Chapter 15: Tensors and Tensor Properties

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15.1 INTRODUCTION

The constitutive variables that appear in the equilibrium thermodynamics of fluids are quantities (entropy, volume, chemical content) and their conjugate intensities (temperature, pressure and chemical potential). These variables have the common feature that they are scalars. While their values may vary from point to point in space (in which
case they form scalar fields) their values do not depend on the particular coordinates that are used to describe space. We can discuss the entropy of a system or the pressure that acts on it without even defining a coordinate system. While we do need a coordinate system to describe the densities of the thermodynamic quantities, the only feature of the coordinate system that is needed for that purpose is its metric (differential volume element).

The constitutive variables become more complicated, however. when we move beyond the equilibrium thermodynamics of simple fluids to treat elastic solids or electromagnetic materials, or even simple fluids that are out of equilibrium. The constitutive variables that must be used to describe these systems include forces and quantities that are vectors, such as the electric field and magnetic fields and the gradients of temperature and chemical potential, and forces and quantities that are described by matrices, such as elastic stress and strain.

The complications that are introduced by matrix variables are of three types. First, constitutive variables like the electric displacement vector, \( \mathbf{D} \), or the elastic strain, \( \mathbf{e} \), are, in fact, groups of variables: the three components of the vector, \( \mathbf{D} \), or the six independent components of the elastic strain, \( \mathbf{e} \). The number of constitutive coordinates increases dramatically when the material has electromagnetic or elastic behavior. Second, the values of these variables depends on the coordinate system that is used to describe the material. For example, the components of a vector change as the underlying coordinates are rotated. Third, the increase in the number of constitutive variables produces an even faster increase in the number of material properties. The number of first-order properties increases with the square of the number of variables. We must proceed with caution lest the number of variables and properties become simply intractable.

Fortunately, there are physical and mathematical principles that let us simplify the coordinates and reduce the number of physical properties that must be measured to characterize mechanical or electromagnetic systems. The vectors and matrices that appear as coordinates and properties are tensors that change with the coordinate system in predictable ways. Moreover, they obey symmetry relations that significantly reduce the number of their independent components.

To understand tensor properties we shall first review the mathematics of tensors. Tensors are matrices whose elements change with the underlying coordinate system so that their physical value remains the same. To understand the properties of tensors we need to formulate their basic transformation laws. To keep these as simple as possible we shall assume that all coordinate systems of interest are Cartesian, which lets us use a Cartesian tensor notation. A more complex notation, the covariant tensor notation, is needed to describe the transformation behavior of tensors in general, curvilinear coordinates.

We shall next discuss the nature of the tensor coordinates and properties that appear in thermodynamics, and explore the symmetry relations that restrict the number of their independent components. The symmetry restrictions on thermodynamic properties have three sources: the inherent symmetry of the constitutive variables themselves, the symmetry of the partial differentials that define the properties, and the symmetry of the materials the
properties govern. Of these, the material symmetries are the most important and complex. The properties of a crystalline solid are governed by its crystallographic point group, and we shall explore how tensor properties are restricted in each of the 32 point groups.

The relationships presented below are accurate in general, but must be used with some caution in the treatment of magnetic properties. Because magnetic fields are produced by currents, which have direction, magnetic properties have more complex symmetries than electrical or mechanical ones. The extra symmetry is associated with the consequences of current reversal, and has the consequence that there are whole sets of additional point group symmetries for magnetic behavior. While the simplest magnetic properties, the magnetic permeability and susceptibility, have the forms that are required by the basic crystallographic point group of the material, more complex properties, such as the ferromagnetic moment and the magnetostrictive coefficients, do not. A discussion of magnetic symmetry is beyond the scope of the present course.

15.2 CARTESIAN TENSORS

15.2.1 Cartesian coordinates and coordinate transformations

Let the space occupied by a material be referred to a Cartesian coordinate system whose axes are defined by the orthogonal, unit vectors, \( \mathbf{e}_i \) \((i = 1,2,3)\), the basis vectors for the coordinate frame. The \( \mathbf{e}_i \) satisfy the orthonormality relations:

\[
\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij} \tag{15.1}
\]

Eq. 15.1 does not uniquely specify the coordinate frame since it does not set the spatial orientation of the basis vectors. A rotated, reflected, or inverted set of coordinates, \( \mathbf{e}'_i \), would be equally satisfactory, so long as they are also orthonormal:

\[
\mathbf{e}'_i \cdot \mathbf{e}'_j = \delta_{ij} \tag{15.2}
\]

Since the basis vectors, \( \mathbf{e}_i \), span three-dimensional space, any alternative set, \( \mathbf{e}'_i \), can be expressed in terms of them

\[
\mathbf{e}'_i = \sum_{j=1}^{3} Q_{ij} \mathbf{e}_j = Q_{ij} \mathbf{e}_j \tag{15.3}
\]

where the \( Q_{ij} \) are the direction cosines,

\[
Q_{ij} = \mathbf{e}'_i \cdot \mathbf{e}_j \tag{15.4}
\]

and we have used the summation convention: indices that are repeated in products like that on the right-hand side of eq. 15.3 are to be summed from 1 to 3. The 3x3 matrix, \( Q \), with
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elements $Q_{ij}$, is the *transformation matrix* that transforms the set of coordinates $e_i$ into the set $e'_i$.

It is equally possible to express the coordinates $e_i$ in terms of the $e'_i$. The transformation equation are

$$e_i = Q^{-1}_{ij} e'_j$$  \hspace{1cm} 15.5

where the elements of the transformation matrix, $Q^{-1}$, are the direction cosines

$$Q^{-1}_{ij} = e_i \cdot e'_j$$  \hspace{1cm} 15.6

The matrix $Q^{-1}$ is the *inverse* of $Q$ in the sense that it reverses the transformation accomplished by $Q$. Since

$$e_i = Q^{-1}_{ij} e'_j = Q^{-1}_{ij} Q_{jk} e_k = \delta_{ik} e_k$$  \hspace{1cm} 15.7

we have

$$Q^{-1}_{ij} Q_{jk} = \delta_{ik}$$  \hspace{1cm} 15.8

Moreover, comparing eqs. 15.4 and 15.6,

$$Q^{-1}_{ij} = Q_{ji}$$  \hspace{1cm} 15.9

The matrix whose elements are obtained from $Q$ by reversing the order of the indices is called the *transpose* of $Q$. Eq. 15.9 states that the transpose of $Q$ is also its inverse.

15.2.2 Tensors and tensor fields

Physical quantities are often described in terms of the coordinate system that is used for the space in which they appear. For example, we speak of the energy density, $E_v(x)$, at the position, $x$, in the material, or the force, $F(x)$, that acts in a certain direction on the material that is located at $x$. But while $E_v$ and $F$ may be described in terms that refer to a particular coordinate system, they are physical quantities, and they have inherent values that must not depend on the way we choose to describe space. Mathematical objects of this type are called *tensors*. Tensors whose values vary with position in space are called *tensor fields*.

15.2.3 Zeroth-order tensors: scalars

A tensor is characterized by its *order*, which is equal to the number of times its components are multiplied by the transformation matrix in a rotation of coordinates. A scalar quantity, like the energy or entropy density, depends on the coordinate system
through the element of volume only (the \textit{metric}), but is unchanged by rotations of the coordinate system since these do not change the metric. If $E_v(x)$ is the value of the energy density at the position, $x = x_i e_i = x_i' e_i'$, then

$$E_v(x) = E_v(x_i) = E_v(x_i')$$ \hspace{1cm} 15.10

Such quantities are called \textit{zeroth-order tensors}, or simply \textit{scalars}.

\textbf{15.2.4 First-order tensors; vectors}

A vector, such as the force, $\mathbf{F}$, can be written in the \textit{dyadic notation}:

$$\mathbf{F} = F_i e_i$$ \hspace{1cm} 15.11

where the $F_i$ ($i = 1,2,3$) are its components, $F_i$, along the three coordinate axes, whose unit vectors are written explicitly. Alternatively, the vector $\mathbf{F}$ can be written in \textit{Cartesian tensor notation} as $F_i$, where the dummy index $i$ ($= 1, 2$ or 3) labels an arbitrary component of $\mathbf{F}$ in a coordinate system whose unit vectors are assumed, but unwritten.

If the coordinate system is changed to one specified by the unit vectors, $e'_i$, then the components of $\mathbf{F}$ must also change if the physical value of $\mathbf{F}$ is to remain the same. To derive the transformation law for the components of $\mathbf{F}$, we use the relations

$$\mathbf{F} = F_i e_i = F'_i e'_i = F_i Q_{ij} e'_j$$ \hspace{1cm} 15.12

which show that the Cartesian components of $\mathbf{F}$ obey the transformation law:

$$F'_j = Q_{ji} F_i$$ \hspace{1cm} 15.13

Since the transformation matrix is used once in the transformation law for the components of a vector, vectors are \textit{first-order tensors}.

It is important to recognize that eq. 15.13 can be read backwards. Suppose that we are given three quantities, $F_i$ ($i = 1,2,3$), whose values depend on the choice of coordinates. If the values of these quantities transform according to eq. 15.12, then the three quantities are the Cartesian components of a vector (first-order tensor), $\mathbf{F}$, whose intrinsic value does not depend on the choice of coordinates.

\textit{Vector algebra}

Vector algebra includes the following important relations.

(1) Vectors add to produce new vectors. If $\mathbf{a}$ and $\mathbf{b}$ are vectors, 

$$(\mathbf{a} + \mathbf{b}) = (\mathbf{b} + \mathbf{a}) = \mathbf{c}$$
(2) A vector, \( \mathbf{a} \), can be multiplied by a scalar, \( k \), to produce a new vector:

\[
ka = \mathbf{c}
\]

\[
ka_i = c_i
\]

(3) Vectors multiply vectors in three different ways. The \textit{scalar} product of the vectors \( \mathbf{a} \) and \( \mathbf{b} \) produces a scalar:

\[
\mathbf{a} \cdot \mathbf{b} = \mathbf{b} \cdot \mathbf{a} = |\mathbf{a}| |\mathbf{b}| \cos(\theta)
\]

\[
= a_i b_j (\mathbf{e}_i \cdot \mathbf{e}_j) = a_i b_i
\]

where \( |\mathbf{a}| \) is the magnitude of the vector, \( \mathbf{a} \):

\[
|\mathbf{a}| = \sqrt{\mathbf{a} \cdot \mathbf{a}} = \sqrt{a_i a_i}
\]

and \( \theta \) is the angle between the vectors \( \mathbf{a} \) and \( \mathbf{b} \). Note that the magnitude of a vector is \textit{invariant} in the sense that it is unchanged by a transformation of coordinates.

