32 crystal classes belonging to one of the seven crystal systems.

Symmetry operator. *See* **generation operator**.

Symmetry transformation. The operation on a property tensor by a generating matrix.

Taylor's series expansion. A convergent power series of a function over a finite interval in which all derivatives or partial derivatives of the function must exist and be continuous in that interval.

Temperature gradient. The gradient of the scalar temperature field T (for absolute temperature), represented by the symbols grad $T = \nabla T$, and pointing in the direction of maximum T.

Tensor. As used in this text, an abstract quantity that is used to study the physical laws of nature, classified by tensor rank r, specified by $3^{(r)}$ components in three-dimensional Euclidean (Cartesian) space, and conforms to a specific transformation law.

Tensor character. The character inherited by its component or defining tensors and may be either cumulative (by addition) or reductive (by cancellation).

Tensor contraction. Tensor contraction occurs when any n subscripts in the product of two tensors of rank r_A and r_B are set equal resulting in a tensor of rank $r_R = (r_A + r_B) - 2n$, where $2n \leq r_A + r_B$.

Tensor field. As used in this text, a physical entity or rank r that is specified by $3^{(r)}$ continuous functions of position (x_1, x_2, x_3) in three-dimensional rectangular Cartesian space and accordingly called a Cartesian tensor field.

Tensor isomer. As used in this text, any tensor for which there is partial symmetry in its subscripts.

Tensor operator. A generalized operator ∂_{ijk} ... of the *n*th order that is used to operate on a field tensor, the most common being the vector operator ∂_i used to yield the gradient of a scalar field and the divergence of a vector field symbolized by $\partial_i\phi$ or grad $\phi = \nabla\phi$ and $\partial_i\psi_i$ or div $\psi = \nabla\cdot\psi$, respectively.

Tensor property. A physical entity that gives the rate of change of an effect tensor parameter with a cause tensor parameter that, in general, varies with direction in a crystal system.

Tensor rank. The total number of subscripts (suffixes) associated with a tensor.

Tetrad. In crystallography, a fourfold (90°) rotation axis of symmetry.

Thermal conductivity. The second-rank, polar tensor transport property that relates a heat current density (flux) to a temperature gradient as in Fourier's law.

Thermal expansion. A symmetrical, polar, second-rank tensor property expressing the rate of change of elastic strain with temperature and whose coefficients are the same as those for the piezocaloric effect.

Thermal resistivity. The inverse of the thermal conductivity tensor.

Thermo-. A prefix that usually denotes the influence of temperature change on a physical property.

Thermocouple effect. The Seebeck effect.

Thermodiffusive effect. Any effect that results from the simultaneous flow of heat and mass.

Thermodynamic equilibrium. A system is in thermodynamic equilibrium if it is simultaneously in electrical, mechanical, thermal, and chemical equilibrium, such that all thermodynamic potentials are constant throughout the system and are the same as those of the surroundings. Thus, the entropy production must be zero for such a system.

Thermodynamic potential. The result of a Legendre transform of the Euler relation that replaces one or more of the extensive parameters by their conjugate intensive parameters.

Thermodynamic tensor symmetry. Applied to the components of the general property compliance and rigidity matrices, it is the self-symmetry of the principle effects and the symmetry expressed by the Maxwell relations as derived from the application of Green's theorem in a plane and the independence of the path principle.

Thermoelectric effect. Any effect that results from the simultaneous flow of electricity and heat.

Thermoelectric heater. A result of the Peltier effect whereby heat is issued to the surroundings from the junction between two dissimilar conductors or semiconductors supporting an electric current.

Thermoelectric power. The rate of change of the electrostatic potential with temperature under open-circuit conditions (zero electric current) when dissimilar conductors are held at different temperatures.

Thermoelectric refrigerator. A result of the Peltier effect whereby heat is absorbed from the surroundings by the junction between two dissimilar conductors or semiconductors supporting an electric current.

Thermogalvanomagnetic effect. A transverse effect that results when electric current flows in the simultaneous presence of an electric field, weak magnetic field, and a temperature gradient but in the absence of mechanical stress and chemical potential gradients.

Thermomagnetic effect. One of several effects that results from the application of a temperature gradient perpendicular to a magnetic field and producing either a transverse electrochemical potential gradient or a transverse temperature gradient. Examples are the Nernst and Leduc–Righi effects.

Thermo-optical effect. A linear first-order or quadratic second-order effect expressing the rate of change of the dielectric impermeability tensor with temperature.

Thermostatics. *See* **thermodynamic equilibrium**.

Thomson effect. The interchange of heat between the surroundings and a uniform homogeneous conducting material carrying both an electric current and a heat current.

Thomson heat. The heat that is interchanged with the surroundings during a Thomson effect process.