The \textit{vector} product of two vectors produces a new vector that is perpendicular to both:

\[
\mathbf{a} \times \mathbf{b} = - (\mathbf{b} \times \mathbf{a}) = e_{ijk} a_j b_k \mathbf{e}_i
\]

\[
(\mathbf{a} \times \mathbf{b})_i = e_{ijk} a_j b_k
\]

where \( e_{ijk} \) is the \textit{permutation tensor}:

\[
e_{ijk} = \begin{cases} 
0 & (ijk) \neq P(123) \\
(-1)^p & (ijk) = P(123)
\end{cases}
\]

that is, \( e_{ijk} = 0 \) unless the numbers \( ijk \) are all different (a permutation of 123), \( e_{ijk} = 1 \) if the order of the permutation is even (\( ijk \) is derived from 123 by making zero or two interchanges of the numbers (123), \( e_{ijk} = -1 \) if the order of the permutation is odd (one interchange of the numbers in the sequence (123)). The vector product, \( \mathbf{a} \times \mathbf{b} \), is perpendicular to both \( \mathbf{a} \) and \( \mathbf{b} \) and is oriented in the direction that a right-hand screw would advance if twisted in the direction that rotates \( \mathbf{a} \) into \( \mathbf{b} \). Its magnitude is

\[
|\mathbf{a} \times \mathbf{b}| = |\mathbf{a}| |\mathbf{b}| \sin(\theta)
\]

where \( \theta \) is the angle between \( \mathbf{a} \) and \( \mathbf{b} \).
The *dyadic* product of two vectors is obtained by multiplying their components:

\[ \mathbf{ab} = a_i b_j \mathbf{e}_i \mathbf{e}_j \]  \hspace{1cm} 15.21

The right-hand side of eq. 15.21 has nine separate terms, whose coefficients can be written

\[ (\mathbf{ab})_{ij} = a_i b_j \]  \hspace{1cm} 15.22

as we shall see, these components form a second-order tensor.

*Vector differentiation*

Finally, note that the derivative of a scalar with respect to a vector is a vector. Let the scalar, \( \mathbf{E} \), be a function of the vector, \( \mathbf{a} \), or, equivalently, of the three components, \( a_i \), of the vector \( \mathbf{a} \). The change in \( \mathbf{E}(\mathbf{a}) \) caused by a small change in the vector, \( \mathbf{a} \), is

\[ \delta \mathbf{E}(\mathbf{a}) = \delta \mathbf{E}(\{a_i\}) = \sum_i \frac{\partial \mathbf{E}(\{a_i\})}{\partial a_i} \delta a_i \]  \hspace{1cm} 15.23

Since

\[ \delta \mathbf{a} = \delta a_i \mathbf{e}_i \]  \hspace{1cm} 15.24

eq. 15.23 can be written

\[ \delta \mathbf{E}(\mathbf{a}) = \left( \frac{\partial \mathbf{E}(\mathbf{a})}{\partial \mathbf{a}} \right) \cdot \delta \mathbf{a} \]  \hspace{1cm} 15.25

where \( \partial \mathbf{E}/\partial \mathbf{a} \) is a vector whose components are the three partial derivatives \( \partial \mathbf{E}/\partial a_i \):

\[ \frac{\partial \mathbf{E}(\mathbf{a})}{\partial \mathbf{a}} = \frac{\partial \mathbf{E}(\{a_i\})}{\partial a_i} \mathbf{e}_i \]  \hspace{1cm} 15.26

It is straightforward to prove the converse: the derivative of a vector-valued function (for example, \( \mathbf{F}(\mathbf{a}, k) \), with respect to a scalar \( k \)) is a vector.

### 15.2.5 Second-order tensors

*Definition and transformation laws*

The simplest way to construct a second-order tensor, \( \mathbf{A} \), is by forming the dyadic product of two vectors, as in eq. 15.21:

\[ \mathbf{A} = \mathbf{ab} = a_i b_j \mathbf{e}_i \mathbf{e}_j = A_{ij} \mathbf{e}_i \mathbf{e}_j \]  \hspace{1cm} 15.27
The right-hand side of eq. 15.27 is the sum of 9 terms, whose coefficients are the 9 components of the 3x3 matrix $A_{ij}$. The dyad, eq. 15.27, is not the most general form for a second-order tensor, but it does make it easy to find the transformation rules these tensors obey. If the coordinates $e_i$ are transformed into coordinates $e'_i$ the coefficients, $A_{ij}$ become $A'_{ij}$, where

$$A = A'_{ij}e'_i e'_j = A_{ij}e_i e_j$$

$$= A_{ij}Q_{ki}e'_k Q_{mj}e'_m = Q_{ki}A_{ij}Q^{-1}_{im}e'_k e'_m$$  \hspace{1cm} 15.28$$

Hence the components, $A_{ij}$, transform according to the rule

$$A'_{km} = Q_{ki}A_{ij}Q^{-1}_{im} = Q_{ki}Q_{mj}A_{ij}$$  \hspace{1cm} 15.29$$

where $Q$ is the transformation matrix. Since the transformation matrix is used twice, $A$ is a second-order tensor.

Eq. 15.29 can also be read backwards, and leads to the general definition of a second-order tensor:

*Any set of nine quantities that can be written as a 3x3 matrix of components, $A_{ij}$, and transform according to eq. 15.29 form a second-order Cartesian tensor, whose inherent value is independent of the choice of coordinates.*

Most of the second-order tensors that we shall encounter are not dyadic products of vectors. However, any second-order tensor can be written in the dyadic notation

$$A = A_{ij}e_i e_j$$  \hspace{1cm} 15.30$$

which identifies both the components and the underlying coordinate set. Alternatively, it can be written in Cartesian tensor notation, $A_{ij}$, which leaves the underlying coordinates unspecified, or simply as the symbol, $A$. In the following we shall use whichever notation is most convenient.

*Symmetric and antisymmetric tensors*

The second-order tensor, $A^T$, with elements, $A_{ji}$, is called the transpose of $A$. The tensor is said to be *symmetric* if $A = A^T$:

$$A_{ij} = A_{ji}$$  \hspace{1cm} 15.31$$

The tensor is *antisymmetric* if $A = -A^T$:
\[ A_{ij} = -A_{ji} \]

from which it follows that the diagonal components of an anti-symmetric tensor are zero. While a general second-order tensor has 9 independent components, a symmetric tensor has 6 and an antisymmetric tensor has only three.

The symmetry of a tensor is preserved in a transformation of coordinates.

**Addition of second-order tensors**

Second-order tensors add according to the normal rules of algebra. If \( \mathbf{A} \) and \( \mathbf{B} \) are second-order tensors,

\[
\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A} = (A_{ij} + B_{ij})\mathbf{e}_i\mathbf{e}_j
\]

\[
(A+B)_{ij} = A_{ij} + B_{ij} \tag{15.33}
\]

It follows that a second-order tensor can always be written as the sum of a symmetric and an antisymmetric tensor

\[
\mathbf{A} = \mathbf{A}^s + \mathbf{A}^a \tag{15.34}
\]

where

\[
A^s_{ij} = \frac{1}{2} \left[ A_{ij} + A_{ji} \right] \tag{15.35}
\]

\[
A^a_{ij} = \frac{1}{2} \left[ A_{ij} - A_{ji} \right] \tag{15.36}
\]

It also follows that one cannot add tensors of different order.

**Tensor multiplication**

One can multiply tensors of different order, and the multiplication rules depend on the order of the tensor that is multiplied. If the scalar, \( K \), multiplies the tensor, \( \mathbf{A} \), the product is a second-order tensor with elements

\[
(K\mathbf{A})_{ij} = KA_{ij} \tag{15.37}
\]

The product of a second-order tensor, \( \mathbf{A} \), and a vector, \( \mathbf{a} \), is defined by the dot product:

\[
\mathbf{A} \cdot \mathbf{a} = A_{ij} \mathbf{e}_i \mathbf{e}_j \cdot a_k \mathbf{e}_k = A_{ij} \mathbf{a}_k \mathbf{e}_i (\mathbf{e}_j \cdot \mathbf{e}_k)
\]

\[
= A_{ij} a_j \mathbf{e}_i = \mathbf{b} \tag{15.38}
\]
and is a vector with components

$$(\mathbf{A} \cdot \mathbf{a})_i = b_i = A_{ij}a_j$$  \hspace{1cm} (15.39)$$

(It is common to describe this multiplication by saying that the tensor, \(\mathbf{A}\), "operates" on the vector, \(\mathbf{a}\), to produce a second vector, \(\mathbf{b}\).) Note that tensor multiplication does not automatically commute:

$$(\mathbf{a} \cdot \mathbf{A})_i = a_jA_{ji} = A^{T}_{ij}a_j$$  \hspace{1cm} (15.40)$$

The rules for multiplying second-order tensors can be found by writing them in dyadic form. If \(\mathbf{A}\) and \(\mathbf{B}\) are second-order tensors,

$$\mathbf{A} \cdot \mathbf{B} = A_{ij}e_i \cdot B_{km}e_k e_m = A_{ij}B_{km}e_i e_m (e_j \cdot e_k)$$

$$= A_{ij}B_{jm}e_i e_m$$  \hspace{1cm} (15.41)$$

Hence the product of two second-order tensors is a second-order tensor with components

$$(\mathbf{A} \cdot \mathbf{B})_{ij} = A_{ik}B_{kj}$$  \hspace{1cm} (15.42)$$

Tensor multiplication only commutes if both tensors are symmetric:

$$(\mathbf{B} \cdot \mathbf{A})_{ij} = B_{ik}A_{kj} = (\mathbf{A}^{T} \cdot \mathbf{B})_{ij}$$  \hspace{1cm} (15.43)$$

Multiplication by the unit tensor, \(\delta\), whose elements are \(\delta_{ij}\), leaves a tensor unchanged:

$$(\mathbf{\delta} \cdot \mathbf{B})_{ij} = \delta_{ik}B_{kj} = B_{ij}$$  \hspace{1cm} (15.44)$$

If the product of \(\mathbf{A}\) and \(\mathbf{B}\) is the unit tensor, \(\mathbf{A}\) is said to be the inverse of \(\mathbf{B}\):

$$(\mathbf{A} \cdot \mathbf{B})_{ij} = \delta_{ij} \Rightarrow \mathbf{A} = \mathbf{B}^{-1}$$  \hspace{1cm} (15.45)$$

One can also form dyadic products with second-order tensors. These produce new tensors of higher order. For example, the dyadic product of a second-order tensor, \(\mathbf{A}\), with a vector, \(\mathbf{b}\), is the tensor

$$\mathbf{T} = \mathbf{A} \mathbf{b} = A_{ij} b_k e_i e_j e_k = T_{ijk} e_i e_j e_k$$  \hspace{1cm} (15.46)$$

as we shall see, the tensor \(\mathbf{T}\) is a third-order tensor whose 27 components, \(T_{ijk}\), can be written as a three-dimensional 3x3x3 matrix. The dyadic product of two second-order tensors, \(\mathbf{A}\) and \(\mathbf{B}\) is

$$\mathbf{S} = \mathbf{A} \mathbf{B} = A_{ij} B_{kl} e_i e_j e_k e_l = S_{ijkl} e_i e_j e_k e_l$$  \hspace{1cm} (15.47)$$
where the 81 components, \( S_{ijkl} \), can be written as a four-dimensional 3\times3\times3\times3 matrix, and form the elements of a fourth-order tensor.

**Second-order tensor invariants**

A combination of the elements of a tensor that is independent of the choice of co-ordinates is called an *invariant* of the tensor, and can be taken to have a physical meaning. As we have seen, a vector, \( \mathbf{a} \), has a single invariant, its magnitude \( |\mathbf{a}| \). A second order tensor has three invariants. While these can be chosen in a number of different ways, a common choice is the *trace* of the tensor, which is the sum of its diagonal elements:

\[
\text{Tr}(\mathbf{A}) = A_{ii}
\]

the *scalar product*:

\[
\mathbf{A} : \mathbf{A} = \text{Tr}(\mathbf{A} \cdot \mathbf{A}) = A_{ij}A_{ji}
\]

and the *determinant*

\[
\text{det}(\mathbf{A}) = |\mathbf{A}| = e_{ijk}A_{1i}A_{2j}A_{3k} = \sum_P (-1)^P A_{1i}A_{2j}A_{3k}
\]

where \( e_{ijk} \) in the first form is the permutation tensor, and the sum in the second form is taken over all permutations, \( P \), of the sequence \( ijk = 123 \), where the exponent, \( P \), is the *order* of the permutation, the number of interchanges of the numbers in the sequence 123 that must be done to obtain the permuted sequence. One advantage of this choice is that the magnitudes of the three invariants scale, respectively, with the first, second and third power of the magnitude of the largest element of \( \mathbf{A} \).