Time reversal (inversion). A nonspatial symmetry operation that represents the quantum mechanical "spin" magnetic moments, such that reversal of these magnetic moments with current reversal correspond to time reversal (inversion).

Trace of a tensor. The sum of the diagonal components of a tensor represented by a square matrix.

Transport property. Any one of a host of properties that arise from irreversible thermodynamic arguments.

Transpose of a matrix. A matrix obtained from a given matrix by the interchange of its rows and columns, that is, by replacing the element A_{ij} by A_{ji}.

Triad. In crystallography, a threefold (120°) rotation axis of symmetry.

Trigonal system. One of three uniaxial crystal systems.

True effect. Usually a first-order or primary effect for which a secondary (false) effect may appear from influences different than those of the primary effect and serving as a correction to the true effect.

True tensor. Same as polar tensor.

Uniaxial crystal. A crystal for which two of the principal property components of a second-rank tensor are the same the third being its optic axis that cannot have double refraction.

Unitary matrix. A square matrix which when multiplied by its complex conjugate transpose yields the identity matrix.

Unit cell. In a crystal having an orderly (periodicity) arrangements of atoms, a single-unit parallelepiped can be identified from which the entire crystal can be imagined to be constructed by close stacking of such units in three dimensions.

Unit (identity) matrix. A square matrix for which the leading diagonal components are +1, all others being zero.

Verdet coefficient. The proportionality constant used in the expression for Faraday rotation angle.

Young's modulus. In a rod of an isotropic solid under uniaxial tension, the ratio of the longitudinal stress to strain in that longitudinal direction.

Glossary of Symbols and Abbreviations

a	An extensive parameter
a_{ij}	Direction cosines symbol used in tensor transformations
$\tilde{a} = a^{\mathrm{T}}$	Transpose of a
A	Amperes
A_{ij}	An asymmetrical second-rank tensor
b	An extensive parameter
B_i	Magnetic flux density
B_{ij}	Dielectric impermeability tensor
C	Specific heat (heat capacity); Base-centered lattice; coulombs of charge
c_{ijkl}	Elastic stiffness modulus tensor
d_{ijkl}	Piezoelectric tensor
D_i	Electric flux density
e	Charge on an electron; extensive parameter
$e\phi$	Electrostatic potential
e_{ijk}	Permutation (alternating) tensor
E	Elastic strain energy
E_i	Electric field strength vector
E_{ijkl}	Elastothermoelectric power tensor
f	Generalized Helmholtz free energy density
f_{ij}	Faraday tensor (second rank)
f_{ijk}	Faraday effect tensor; thermomagneto-optical tensor
F	Helmholtz free energy; face-centered lattice
F_{ijkl}	Quadratic magneto-optical coefficient (Cotton–Mouton) tensor
g	Generalized Gibbs free energy density
G	Gibb free energy; modulus of rigidity
h	Generalized enthalpy density
h_i	A dependent pyroelectric effect vector
H	Enthalpy
H_i	Magnetic field strength

I	Intensive parameter; body-centered lattice; electric current; total magnetic dipole moment
I_m	Total magnetic dipole moment; intensive parameter
J	Joules of energy; generalized flux
J^n	Electric current density
J^q	Heat current density
J_i	Flux (current density) vector
K_{ij}	Dielectric constant (relative permittivity) tensor; generalized conductivity
k_{ij}	Thermal conductivity tensor
l	Length (e.g., in meters, m)
$L^{\alpha\beta}$	Phenomenological coefficient
m	Plane of symmetry (mirror plane); meters
m_{ijk}	Dependent magnetoelastic tensor
m_{ijkl}	Magneto-electro-optical tensor
M_i	Total magnetic dipole moment per unit volume (magnetization)
n	Refractive index
n°	Refractive index in the absence of all external fields
N	Mole number; newton
P_{ijkl}	Elasto-optical tensor
P_{ijkl}	Piezoresistance tensor
P	Primitive lattice
$\hat{P}$	Total electric dipole moment
P_i	Total electric dipole moment per unit volume (polarization)
Q_{ijk}	Piezomagnetic tensor
Q_{ijkl}	Piezomagnetoelectric tensor
r_{ij}	Thermal resistivity tensor
r_{ijk}	Linear electro-optical tensor; thermo-electro-optical tensor
R	Hall constant; rhombohedral lattice; gas constant
$\mathfrak{R}$	Time inversion (reversal) operator
R_{mn}	General property rigidity coefficient
R_{ijk}	Hall tensor
R_{ijkl}	Quadratic electro-optical (Kerr effect) tensor
S	Entropy
s	Entropy density
$s^{(n)}$	The *n*th generating matrix used to determine crystal symmetry effects on tensor properties
$\dot{s}$	Entropy density production
s_{ijkl}	Elastic compliance tensor

t	Time (e.g., in seconds, s)
t_{ij}	Dependent elastocaloric (thermal stress) tensor; linear thermo-optical tensor
T	Absolute temperature (e.g., in degrees kelvin, °K); tesla, the SI unit for magnetic flux density
T_{ij}	Quadratic thermo-optical tensor
$T_{ijk\cdots}$	Tensor of arbitrary rank
u	Internal energy density
U	Internal energy
V	Volume; volt
V_0	Instantaneous volume of the solid phase
w	Elastic strain energy density
w_{ijklm}	Piezo-magneto-optical tensor
x	Crystallographic axis
X	Driving force (affinity); *n*-fold rotation axis of symmetry
X_i	Mole fraction of *i*th component
$\bar{X}$	*n*-fold rotoinversion axis of symmetry
Xm	Rotation axis with a mirror parallel to it
Xmm	Rotation axis with two mirror planes parallel to it
$\bar{X}m$	Rotoinversion axis with a mirror plane parallel to it
X/m	Rotation axis with a mirror plane normal to it
X/mmm	Rotation axis with mirror plane normal to it and two mirror planes parallel to it
Y	Young's Modulus
z_{ijklm}	Piezo-electro-optical tensor
$\text{đ}Q$	Thermal energy (Pfaffian) transferred to the system
$\text{đ}W$	External work (Pfaffian) done on the system

Greek Symbols

α	Quadratic transformation form for symmetrical second-rank tensors; an intensive parameter
α_{ij}	Thermal expansion tensor
β	Quadratic transformation form for asymmetrical second-rank tensors; an intensive parameter
χ_{ij}	Dielectric susceptibility tensor
δ_{ij}	Kronecker delta
ε_{ij}	Elastic strain tensor
ε_{ijk}	Ettingshausen tensor; dependent electroelastic effect tensor
ϕ	Scalar field potential; a thermodynamic potential
γ_{ij}	Magnetoelectric susceptibility tensor; Grüneisen tensor
γ_{ijkl}	Second-order electrostrictive tensor
η_i	Dependent magnetocaloric tensor
η_{ijk}	Nernst tensor
κ_0	Permittivity in a vacuum
μ_0	Permeability in a vacuum
μ_c	Chemical potential
$\bar{\mu}$	Electrochemical potential (Fermi level in equilibrium state)
ν	Poisson's ratio
υ_{ij}	Dependent magnetoelectric tensor
π_{ijkl}	Linear piezo-optical tensor; thermo-piezo-optical tensor
Π_{ij}	Peltier tensor
Π_{ijkl}	Piezothermoelectric power tensor
Π_{ijklmn}	Quadratic piezo-optical tensor
θ_F	Faraday rotation angle
ρ_{ij}	Resistivity tensor
ρ_{ijkl}	Magnetoresistance tensor
ρ_{ijklmn}	Piezomagnetoresistance tensor
σ_{ij}	Electrical conductivity tensor; stress tensor
$\sigma^{(n)}$	Quadratic form of $s^{(n)}$
Σ_{ij}	Thermoelectric power tensor

τ_{ij}	Thomson heat tensor
ψ_{ij}	Magnetic susceptibility tensor
ζ_{ijk}	Leduc–Righi tensor
∇_i	Gradient operator
$\nabla_i\phi$	Scalar field gradient
$\partial_{ijk\cdots}$	n^{th}-order operator of rank n

Author Biography

Richard F. Tinder's teaching interests have been highly variable during his tenure at Washington State University. They have included crystallography, thermodynamics of solids (both equilibrium and irreversible thermodynamics), tensor properties of crystals, dislocation theory, solid-state direct energy conversion (mainly solar cell theory, thermoelectric effects, and fuel cells), general materials science, advanced reaction kinetics in solids, electromagnetics, and analog and digital circuit theory. In recent years, he has taught logic design at the entry, intermediate, and advanced levels and has published a major text, *Engineering Digital Design*, on that subject. He has conducted research and published in the areas of tensor properties of solids, surface physics, shock dynamics of solids, milli–micro plastic flow in metallic single crystals, high-speed asynchronous (clock-independent) state machine design, and Boolean algebra (specifically XOR algebra and graphics). Most recently, Prof. Tinder has published an e-book, *Relativistic Flight Mechanics and Space Travel* (Morgan & Claypool Publishers, 2007). Prof. Tinder holds bachelor of science, master of science, and doctor of philosophy degrees, all from the University of California, Berkeley.

He has spent one year as a visiting faculty member at the University of California, Davis, in what was then the Department of Mechanical Engineering and Materials Science. Currently, he is professor emeritus of the School of Electrical Engineering and Computer Science at Washington State University where he has been a major contributor to the computer engineering program there during a period of nearly two decades.

Index