If \( \mathbf{A} \) is antisymmetric, both its trace and its determinant vanish. Hence an antisymmetric tensor has a single invariant, its scalar product.

The trace of a sum of second-order tensors is the sum of the traces:

\[
\text{Tr}(\mathbf{A} + \mathbf{B}) = \text{Tr}(\mathbf{A}) + \text{Tr}(\mathbf{B}) = A_{ii} + B_{ii}
\]

The trace of a product of second-order tensors is their scalar product:

\[
\text{Tr}(\mathbf{A} \cdot \mathbf{B}) = \mathbf{A} : \mathbf{B} = A_{ij}B_{ji}
\]

The scalar product vanishes when one tensor is symmetric and the other is antisymmetric. Hence, writing \( \mathbf{A} \) and \( \mathbf{B} \) as the sum of their symmetric and antisymmetric parts,

\[
\mathbf{A} : \mathbf{B} = \mathbf{A}^s : \mathbf{B}^s + \mathbf{A}^a : \mathbf{B}^a
\]

The determinant of a sum or product of tensors is the sum or product of the determinants:
It follows that the determinant of a second-order tensor is the determinant of its symmetric part.

**Minors and cofactors**

The *minor* of an element, \( A_{ij} \), of a determinant, \(|A|\), is the determinant of the 2x2 matrix formed by eliminating the \( i \)th row and \( j \)th column from \( A \). For example,

\[
M(A_{11}) = A_{22}A_{33} - A_{23}A_{32}
\]

\[
M(A_{12}) = A_{21}A_{33} - A_{23}A_{31}
\]

The cofactor of a second-order tensor is the tensor, \( A^c \), whose elements, \( A^c_{ij} \), are

\[
A^c_{ij} = (-1)^{i+j}M(A_{ij})
\]

The product of a second-order tensor and the transpose of its cofactor obeys the relation:

\[
A \cdot A^c^T = A_{ij}A^c_{jk} = |A| \delta_{jk}
\]

Hence the inverse of \( A \), \( A^{-1} \), is equal to the transposed cofactor divided by the determinant:

\[
A^{-1}_{ij} = \frac{A^c_{ij}}{|A|}
\]

Eq. 15.60 can be used to invert the action of a second-order tensor on a vector, that is, to find the vector, \( a \), that produces the vector, \( b \), under the action of the tensor, \( A \). If

\[
A_{ij}a_j = b_i
\]

\[
a_j = A^{-1}_{ji}b_i = \frac{1}{|A|} A^c_{ji}b_i
\]

If the vector, \( b \), is zero for non-zero values of the \( a_i \), the determinant of \( A \) must vanish:

\[
A \cdot a = 0 \implies |A| = 0
\]
Eigenvalues and eigenvectors

A tensor that has only diagonal elements is said to have a diagonal form. When a tensor, \( \mathbf{A} \), is symmetric, it is always possible to find a coordinate transformation that will bring it into diagonal form. The diagonal elements are the eigenvalues of the tensor. The unit vectors that bring it into diagonal form are its eigenvectors.

To find the eigenvalues and eigenvectors of a symmetric tensor, \( \mathbf{A} \), let \( \mathbf{e}_i^0 \) be the normalized eigenvectors. The tensor, \( \mathbf{A} \), is diagonal in the coordinate system defined by \( \mathbf{e}_i^0 \). Let its elements be \( \lambda_i \), \( i = 1,2,3 \). Let the vector, \( \mathbf{a} \), be parallel to one of the eigenvectors (leaving the particular eigenvector arbitrary since we do not yet know what the eigenvectors are). Then

\[
\mathbf{A} \cdot \mathbf{a} = \lambda \mathbf{a}
\]

or

\[
[\mathbf{A} - \lambda \mathbf{I}] \cdot \mathbf{a} = 0
\]

where \( \lambda \) is one of the eigenvalues, \( \lambda_i \), and \( \mathbf{I} \) is the unit tensor. It then follows from eq. 15.63 that

\[
\det[\mathbf{A} - \lambda \mathbf{I}] = 0
\]

Eq. 15.66 is a cubic equation for \( \lambda \). When \( \mathbf{A} \) is symmetric, this equation has three real roots, which are the eigenvalues of \( \mathbf{A} \).

Since a determinant is invariant, eq. 15.66 holds for any choice of coordinates. If we know the elements of \( \Lambda_{ij} \) in some coordinate system (the reference coordinate system), then the eigenvalues are the three solutions to the cubic equation

\[
\det[\Lambda_{ij} - \lambda \delta_{ij}] = 0
\]

To find the eigenvectors, let \( [\mathbf{e}_i^0] \) be the components of the first eigenvector, \( \mathbf{e}_1^0 \), in the reference coordinate system. Writing

\[
\Lambda'_{ij} = \Lambda_{ij} - \lambda \delta_{ij}
\]

we have

\[
\Lambda'_{ij} [\mathbf{e}_1^0]_j = 0
\]

Since \( |\mathbf{A}'| = 0 \), this set of homogeneous equations has a solution. To find a solution, let
\[
[e_1^0]_j = cA'_{ij}^c
\]  

15.70

where \( A'_{ij}^c \) is the cofactor of \( A' \) and \( c \) is an arbitrary constant. By eq. 15.59,

\[
A_{ij} A_{ij}^c = |A'|\delta_{i1} = 0
\]

15.59

and eq. 15.69 is satisfied for all \( i \). The constant, \( c \), in eq. 15.70 is then used to normalize \( e_1^0 \). If the eigenvalues, \( \lambda_i \), are all different then the three eigenvectors can be found by successively substituting the values of \( \lambda_i \) into eq. 15.68. The three eigenvectors are automatically orthogonal; since \( A \) is symmetric, \( A \cdot a = a \cdot A \), and

\[
e_i^0 \cdot A \cdot e_j^0 - e_j^0 \cdot A \cdot e_i^0 = (\lambda_j - \lambda_i)(e_i^0 \cdot e_j^0) = 0
\]

15.71

which holds for \( \lambda_i \neq \lambda_j \) if and only if \( e_i^0 \cdot e_j^0 = 0 \).

When two or more of the eigenvalues are the same (that is, when the eigenvalues are degenerate) their directions are not so rigidly fixed. In the extreme case, all three eigenvalues of \( A \) are the same: \( \lambda_1 = \lambda_2 = \lambda_3 = \lambda \). In this case, the diagonal form of \( A \) is

\[
A = \lambda \delta
\]

15.72

But the unit tensor, \( \delta \), is the same in every coordinate system. A tensor that has the form 15.72 is said to have spherical symmetry. Any unit vector is an eigenvector of a spherical tensor, and any three orthogonal vectors can be used as the set of eigenvectors.

Now let two of the eigenvectors be the same: \( \lambda_1 = \lambda_2 = \lambda \). It follows from eq. 15.71 that the eigenvector, \( e_3^0 \), that is associated with the unique eigenvalue, \( \lambda_3 \), is orthogonal to both \( e_1^0 \) and \( e_2^0 \), the two eigenvectors associated with the eigenvalue, \( \lambda \). However, it can be easily shown that any vector that lies in the plane perpendicular to \( e_1^0 \) is an eigenvector of \( A \) with the eigenvalue, \( \lambda \). It follows that any two orthogonal unit vectors that lie in the plane perpendicular to \( e_3^0 \) are suitable choices for \( e_1^0 \) and \( e_2^0 \). A tensor of this type is said to have circular symmetry in the plane perpendicular to \( e_3^0 \).

Second-order tensors produced by differentiation

The second-order tensor properties that we shall treat in the balance of this chapter are obtained by differentiation. There are four distinct cases in which differentiation produces a second-order tensor.

(1) Let \( E(a) \) be a scalar function of the vector, \( a \). If the components of \( a \) are changed incrementally, the change in \( E \) is, to second order,

\[
\delta E = \left[ \frac{\partial E}{\partial a_i} \right] \delta a_i + \frac{1}{2} \left[ \frac{\partial^2 E}{\partial a_i \partial a_j} \right] \delta a_i \delta a_j + ...
\]
Since the variation, $\delta a$, is a vector, the coefficients,

$$\left[ \frac{\partial^2 E}{\partial a_j \partial a_j} \right] = \left[ \frac{\partial^2 E}{\partial a \partial a} \right]_{ji}$$

form a symmetric second-order tensor; the second derivative of a scalar with respect to a vector is a second-order tensor.

(2) Let $E(A)$ be a scalar function of the second-order tensor, $A$. An example is the energy density in an elastic solid, which depends on the strain tensor, $\varepsilon$. An incremental change in the elements, $A_{ij}$, of $A$ changes the value of $E$ by

$$\delta E = \left[ \frac{\partial E}{\partial A_{ij}} \right] A_{ij} = \left[ \frac{\partial E}{\partial A} \right]_{ji} \delta A_{ij}$$

Hence $\partial E/\partial A_{ij}$ is the $(ij)$ element of the second-order tensor, $\partial E/\partial A$. The tensor, $\partial E/\partial A$, has the symmetry of the tensor, $A$.

(3) Let $b$ be a vector that is a function of the vector, $a$: $b = b(a)$. An example is the electric displacement vector, $D$, which can be regarded as a function of the electric field, $D(E)$. The change in the element, $b_i$, when the elements, $a_j$, of $a$ are changed incrementally is

$$\delta b_i = \left[ \frac{\partial b_i}{\partial a_j} \right] \delta a_j = \left[ \frac{\partial b}{\partial a} \right]_{ij} \delta a_j$$

Hence $\partial b_i/\partial a_j$ is the $(ij)$ element of the second-order tensor $[\partial b/\partial a]$.

(4) Finally, let a second-order tensor, $A$, be a function of a scalar, $T$. A simple example occurs in a solid with an anisotropic thermal expansion coefficient; the strain, $\varepsilon$, depends on the temperature, $T$. The variation of the $(ij)$ element of $A$, $\delta A_{ij}$, with $\delta T$ is

$$\delta A_{ij} = \left[ \frac{\partial A_{ij}}{\partial T} \right] \delta T$$

Hence $\partial A_{ij}/\partial T$ is the $(ij)$ element of the second-order tensor, $\partial A/\partial T$.

### 15.2.6 Third- and fourth-order tensors

The dyadic product of three vectors $(abc)$, or the dyadic product of a second-order tensor and a vector $(Aa)$ produces a third-order tensor. The components of a third-order tensor, $B$, form a $3 \times 3 \times 3$ matrix of 27 elements, which transform according to the relation

$$B'_{ijk} = Q_{ip} Q_{jq} Q_{kr} B_{pqr}$$
Any 3x3x3 matrix whose elements transform according to eq. 15.77 is a third-order tensor, whether or not it can be written as the dyadic product of tensors of lower order.

Third-order tensor properties result from differentiation. For example, the third derivative of a scalar with respect to a vector, the cross-derivative of a scalar with respect to a vector and a second-order tensor, and the derivative of a vector with respect to a second-order tensor are all third-order tensors. An example of a third-order tensor that is important in materials science is the tensor of piezoelectric moduli:

\[
\mathbf{d} = \left[ \frac{\partial \mathbf{P}}{\partial \mathbf{\sigma}} \right]
\]

which governs the change in the electric polarization, \( \mathbf{P} \), of a body with a change in the applied stress, \( \mathbf{\sigma} \). Since \( \mathbf{P} \) is a vector and \( \mathbf{\sigma} \) is a second-order tensor, \( \mathbf{d} \) is a third-order tensor.

The transformation laws for fourth-order tensors can be found by forming one from the dyadic product of four vectors (\( \mathbf{abcd} \)) or the dyadic product of two second order tensors (\( \mathbf{AB} \)). A fourth-order tensor is a 3x3x3x3 matrix of 81 elements that transform according to the relation

\[
\lambda'_{ijkl} = Q_{ip}Q_{jq}Q_{kr}Q_{ls}\lambda_{pqrs}
\]

Any set of 81 elements that transform according to eq. 15.79 form a second-order tensor.

The fourth-order tensors that are most commonly encountered in materials science are the second derivatives of scalars with respect to second-order tensors, or the derivatives of second order tensors with respect to one another. The most common example is the tensor of elastic constants,

\[
\lambda_{ijkl} = \frac{\partial^2 F}{\partial E_{ij} \partial E_{kl}} = \left[ \frac{\partial \sigma_{ij}}{\partial E_{kl}} \right]
\]

which governs the change of stress with strain.

15.3 TENSORS PROPERTIES

15.3.1 Prototypic example of a system with tensor properties

The important properties of materials include tensors of the first through fourth orders.

We can find most of the interesting features of tensor coordinates, forces and properties by examining a specific example. Consider the behavior of a dielectric solid,
such as quartz (SiO₂) or rocksalt (NaCl). As we shall see, the constitutive coordinates that are needed to describe such a material include the conventional variables for the multicomponent fluid, but also include variables that describes the elastic strain, and variables that describes the electric field. The free energy density within a dielectric solid has the natural form:

\[ F_V = \tilde{F}_V(T,\{n\},D,\varepsilon) \]  

where \( F_V \) is the free energy per unit volume of the reference (unstrained) state, \( D \) is the electric displacement vector, and \( \varepsilon \) is the second-order tensor strain. The forces conjugate to the constitutive variables, \( D \) and \( \varepsilon \) are:

\[
\frac{\partial \tilde{F}_V}{\partial D} = E \tag{15.82}
\]

\[
\frac{\partial \tilde{F}_V}{\partial \varepsilon} = \sigma \tag{15.83}
\]

where the electric field, \( E \), is a vector (the vector derivative of a scalar) and the stress, \( \sigma \), is a second-order tensor (derivative of a scalar with respect to a second-order tensor).

In the most general case the dielectric solid has tensor properties of order zero to four. The scalar properties are the second derivatives and cross-derivatives with respect to the scalar coordinates \( T \) and \( \{n\} \), for example,

\[
f_{TT} = \frac{\partial^2 \tilde{F}_V}{\partial T^2} = \left[ \frac{\partial S_V}{\partial T} \right]_{\{n\},D} = c_v \frac{\varepsilon}{T} \tag{15.84}
\]

The vector properties are cross-derivatives between scalars and vectors, for example,

\[
f_{TD} = \left[ \frac{\partial^2 \tilde{F}_V}{\partial T \partial D} \right] = \left[ \frac{\partial S_V}{\partial T} \right]_{\{n\},\varepsilon} = \left[ \frac{\partial E}{\partial T} \right]_{\{n\},\varepsilon} \tag{15.85}
\]

The second-order tensor properties are second derivatives with respect to vectors, and cross-derivatives between scalars and second-order tensors, for example:

\[
f_{DD} = \left[ \frac{\partial^2 \tilde{F}_V}{\partial \varepsilon} \right] = \left[ \frac{\partial E}{\partial \varepsilon} \right]_{T,\{n\},\varepsilon} = (\varepsilon_0 \varepsilon)^{-1} \tag{15.86}
\]

where \( \varepsilon_0 \) is the permittivity of free space and \( \varepsilon \) is the second-order tensor of dielectric constants, and
\[
\begin{align*}
\mathbf{f}_\mathbf{T}\mathbf{e} &= \left[ \frac{\partial^2 \bar{F}_V}{\partial T \partial \mathbf{e}} \right] - \left[ \frac{\partial \mathbf{S}_V}{\partial \mathbf{e}} \right]_{\mathbf{T},\{n\},\mathbf{D}} = \left[ \frac{\partial \mathbf{\sigma}}{\partial T} \right]_{\{n\},\mathbf{e},\mathbf{D}} \quad 15.87
\end{align*}
\]

The third-order tensor properties are cross-derivatives between vectors and second-order tensors, for example,

\[
\begin{align*}
\mathbf{f}_\mathbf{D}\mathbf{e} &= \left[ \frac{\partial^2 \bar{F}_V}{\partial \mathbf{D} \partial \mathbf{e}} \right] - \left[ \frac{\partial \mathbf{E}}{\partial \mathbf{e}} \right]_{\mathbf{T},\{n\},\mathbf{D}} = \left[ \frac{\partial \mathbf{\sigma}}{\partial \mathbf{D}} \right]_{\{n\},\mathbf{e}} = \mathbf{\gamma} \quad 15.88
\end{align*}
\]

where \( \mathbf{\gamma} \) is a third-order tensor of piezoelectric constants. The fourth-order tensor properties are second derivatives with respect to second-order tensors, for example,

\[
\begin{align*}
\mathbf{f}_\mathbf{e}\mathbf{e} &= \left[ \frac{\partial^2 \bar{F}_V}{\partial \mathbf{e} \partial \mathbf{e}} \right] - \left[ \frac{\partial \mathbf{\sigma}}{\partial \mathbf{e}} \right]_{\mathbf{T},\{n\},\mathbf{D}} = \lambda \quad 15.89
\end{align*}
\]

where \( \lambda \) is the fourth-order tensor of elastic constants. While tensors of even higher order are needed for particular problems, tensors of order four or less are adequate for the vast majority of the problems of interest in materials science.

### 15.3.2 Two-dimensional matrix representation of tensor properties

It is useful to have a systematic method for representing third- and fourth-order tensors as two-dimensional matrices that can be visualized and compared. The tensor properties that we need to represent are third-order properties like the \( \mathbf{\gamma} \) defined in eq. 15.88, which relates stress to electric displacement (or electric field to strain):

\[
d\sigma_{ij} = \gamma_{ijk} dD_k \quad 15.90
\]

and fourth-order tensors like the \( \lambda \) defined in eq. 15.89, which relates elastic strain to stress:

\[
d\sigma_{ij} = \lambda_{ijkl} d\varepsilon_{kl} \quad 15.91
\]

**Fourth-order tensor properties: stiffness and compliance**

We begin with the fourth-order tensor, \( \lambda \). We represent it as a two-dimensional matrix whose elements relate the components of \( \mathbf{\sigma} \) to those of \( \mathbf{\varepsilon} \). The nine elements of \( \mathbf{\sigma} \) and \( \mathbf{\varepsilon} \) are written as (1x9) column matrices, \( \sigma_i \) and \( \varepsilon_i \) (\( i = 1,...,9 \)), by making the following identifications:
Notes on the Thermodynamics of Solids  

J.W. Morris, Jr: Fall, 2008

\[
\begin{bmatrix}
11 & 1 \\
22 & 2 \\
33 & 3 \\
23 & 4 \\
13 & \rightarrow 5 \\
12 & 6 \\
32 & 7 \\
31 & 8 \\
21 & 9 \\
\end{bmatrix}
\]

We then define the matrix of elastic moduli, \( \mathbf{\lambda} \), by the relations

\[ \sigma_i = \lambda_{ij} \varepsilon_{ij} \]  

With this definition the subscripts \( i \) and \( j \) in \( \lambda_{ij} \) replace the pairs \((kl)\) and \((mn)\) in \( \lambda_{klmn} \) according to the recipe given in eq. 15.92; the element, \( \lambda_{11} \), of the matrix is the \( \lambda_{1111} \) element of \( \mathbf{\lambda} \), the element \( \lambda_{47} \) is \( \lambda_{2332} \), etc.

In the example given in eq. 15.91, as in most of the cases of interest to us, the tensors \( \boldsymbol{\sigma} \) and \( \varepsilon \) are symmetric. It follows that the fourth-order tensor, \( \lambda_{ijkl} \), is symmetric with respect to interchange of the indices in either the pair \((ij)\) or the pair \((jk)\):

\[ \lambda_{ijkl} = \lambda_{ijkl} = \lambda_{ijlk} = \lambda_{jil} \]  

and only 36 of its 81 components are independent. In the matrix notation, the elements of the \((9\times9)\) matrix whose indices contain the values 7, 8 or 9 are unchanged in value if 7 is replaced by 4, 8 by 5 and 9 by 6:

\[ \lambda_{7j} = \lambda_{4j} \quad (j = 1, \ldots, 9) \]  

and so on. We can, therefore, write the independent elements of \( \mathbf{\lambda} \) as a \((6\times6)\) matrix, \( \mathbf{c} \), that uses only the first 6 indices in the column on the left of eq. 15.92:

\[
\mathbf{c} = \begin{bmatrix}
c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\
c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\
c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\
c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\
c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\
c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \\
\end{bmatrix}
\]

However, the matrix \( \mathbf{c} \) cannot simply replace \( \mathbf{\lambda} \). If we set \( c_{ij} = \lambda_{ij} \) in eq. 15.93,
\[ \mathrm{d} \sigma_i = \sum_{j=1}^{9} \lambda_{ij} \mathrm{d} \epsilon_j = \sum_{j=1}^{3} \lambda_{ij} \mathrm{d} \epsilon_j + 2 \sum_{j=4}^{6} \lambda_{ij} \mathrm{d} \epsilon_j + \sum_{j=7}^{9} c_{ij} \mathrm{d} \epsilon_j \]  

15.97

So we must adjust the definition of the matrix, \( \mathbf{c} \), or the definition of \( \epsilon \) or \( \mathbf{\sigma} \) to reduce the matrix of properties to the (6x6) form. In the theory of elasticity it is conventional to correct eq. 15.97 by incorporating the factor, 2, into the affected elements of the strain, \( \epsilon \). Defining the three pure shears, \( \gamma_i \), by the relations

\[ \gamma_i = 2 \epsilon_i \quad (i = 4,5,6) \]  

15.98

we have

\[ \mathrm{d} \sigma_i = \sum_{j=1}^{3} c_{ij} \mathrm{d} \epsilon_j + \sum_{j=4}^{6} c_{ij} \mathrm{d} \gamma_j \Rightarrow c_{ij} \mathrm{d} \epsilon_j \]  

15.99

where we have adopted a notation in which \( \epsilon_i \) is to replaced by \( \gamma_i \) for \( i \geq 4 \) in any sum. The matrix, \( \mathbf{c} \), is known as the elastic stiffness matrix. Its elements, \( c_{ij} \), are called the elastic constant, or the Voigt constants.

While the choice made in eq. 15.98 simplifies the matrix of elastic constants, it does so at the cost of complicating the inverse matrix, the compliance matrix, \( \mathbf{s} = \mathbf{c}^{-1} \), that governs the inverse relations.

\[ \mathrm{d} \epsilon_i = s_{ij} \mathrm{d} \sigma_j \]  

(j = 1,2,3)

\[ \mathrm{d} \gamma_i = s_{ij} \mathrm{d} \sigma_j \]  

(j = 4,5,6)  

15.100

If \( \mathbf{c} \) is known, the compliance matrix, \( \mathbf{s} \), can be found directly by inverting it. The (6x6) matrix, \( \mathbf{s} \), is the two-dimensional matrix representation of the fourth-order compliance tensor,

\[ \mathbf{S} = \mathbf{\lambda}^{-1} \]  

15.101

which follows from the tensor relations:

\[ \mathrm{d} \epsilon_{ij} = S_{ijkl} \mathrm{d} \sigma_{kl} \]  

15.102

Let \( S_{ij} \) be the two-dimensional matrix representation of the tensor elements, \( S_{ijkl} \), according to eq. 15.92. While the stiffnesses, \( c_{ij} = \lambda_{ij} \), the compliances obey the more complicated set of relations:

\[ s_{ij} = (2)^q S_{ij} \quad q = \begin{cases} 0 & \text{i and j} = 1,2,3 \\ 1 & \text{i or j} = 4,5,6 \\ 2 & \text{i and j} = 4,5,6 \end{cases} \]  

15.103
This behavior is general: if the elements of a (6x6) matrix representation of a fourth-order tensor are equal to corresponding elements of the tensor, the elements of the inverse matrix will not be.

**Third-order tensors: piezoelectric coefficients**

Consider the third-order property tensor, \( \gamma \), of piezoelectric constants, which is defined in eq. 15.90:

\[
d\sigma_{ij} = \gamma_{ijk} dD_k
\]

If we replace the elements, \( \sigma_{ij} \), by the six stresses, \( \sigma_i \), and replace the first two indices of the \( \gamma_{ijk} \) by the six coefficients, \( \gamma_m \), that are determined by the recipe given in eq. 15.90, the result is

\[
d\sigma_m = \gamma_{mk} D_k
\]

where the \( \gamma_{mk} \) form the (6x3) matrix of coefficients:

\[
\gamma = \begin{bmatrix}
\gamma_{11} & \gamma_{12} & \gamma_{13} \\
\gamma_{21} & \gamma_{22} & \gamma_{23} \\
\gamma_{31} & \gamma_{32} & \gamma_{33} \\
\gamma_{41} & \gamma_{42} & \gamma_{43} \\
\gamma_{51} & \gamma_{52} & \gamma_{53} \\
\gamma_{61} & \gamma_{62} & \gamma_{63}
\end{bmatrix}
\]

**15.4 Symmetry Restrictions on Tensor Properties**

The number of separate elements of a tensor increases as \( 3^n \), where \( n \) is the order of the tensor. If all of the elements of a second, third and fourth-order tensor property were independent a very large number of separate properties would have to be measured or computed to predict the behavior of even relatively simple systems. Fortunately, the tensor properties obey symmetry relations that substantially reduce the number of independent elements. The symmetry relations have three sources: the symmetry of the partial differential that defines the property, the symmetry of the tensor variables that determine the property, and the symmetry of the material that exhibits the property.

**15.4.1 Symmetry imposed by differentiation**

As we have already discussed, the equilibrium thermodynamic properties are second derivatives of the thermodynamic potentials. As we shall see later, the important
kinetic properties can be defined in a very similar way, as second derivatives of the rate of change of the thermodynamic potential. Properties that are defined by multiple differentiation are symmetric with respect to a change in the order of differentiation. This symmetry limits the number of independent tensor properties that can be defined by cross-differentiation, and limits the number of independent elements of tensor properties that are defined by repeated differentiation.

**Cross-derivatives**

Let a tensor property be defined by the cross-derivative of a potential with respect to two or more tensors. For example, if the potential is $\Phi(a, b)$, where $a$ and $b$ are vectors, the cross-derivatives define the 18 second-order tensor properties

$$[\Phi_{ab}]_{ij} = \left[ \frac{\partial^2 \Phi}{\partial a_i \partial b_j} \right]$$  \hspace{1cm} (15.106)

$$[\Phi_{ba}]_{ij} = \left[ \frac{\partial^2 \Phi}{\partial b_i \partial a_j} \right]$$  \hspace{1cm} (15.107)

However, given the symmetry of the second derivative,

$$[\Phi_{ba}]_{ij} = [\Phi_{ab}]_{ji} = [\Phi_{ab}^T]_{ij}$$  \hspace{1cm} (15.108)

and only one of the two tensors is independent. A similar result holds for all tensor properties; if $\Phi_{BA}$ and $\Phi_{AB}$ are properties determined by cross-differentiation with respect to tensors of any order, the elements of one cross-derivative, e.g., $\Phi_{AB}$, are sufficient to determine the elements of the other. If $\Phi_{ABC}$ is the tensor property that results from successive differentiation by the tensors $A$, $B$ and $C$, the elements of $\Phi_{ABC}$ determine those of the cross-derivatives with respect to $A$, $B$ and $C$ in any order.

**Repeated differentiation**

When a tensor property is defined by repeated differentiation with respect to a single tensor, symmetry relations restrict the number of independent elements.

Let a second-order tensor property, $\Phi_{aa}$, be defined by the second derivative of a potential ($\Phi$) with respect to a vector, $a$. Since

$$\left[ \frac{\partial^2 \Phi}{\partial a_i \partial a_j} \right] = \left[ \frac{\partial^2 \Phi}{\partial a_j \partial a_i} \right]$$  \hspace{1cm} (15.109)

the tensor, $\Phi_{aa}$, is symmetric,

$$[\Phi_{aa}]_{ij} = [\Phi_{aa}]_{ji}$$  \hspace{1cm} (15.110)
and has only six independent elements.

A third-order tensor property, \( \Phi_{\text{aaa}} \), that is defined by differentiation with respect to the vector, \( \mathbf{a} \), has elements, \([\Phi_{\text{aaa}}]_{ijk}\) that are symmetric with respect to any permutation of the indices \( i,j,k \). Such a tensor has only 10 separate elements. In the representation given in eq. 15.105:

\[
\Phi_{\text{aaa}} = \gamma = \begin{bmatrix}
\gamma_{11} & \gamma_{12} & \gamma_{13} \\
\gamma_{21} & \gamma_{22} & \gamma_{23} \\
\gamma_{31} & \gamma_{32} & \gamma_{33} \\
\gamma_{41} & \gamma_{23} & \gamma_{32} \\
\gamma_{13} & \gamma_{41} & \gamma_{31} \\
\gamma_{12} & \gamma_{21} & \gamma_{41}
\end{bmatrix}
\]

A fourth-order tensor, \( \lambda \), that is defined by double differentiation with respect to a second order tensor, \( \mathbf{A} \), has elements that satisfy the symmetry relations

\[
\lambda_{ijkl} = \lambda_{klij}
\]

It follows that the (9x9) matrix representation of the tensor is symmetric. For any matrix indices, \( i \) and \( j \), chosen from the list in eq. 15.92,

\[
\lambda_{ij} = \lambda_{ji}
\]

It follows that a tensor whose elements are set by equations of the form

\[
\lambda_{ijkl} = \left[ \frac{\partial^2 \Phi}{\partial A_{ij} \partial A_{kl}} \right]
\]

has a maximum of 45 independent elements, the independent elements of the symmetric (9x9) matrix of the \( \lambda_{ij} \).

**15.4.2 Symmetry imposed by the underlying tensor**

If the second-order tensor, \( \mathbf{A} \), is symmetric, then the tensor derivative,

\[
\Phi_{\mathbf{A}} = \left[ \frac{\partial \Phi}{\partial \mathbf{A}} \right]
\]

is symmetric also, and has only 6 independent elements.
The third order tensor, \( \gamma = \Phi_{Aa} \), satisfies the symmetry relations

\[ \gamma_{ijkl} = \gamma_{ijlk} \]

and has a maximum of 18 independent elements. It can be represented by the (6x3) matrix given in eq. 15.105. It is sometimes useful to write the tensor in the differential notation, \( \gamma_{ijkl} \), so that it is evident which of the three indices are symmetric. To see how this notation avoids confusion, note that by differential symmetry,

\[ \gamma_{ijkl} = \gamma_{klij} \]

but, at least in the general case,

\[ \gamma_{ijkl} \neq \gamma_{klij} \]

If \( A \) and \( B \) are both symmetric tensors the fourth-order tensor, \( \lambda = \Phi_{AB} \) satisfies the symmetry relations

\[ \lambda_{ijkl} = \lambda_{jikl} = \lambda_{ijlk} = \lambda_{jilk} \]

The tensor, \( \lambda \), has a maximum of 36 independent elements, and can be represented by the (6x6) matrix shown in eq. 15.96. When \( A = B \), the elements of \( \lambda \) satisfy the additional symmetry relation

\[ \lambda_{ijkl} = \lambda_{klij} \]

The (6x6) matrix representation of \( \lambda \) is symmetric (\( \lambda_{ij} = \lambda_{ji} \)) and has only 21 independent elements. It can be written

\[
\lambda = \begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & \lambda_{14} & \lambda_{15} & \lambda_{16} \\
• & \lambda_{22} & \lambda_{23} & \lambda_{24} & \lambda_{25} & \lambda_{26} \\
• & • & \lambda_{33} & \lambda_{34} & \lambda_{35} & \lambda_{36} \\
• & • & • & \lambda_{44} & \lambda_{45} & \lambda_{46} \\
• & • & • & • & \lambda_{55} & \lambda_{56} \\
• & • & • & • & • & \lambda_{66}
\end{bmatrix}
\]

where the matrix elements that are represented by dots are symmetric with the elements shown.

15.4.3 Symmetry imposed by the material

The third set of constraints on tensor properties are due to the symmetry of the material. The concept of material symmetry is a very useful one. It derives from the
observation that, for most materials, there is a set of geometric operations that do not change the material in any observable way, that is, there is no observation that could be made that would reveal whether or not the geometric operation had been performed.

As a simple illustration of what this means, consider a perfect square that has been cut from a piece of cardboard and placed on the surface of a table. Carefully note the position and orientation of the square, leave the room and return some time later. The question you will then be asked is whether the square has been rotated by 90° while you were gone. If the square is perfect and its edges and surface are featureless, there is no way to answer the question. We therefore say that the square is symmetric with respect to a rotation through 90°, or, equivalently, that the geometric operation, 90° rotation, is a symmetry element of the square.

**Symmetry restrictions on tensor properties**

The fact that the symmetry of a material restricts its tensor properties can be illustrated by the following simple example. Let a material be symmetric with respect to 90° rotation about a given axis (for example, the z-axis in Fig. 15.1). Let a vector force, for example, the electric field, \( \mathbf{E} \), act in the x-direction. The electric field, \( \mathbf{E} \), induces a polarization, \( \mathbf{P} \), that is given by

\[
P_1 = \chi_{ij} \varepsilon_0 E_j
\]

where \( \varepsilon_0 \) is a constant (the permittivity of free space) and \( \chi \) is the electrical susceptibility, a second-order tensor property of the material. A hypothetical relation between \( \mathbf{P} \) and \( \mathbf{E} \) for \( \mathbf{E} \) in the x-direction is shown in Fig. 15.1(a). Now let the material be rotated by 90° while the field, \( \mathbf{E} \), remains the same. The x- and y-axes, which are fixed in the material, rotate into the configurations shown in Fig. 15.1(b). Since the material is symmetric under this rotation, it must be impossible to tell whether the rotation has been performed. If \( \mathbf{E} \) has the same magnitude and direction in space, \( \mathbf{P} \) must also be the same (Fig. 15.1(b)). While the vectors \( \mathbf{E} \) and \( \mathbf{P} \) are fixed in space, from the perspective of the material they have rotated so that \( \mathbf{E} \) now lies along the y-axis, as shown in Fig. 15.1(c).

![Fig. 15.1: The relation between force (\( \mathbf{E} \)) and response (\( \mathbf{P} \)) in a material that is symmetric with respect to a 90° rotation: (a) \( \mathbf{E} \) in x-](image_url)

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**Notes on the Thermodynamics of Solids**

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direction; (b) \( E \) in y-direction after rotation by 90\(^\circ\); (c) \( E \) in y-direction.

The same result could have been achieved by keeping the material fixed and rotating the vector \( E \) by 90\(^\circ\) in space, as in Fig. 15.1(c). It follows that if \( E \) is changed by an operation that conforms to the symmetry of the material, the relation of \( P \) to \( E \) is unchanged.

Since the relation between the vectors \( P \) and \( E \) is governed by the tensor, \( \chi \), this tensor must have a mathematical form that guarantees the identity of the situations diagrammed in Fig. 15.1. First, let \( Q \) be the transformation matrix for the rotation that takes 15.1(a) to 15.1(b). The rotation changes \( \chi \) to \( \chi' \), where, according to eq. 15.29,

\[
\chi'_{ij} = Q_{ik}Q_{jm}\chi_{km}
\]

But if the relation between \( P \) and \( E \) is unchanged, \( \chi' = \chi \). Hence, if the material is symmetric under the operation, \( Q \), we must have

\[
Q_{ik}Q_{jm}\chi_{km} = \chi_{ij}
\]

Second, let \( Q' \) be the transformation matrix that takes \( E \) from its orientation in Fig. 15.1(a) to 15.1(c). Since \( P \) undergoes the same rotation,

\[
Q'_{kl}P_l = \varepsilon_0\chi_{km}Q'_{mj}E_j
\]

or

\[
P_j = \varepsilon_0[Q'_{kl}Q'_{mj}\chi_{km}]E_j
= \varepsilon_0\chi_{ij}E_j
\]

By eq. 15.9, \( Q' = Q^{-1} \), where \( Q^{-1} \) is the operation that reverses \( Q \). This relation is geometrically apparent from Fig. 15.1; rotating the vector, \( E \), while keeping the material fixed in space has the same effect as fixing the vector, \( E \), in space and rotating the material in the opposite sense. It follows that if a material is symmetric under the transformation, \( Q \), it is also symmetric under the inverse transformation, \( Q^{-1} \).

**Symmetry elements**

As you probably know from the study of crystallography, the geometric operations that may leave a material unchanged include the *point symmetry operations* that are illustrated in Fig. 15.2 (rotation about an axis, reflection through a plane, and inversion through a center of symmetry) and *translation symmetry operations* that move a reference point from place to place within the material. Since a tensor property (e.g., a vector property) has magnitude and orientation in space, but has no fixed origin, the symmetry of material properties is governed by the point symmetry operations;
Fig. 15.2: Reorientation of a vector in the unit cube under inversion, reflection, and proper or improper rotation.

The four basic point symmetry operations are inversion, reflection, and proper or improper rotation. The point symmetry operations can be visualized as acting on a point in space (the perspective taken in crystallography), as acting on a vector that extends from the origin to a point in space, as in Fig. 15.2, or as acting on the coordinate system itself.

The \textit{inversion} operator can be symbolized by $Q_I$, and takes a vector into the negative of itself:

$$Q_I \cdot \mathbf{a} = - \mathbf{a}$$

$$Q_I = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$  \hspace{1cm} 15.127

The \textit{reflection} operator, $Q_r^n$, reflects a vector through the plane normal to the vector, $\mathbf{n}$. The operation illustrated in Fig. 15.2 is reflection through the (xy) plane, perpendicular to $\mathbf{e}_z$, and is accomplished by the operator

$$Q_r^z \cdot (x\mathbf{e}_x + y\mathbf{e}_y + z\mathbf{e}_z) = x\mathbf{e}_x + y\mathbf{e}_y - z\mathbf{e}_z$$

$$Q_r^z = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$  \hspace{1cm} 15.128
The rotation operator, $Q_{\theta}^e$, rotates a vector through the angle, $\theta$, about the axis, $e$. The operation illustrated in Fig. 15.2 is rotation about the z-axis:

$$Q_{\theta}^z \cdot (xe_x + ye_y + ze_z) = [\cos(\theta) - \sin(\theta)]e_x + [\cos(\theta) + \sin(\theta)]e_y + ze_z$$

$$Q_{\theta}^z = \begin{bmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The improper rotation operator, $Q_{\theta}^{\pi}$, causes a rotation through the angle $\theta$ about the axis, $e$, followed by an inversion through the origin. For rotation about the z-axis,

$$Q_{\theta}^{\pi} \cdot (xe_x + ye_y + ze_z) = -[\cos(\theta) - \sin(\theta)]e_x - [\cos(\theta) + \sin(\theta)]e_y - ze_z$$

$$Q_{\theta}^{\pi} = \begin{bmatrix} -\cos(\theta) & \sin(\theta) & 0 \\ -\sin(\theta) & -\cos(\theta) & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Note that, as illustrated in Fig. 15.2, an improper rotation about the axis, $e$, through the angle, $\pi$, is the same as a simple reflection through the plane perpendicular to $e$:

$$Q_{\pi}^e = Q_{\theta}^e$$

Moreover, an inversion is an improper rotation through the angle $0$:

$$Q_{0}^e = Q_{I}$$

where the axis, $e$, is arbitrary. It follows that all point operations can be represented by proper and improper rotations.

Finally, note that if a material is symmetric with respect to an operation, $Q$, it is necessarily symmetric to the inverse operation, $Q^{-1}$. The state reached by $Q^{-1}$ must be a symmetry transformation of the original state since it transforms into the original state under the operation, $Q$. Moreover, if both $Q_1$ and $Q_2$ are symmetry elements of a material, then their product, $Q_3 = (Q_1 \cdot Q_2)$ is also a symmetry element. The change accomplished by the operation $Q_3$ is the same as that made by sequential application of $Q_1$ and $Q_2$. But since $Q_1$ and $Q_2$ are symmetry operations they produce states that are indistinguishable from the original. Hence $Q_3$ also produces an indistinguishable state and is, therefore, a symmetry operation.
Symmetry groups

The set of all the point symmetry operations that leave a material unchanged is called its point group,

\[ g = \{ Q \} \]

where \( Q \) is a general notation for a symmetry operation. The mathematical restrictions on the tensor properties of materials follow from the condition that relations like that given by eq. 15.124 and its straightforward generalization to tensor properties of any order must hold simultaneously for every operation, \( Q \), in \( g \):

Let a material have a vector property, \( \alpha \), a second-order tensor property, \( \beta \), a third-order tensor property, \( \gamma \), and a fourth-order tensor property, \( \lambda \). Let the material have point symmetry \( g \). Then, for every symmetry element \( Q \) in \( g \):

\[
\alpha_i = Q_{ij} \alpha_j \\
\beta_{ij} = Q_{ik} Q_{jm} \beta_{km} \\
\gamma_{ijk} = Q_{iq} Q_{jr} Q_{ks} \gamma_{qrs} \\
\lambda_{ijkl} = Q_{iq} Q_{jr} Q_{ks} Q_{lt} \lambda_{qrst}
\]

For crystalline materials, there are precisely 32 point groups. Non-crystalline materials may have other point symmetries (for example, they may have five-fold or seven-fold rotation axes that are prohibited in crystals) but these symmetries are rarely of interest. Most of the point groups contain a number of different symmetry elements, with the result that eq. 15.134 severely restricts the number of independent properties. We shall derive these restrictions below. Some of the results are tabulated in Table 15.1, which shows the number of independent elements of tensor properties of orders one to four for the 32 crystallographic point groups and the isotropic group. This is the number of properties that one would have to measure to determine the full property tensor. Note that relatively few of the crystallographic point groups permit tensor properties of odd order. Also note the dramatic reduction in the number of independent properties as the symmetry changes from triclinic to isotropic.

The underlying symmetry of a crystalline material is the symmetry of its basic crystal structure. However, this underlying symmetry is often modified in two ways: the material may be polycrystalline, or the material may be subject to forces or deformations that perturb the symmetry of its crystal structure.
Table 15.1:
Number of independent elements of tensor properties of orders 1-4 for the 32 crystallographic point groups.

<table>
<thead>
<tr>
<th>Bravais lattice</th>
<th>Group symbol</th>
<th>International</th>
<th>Schoenflies</th>
<th>1st order</th>
<th>2nd order</th>
<th>3rd order</th>
<th>4th order</th>
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<tbody>
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<td>18</td>
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<tr>
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<td>1</td>
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<td>0</td>
<td>21</td>
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<td>8</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>m</td>
<td>C1h</td>
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<td>4</td>
<td>10</td>
<td>13</td>
<td></td>
</tr>
<tr>
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<td>2/m</td>
<td>C2h</td>
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<td>9</td>
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</tr>
<tr>
<td></td>
<td>mm2</td>
<td>C2v</td>
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<td>3</td>
<td>5</td>
<td>9</td>
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</tr>
<tr>
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<td>mmm</td>
<td>D2h</td>
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<tr>
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<td>4/mmm</td>
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<tr>
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</tr>
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<tr>
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<td>C6v</td>
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</tr>
<tr>
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<td>O₃h</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

Polygranular materials

A polycrystal has at least the symmetry elements that are common to the crystal structures of the phases it contains, and, in general, has additional symmetry elements that result from the fact that the individual crystals are distributed over many orientations. A polygranular body that contains a very large number of individual grains in random orientation is isotropic, whatever its crystal structure. A polygranular body that has a def-
inite crystallographic texture has a symmetry that reflects both that texture and the symmetry of the underlying crystals.

A detailed discussion of the symmetries of textured polycrystals is beyond the scope of this course, but a simple example may help clarify the physics of the problem. As we shall see below, a material cannot have a vector property unless it has a unique axis. A random polycrystal has no unique axis, and, therefore, cannot have a vector property. If the material is drawn into a wire, however, the axis of the wire is a unique axis, and the act of drawing the wire will ordinarily introduce a crystallographic texture such that some crystal axis is preferentially oriented along the axis of the wire. It is, therefore, possible for a drawn wire to have a vector property. But this will only happen if the underlying crystal has a vector property, and if that vector property has a non-zero component in the direction that is textured parallel to the wire axis. Most common crystalline solids do not have vector properties (Table 15.1), so the wires drawn from these solids have no vector properties either.

**Perturbed symmetries; reference symmetries**

The symmetry of a material is also changed by forces or displacements that distort its crystal structure. For example, a cubic material that is sheared is no longer cubic, and has fewer symmetry elements than were present in its relaxed state. Fortunately, the tensor forces and displacements that ordinarily concern us are small in magnitude and effect, and we can usually account for them by expansion about a relaxed reference state whose symmetry is known. As a specific example, let the material be a solid dielectric whose free energy density depends on both the local electric displacement, \( \mathbf{D} \), and the local elastic strain, \( \mathbf{e} \). If \( \mathbf{D} \) and \( \mathbf{e} \) are small in effect (as they almost always are) we approximate the free energy density by expanding about the relaxed state. The result is, to second order,

\[
\tilde{F}_V(T, \{n\}, \mathbf{D}, \mathbf{e}) = \tilde{F}_V(T, \{n\}) + \left[ \frac{\partial \tilde{F}_V}{\partial D_i} \right]_0 D_i + \left[ \frac{\partial \tilde{F}_V}{\partial \varepsilon_{ij}} \right]_0 \varepsilon_{ij} + \frac{1}{2} \left[ \frac{\partial^2 \tilde{F}_V}{\partial D_i \partial D_j} \right]_0 D_i D_j +
\]

\[
+ \left[ \frac{\partial^2 \tilde{F}_V}{\partial \varepsilon_{ij} \partial D_k} \right]_0 \varepsilon_{ij} D_k + \frac{1}{2} \left[ \frac{\partial^2 \tilde{F}_V}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right]_0 \varepsilon_{ij} \varepsilon_{kl}
\]

where \( \tilde{F}_V(T, \{n\}) \) is the free energy density when \( \mathbf{D} = 0, \mathbf{e} = 0 \) and the subscript zeros have the meaning that the partial derivatives are taken at \( \mathbf{D} = 0, \mathbf{e} = 0 \).

The partial derivative, \( \left[ \frac{\partial \tilde{F}_V}{\partial D_i} \right]_0 \), is a vector property that must be compatible with the symmetry of the material in its relaxed state. Physically, it can be shown that

\[
\left[ \frac{\partial \tilde{F}_V}{\partial D_i} \right]_0 = E_i^0
\]

where \( E^0 \) is the residual electric field within the body when the applied field, as measured by the electric displacement, \( \mathbf{D} = 0 \). Since \( E^0 \) is a vector property, it must vanish unless the
symmetry of the material in its relaxed state permits a vector property. Materials that have a non-vanishing residual field, \( \mathbf{E}^0 \), in the absence of an applied field are said to be pyroelectric. Table 15.1 shows that pyroelectric materials must have one of only 10 of the 32 point group symmetries. No cubic material can be pyroelectric. It is, therefore, not surprising that pyroelectric materials are uncommon.

There is, however, a broader class of materials that become "pyroelectric" if they are given an appropriate elastic strain. According to eq. 15.135, the residual field in a strained material is

\[
E_i^0 = \left[ \frac{\partial \mathbf{F}_V}{\partial D_{1j}}, \varepsilon \right] + \left[ \frac{\partial^2 \mathbf{F}_V}{\partial \varepsilon_{jk} \partial D_{1j}} \right] \varepsilon_{jk} \tag{15.137}
\]

where the subscript \( \varepsilon \) on the partial derivative means that it is to be taken at \( D = 0, \varepsilon \neq 0 \). The derivative \( \left[ \frac{\partial^2 \mathbf{F}_V}{\partial \varepsilon_{jk} \partial D_{1j}} \right] \) is a third-order tensor property of the relaxed state. Eq. 15.137 shows that a material that is not pyroelectric in the relaxed state becomes so if its symmetry allows third-order tensor properties that couple the electric field and the elastic strain. Reference to Table 15.1 shows that there a number of point group symmetries that forbid pyroelectricity in the relaxed state, but permit it in a properly strained state. Such materials develop spontaneous electric fields when they are strained, and are said to be piezoelectric. Two of the point groups of the cubic system have this property.

There is still another class of materials that are neither pyro- nor piezoelectric at high temperature, but spontaneously develop pyroelectricity when cooled below a critical temperature, called the Curie temperature, \( T_c \). These materials are said to be ferroelectric. Symmetry considerations show that the ferroelectric transition must be a structural transition, from a high-temperature structure whose symmetry does not permit vector properties to a low-temperature structure that corresponds to one of the 10 pyroelectric point groups. In practice, the ferroelectric transition is a mutation, and the change in structure at the Curie temperature is caused by the cooperative, infinitesimal displacement of ions in adjacent cells (a symmetry element is eliminated by atomic displacements that are incompatible with it, however small these may be).

### 15.5 Consequences of the Basic Symmetry Operations

In this section we shall systematically explore the restrictions that are imposed on tensor properties by the basic symmetry operations that appear in the crystallographic point groups. These operations include (1) inversion, (2) reflection through a plane, (3) rotation through the angle \( \pi \), (4-5) proper or improper rotation through the angle \( \pi/2 \), (6-7) proper or improper rotation through the angle \( 2\pi/3 \), (7-8) proper or improper rotation through the angle \( \pi/3 \).

We shall assume a Cartesian coordinate system that is specified by the orthogonal unit vectors \( \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3 \), and shall assume that \( \mathbf{e}_3 \) is the axis of symmetry (the rotation axis for rotations, the vector perpendicular to the mirror plane for reflections). We shall only
consider properties that are obtained by differentiating the fundamental equation with respect to vectors or symmetric second-order tensors, and, hence, have the symmetries

\[\beta_{ij} = \beta_{ji}\] (6 independent elements)  
\[\gamma_{ijkl} = \gamma_{ijlk}\] (18 independent elements)  
\[\lambda_{ijkl} = \lambda_{ijkl} = \lambda_{ijlk} = \lambda_{klij}\] (21 independent elements)  

15.5.1 Inversion

The symbol for inversion symmetry is \(\tilde{I}\) (International system) or \(S_2\) (Schoenflies system). The center of symmetry is assumed to lie at the origin of the coordinate system. Inverting the coordinate system changes the unit vectors into their negatives:

\[[\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3] \rightarrow [-\mathbf{e}_1, -\mathbf{e}_2, -\mathbf{e}_3]\]

and is represented by the transformation matrix:

\[[Q_I]_{ij} = -\delta_{ij}\]

A material whose symmetry group contains the inversion cannot have tensor properties of odd order. If \(\alpha\) is a vector property then we must have

\[Q_I \cdot \alpha = -\alpha = \alpha\]

which is only satisfied if

\[\alpha = 0\]

An arbitrary element of the third-order tensor property, \(\gamma\), is, in dyadic form, \(\gamma_{ijk}\mathbf{e}_i\mathbf{e}_j\mathbf{e}_k\). Symmetry with respect to an inversion of the coordinate system requires that

\[\gamma_{ijk} = -\gamma_{ijk} = 0\]

so that

\[\gamma = 0\]

On the other hand, inversion places no restrictions on tensor properties of even order. For example, an arbitrary element of the second-order tensor property, \(\beta\), is, in dyadic form, \(\beta_{ij}\mathbf{e}_i\mathbf{e}_j\), and is unchanged if the coordinates are inverted. The same result holds for the fourth-order tensor, \(\lambda\):

\[\beta_{ij} = \beta_{ij} \quad \Rightarrow \beta \text{ unaffected} \quad (6 \text{ independent elements})\]
\[ \lambda_{ijkl} = \lambda_{ijkl} \implies \lambda \text{ unaffected (21 independent elements)} \] 15.148

### 15.5.2 Reflection

The symbol for reflection symmetry is \( m \) (international) or \( C_{1h} \) (Schoenflies). The mirror plane will be assumed perpendicular to \( e_3 \). If the coordinate system is reflected through this plane the unit vectors are changed by

\[ [e_1, e_2, e_3] \rightarrow [e_1, e_2, -e_3] \]

so the transformation matrix is

\[ Q_r^3 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \]

15.150

The transformation 15.149 has the effect of reversing the sign of any tensor element whose dyadic form contains \( e_3 \) an odd number of times. Other elements are unaffected. It follows that the most general forms for the tensor properties \( \alpha, \beta, \gamma \) and \( \lambda \) are:

\[ \alpha = \alpha_1 e_1 + \alpha_2 e_2 \] (2 independent elements) 15.151

\[ \beta = \begin{bmatrix} \beta_{11} & \beta_{12} & 0 \\ \beta_{12} & \beta_{22} & 0 \\ 0 & 0 & \beta_{33} \end{bmatrix} \] (4 elements) 15.152

\[ \gamma = \begin{bmatrix} \gamma_{11} & \gamma_{12} & 0 \\ \gamma_{21} & \gamma_{22} & 0 \\ \gamma_{31} & \gamma_{32} & 0 \\ 0 & 0 & \gamma_{43} \\ 0 & 0 & \gamma_{53} \\ \gamma_{61} & \gamma_{62} & 0 \end{bmatrix} \] (10 elements) 15.153

\[ \lambda = \begin{bmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & \lambda_{16} \\ \lambda_{12} & \lambda_{22} & \lambda_{23} & 0 & 0 & \lambda_{26} \\ \lambda_{13} & \lambda_{23} & \lambda_{33} & 0 & 0 & \lambda_{36} \\ 0 & 0 & 0 & \lambda_{44} & \lambda_{45} & 0 \\ 0 & 0 & 0 & \lambda_{45} & \lambda_{55} & 0 \\ \lambda_{61} & \lambda_{26} & \lambda_{36} & 0 & 0 & \lambda_{66} \end{bmatrix} \] (13 elements) 15.154
15.5.3 Two-fold rotation about $e_3$

The symbol for rotation through $\pi$ is $2$ (international) or $C_2$ (Schoenflies). If $e_3$ is the axis of symmetry for rotation through $\pi$, it is called a two-fold axis. Rotating the coordinate system through $\pi$ about $e_3$ changes the set of unit vectors as follows:

$$[e_1, e_2, e_3] \rightarrow [-e_1, -e_2, e_3]$$  \hspace{1cm} (15.155)

The transformation matrix is

$$Q_\pi^3 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$  \hspace{1cm} (15.156)

The transformation $15.155$ has the effect of reversing the sign of any tensor element whose dyadic form contains $e_1$ and/or $e_2$ an odd number of times. Other elements are unaffected. It follows that the most general forms for the tensor properties $\alpha$, $\beta$, $\gamma$ and $\lambda$ are:

$$\alpha = \alpha_3 e_3$$  \hspace{1cm} (1 element)  \hspace{1cm} (15.157)

$$\beta = \begin{bmatrix} \beta_{11} & \beta_{12} & 0 \\ \beta_{12} & \beta_{22} & 0 \\ 0 & 0 & \beta_{33} \end{bmatrix}$$  \hspace{1cm} (4 elements)  \hspace{1cm} (15.158)

$$\gamma = \begin{bmatrix} 0 & 0 & \gamma_{13} \\ 0 & 0 & \gamma_{23} \\ 0 & 0 & \gamma_{33} \\ \gamma_{41} & \gamma_{42} & 0 \\ \gamma_{51} & \gamma_{52} & 0 \\ 0 & 0 & \gamma_{63} \end{bmatrix}$$  \hspace{1cm} (8 elements)  \hspace{1cm} (15.159)

$$\lambda = \begin{bmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & \lambda_{16} \\ \lambda_{12} & \lambda_{22} & \lambda_{23} & 0 & 0 & \lambda_{26} \\ \lambda_{13} & \lambda_{23} & \lambda_{33} & 0 & 0 & \lambda_{36} \\ 0 & 0 & 0 & \lambda_{44} & \lambda_{45} & 0 \\ 0 & 0 & 0 & \lambda_{45} & \lambda_{55} & 0 \\ \lambda_{16} & \lambda_{26} & \lambda_{36} & 0 & 0 & \lambda_{66} \end{bmatrix}$$  \hspace{1cm} (13 elements)  \hspace{1cm} (15.160)
Note that the restrictions on $\beta$ and $\lambda$, are the same as those imposed by a mirror plane perpendicular to $e_3$, but the restrictions on $\alpha$ and $\gamma$ are different.

### 15.5.4 Four-fold rotation about $e_3$

The symbol for rotation through $\pi/2$ is 4 (international) or $C_4$ (Schoenflies). If a material is symmetric under a rotation by $\pi/2$ about $e_3$ then it is also symmetric under rotation by $\pi$ or $3\pi/4$; the axis $e_3$ is called a *four-fold axis*. If the coordinate system is rotated through $\pi/4$ about $e_3$ the unit vectors are changed by

$$[e_1, e_2, e_3] \rightarrow [e_2, -e_1, e_3]$$

so the transformation matrix is

$$Q_{\pi/2}^3 = \begin{bmatrix}
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{bmatrix}$$

The transformation 15.162 has the effect of interchanging the 1- and 2-axes, and changing the sign of $e_1$. It is straightforward to show that most general forms for the tensor properties $\alpha, \beta, \gamma$ and $\lambda$ are:

$$\alpha = \alpha_3 e_3$$  \hspace{1cm} (1 element)  \hspace{1cm} 15.163$$

$$\beta = \begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{11} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix}$$  \hspace{1cm} (3 elements)  \hspace{1cm} 15.164$$

$$\gamma = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{41} & \gamma_{42} & 0 \\
\gamma_{42} & -\gamma_{41} & 0 \\
0 & 0 & 0
\end{bmatrix}$$  \hspace{1cm} (4 elements)  \hspace{1cm} 15.165$$
\[ \lambda = \begin{bmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & \lambda_{16} \\ \lambda_{12} & \lambda_{11} & \lambda_{13} & 0 & 0 & -\lambda_{16} \\ \lambda_{13} & \lambda_{13} & \lambda_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & \lambda_{44} & 0 \\ \lambda_{16} & -\lambda_{16} & 0 & 0 & 0 & \lambda_{66} \end{bmatrix} \quad \text{(7 elements)} \]

15.5.5 Four-fold improper rotation about \( e_3 \)

The symbol for an improper rotation through \( \pi/4 \) is \( \bar{4} \) (international) or \( S_4 \) (Schoenflies). If the coordinate system is rotated through \( \pi/4 \) about \( e_3 \) and then inverted through the origin the transformation is

\[ [e_1, e_2, e_3] \to [-e_2, e_1, -e_3] \]

and the transformation matrix is

\[ Q_{\pi/2}^3 = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \]

Since inversion does not affect tensors of even order, the restrictions on \( \beta \) and \( \lambda \) are the same as for the proper 4-fold rotation. The vector property, \( \alpha \), must vanish:

\[ \alpha = 0 \quad \text{(0 elements)} \]

The third-order tensor, \( \gamma \), need not vanish, but takes the simple form

\[ \gamma = \begin{bmatrix} 0 & 0 & \gamma_{13} \\ 0 & 0 & -\gamma_{13} \\ \gamma_{41} & \gamma_{42} & 0 \\ -\gamma_{42} & \gamma_{41} & 0 \\ 0 & 0 & \gamma_{63} \end{bmatrix} \quad \text{(4 elements)} \]

The fact that \( \gamma \) can have non-zero elements may seem surprising, since we found (sec. 15.5.1) that \( \gamma = 0 \) when the material is symmetric to inversion. However, as illustrated in fig. 15.3, a four-fold axis of improper rotations does not include a simple inversion. A material that is symmetric to a four-fold improper rotation is not necessarily symmetric.
under inversion. The result is that such a material cannot have a vector property, but can have a third-order tensor property unless other symmetry elements forbid it.

Fig. 15.3: The four vectors generated by a four-fold improper rotation about the axis shown. Note that the inverse vectors do not appear.

15.5.6 Three-fold rotation about $e_3$

The symbol for rotation through $2\pi/3$ is $3$ (international) or $C_3$ (Schoenflies). If a material is symmetric under a rotation by $2\pi/3$ about $e_3$ then it is also symmetric to rotation by $4\pi/3$; the axis $e_3$ is called a three-fold axis. If the coordinate system is rotated through $2\pi/3$ about $e_3$ the unit vectors change as

$$[e_1, e_2, e_3] \rightarrow \left[ \begin{array}{c} \frac{1}{2} e_1 + \frac{\sqrt{3}}{2} e_2, -\frac{\sqrt{3}}{2} e_1 + \frac{1}{2} e_1, e_3 \end{array} \right]$$

15.171

The transformation matrix is

$$Q_{2\pi/3}^3 = \begin{bmatrix} 1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

15.172

The transformation 15.171 commingles the 1- and 2-axes. It is algebraically tedious to find the restrictions that result from this transformation, particularly for third- and fourth-order tensor properties. However, the algebra can be done. The most general forms for the tensor properties $\alpha$, $\beta$, $\gamma$ and $\lambda$ are:

$$\alpha = \alpha e_3$$

(1 element) 15.173
\[
\beta = \begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{11} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix} \quad (2 \text{ elements})
\]

\[
\gamma = \begin{bmatrix}
\gamma_{11} & -\gamma_{22} & \gamma_{13} \\
-\gamma_{11} & \gamma_{22} & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{41} & \gamma_{51} & 0 \\
\gamma_{51} & -\gamma_{41} & 0 \\
-2\gamma_{22} & -2\gamma_{11} & 0
\end{bmatrix} \quad (6 \text{ elements})
\]

\[
\lambda = \begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & \lambda_{14} & -\lambda_{25} & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{13} & -\lambda_{14} & \lambda_{25} & 0 \\
\lambda_{13} & \lambda_{13} & \lambda_{33} & 0 & 0 & 0 \\
-\lambda_{14} & -\lambda_{14} & 0 & \lambda_{44} & 0 & \lambda_{25} \\
-\lambda_{25} & \lambda_{25} & 0 & 0 & \lambda_{44} & \lambda_{14} \\
0 & 0 & 0 & \lambda_{25} & \lambda_{14} & \frac{1}{2}(\lambda_{11} - \lambda_{12})
\end{bmatrix} \quad (7 \text{ elements})
\]

15.5.7 Three-fold improper rotation about \( e_3 \)

The symbol for a 3-fold axis of improper rotations is \( \bar{3} \) (international) or \( S_6 \) (Schoenflies). An improper rotation of the coordinates through \( 2\pi/3 \) about \( e_3 \) changes the set of coordinates as follows:

\[
[e_1, e_2, e_3] \rightarrow \begin{bmatrix}
\frac{1}{2} e_1 + \frac{\sqrt{3}}{2} e_2, \quad -\frac{\sqrt{3}}{2} e_1 + \frac{1}{2} e_1, e_3
\end{bmatrix}
\]

The transformation matrix is

\[
Q^3_{2\pi/3} = \begin{bmatrix}
-1/2 & -\sqrt{3}/2 & 0 \\
\sqrt{3}/2 & -1/2 & 0 \\
0 & 0 & -1
\end{bmatrix}
\]
Fig. 15.4: Vectors related by improper rotations about a 3-fold axis. Note that the inverse of each vector is included in the set.

While the transformation specified by 15.177 is complicated, the restrictions it imposes can be obtained by inspection from the result for the 3-fold axis of proper rotations. The second- and fourth order tensors, $\mathbf{\beta}$ and $\mathbf{\lambda}$, have the same forms given in eqs. 15.174 and 15.176; the addition of an inversion to each rotation does not change tensors of even order. The first- and third-order tensors, $\mathbf{\alpha}$ and $\mathbf{\gamma}$, vanish:

$$\mathbf{\alpha} = 0$$  \hspace{1cm} (15.179)

$$\mathbf{\gamma} = 0$$  \hspace{1cm} (15.180)

The simple reason that odd-order tensors vanish is illustrated in Fig. 15.4, which shows the vectors generated from a single vector by improper rotations about a 3-fold axis. The inverse of each vector is included in the set. It follows that a material that has a 3-fold symmetry axis of improper rotations is also symmetric under inversion and cannot have tensor properties of odd order.

### 15.5.8 Six-fold rotation about $e_3$

A 6-fold symmetry axis is generated by rotation through $\pi/3$. The symbol is 6 (international) or $C_6$ (Schoenflies). If the coordinate system is rotated through $\pi/3$ about $e_3$, the unit vectors change as

$$\begin{bmatrix} e_1, e_2, e_3 \end{bmatrix} \rightarrow \begin{bmatrix} \frac{\sqrt{3}}{2} e_1 + \frac{1}{2} e_2, -\frac{1}{2} e_1 + \frac{\sqrt{3}}{2} e_2, e_3 \end{bmatrix}$$  \hspace{1cm} (15.181)

The transformation matrix is

$$Q_{\pi/3}^3 = \begin{bmatrix} \frac{\sqrt{3}}{2} & 1/2 & 0 \\ -1/2 & \sqrt{3}/2 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$  \hspace{1cm} (15.182)
The transformation 15.181 again commingles the 1- and 2-axes. The most general forms for the first- and second-order tensor properties, \( \alpha \) and \( \beta \), are the same as those set by a 3-fold axis:

\[
\alpha = \alpha e_3 \\
\beta = \begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{11} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix}
\]

(1 element) 15.183  
(2 elements) 15.184

The third- and fourth-order tensor properties are simpler than in the 3-fold case:

\[
\gamma = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{41} & \gamma_{51} & 0 \\
\gamma_{51} & \gamma_{41} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

(4 elements) 15.185

\[
\lambda = \begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{13} & 0 & 0 & 0 \\
\lambda_{13} & \lambda_{13} & \lambda_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{2}(\lambda_{11}-\lambda_{12})
\end{bmatrix}
\]

(5 elements) 15.186

15.5.9 Six-fold improper rotation about \( e_3 \)

The symbol for a 6-fold axis of improper rotations is \( \bar{e} \) (international) or \( C_{3h} \) (Schoenflies). An improper rotation of the coordinates through \( \pi/3 \) about \( e_3 \) changes the set of coordinates as follows:

\[
[e_1, e_2, e_3] \rightarrow \begin{bmatrix}
-\frac{\sqrt{3}}{2}e_1 - \frac{1}{2}e_2, \\
\frac{1}{2}e_1 - \frac{\sqrt{3}}{2}e_2, \\
-e_3
\end{bmatrix}
\]

15.187

The transformation matrix is
\[ Q_{\pi/3}^3 = \begin{bmatrix} -\sqrt{3}/2 & -1/2 & 0 \\ 1/2 & -\sqrt{3}/2 & 0 \\ 0 & 0 & -1 \end{bmatrix} \]

15.188

While the transformation specified by 15.177 is complicated, the restrictions it imposes can be found by inspection from results obtained above. The second- and fourth order tensors, \( \mathbf{\beta} \) and \( \mathbf{\lambda} \), have the forms given in eqs. 15.184 and 15.186; the addition of an inversion to each rotation does not change tensors of even order.

\[ \text{Fig. 15.5: The set of vectors related by improper rotations about a six-fold axis. Note that the inversion is not included, but the symmetry does include both a 3-fold axis and a mirror plane.} \]

To evaluate the odd-order tensors we examine the symmetry about a 6-fold axis of improper rotations (Fig. 15.5). While simple inversion is not included, the symmetry of a six-fold axis of improper rotations is the sum of two simpler symmetries: a 3-fold rotation axis and a perpendicular mirror plane. It follows that the tensor properties of \( C_{3h} \) must simultaneously have the forms dictated by the symmetries \( C_3 \) and \( C_{1h} \). For the vector property, \( \mathbf{\alpha} \), eqs. 15.151 and 15.173 require that

\[ \mathbf{\alpha} = \alpha_1 \mathbf{e}_1 + \alpha_2 \mathbf{e}_2 = \alpha_3 \mathbf{e}_3 \]

15.189

which can only be satisfied if

\[ \mathbf{\alpha} = 0 \]

15.190

That is, a material with symmetry \( C_{3h} \) cannot have a vector property.

For the third-order tensor, \( \mathbf{\gamma} \), eqs. 15.153 and 15.175 require that
Notes on the Thermodynamics of Solids

15.5.10 Materials with higher symmetry; cubic materials

Each of the elementary symmetry elements treated above defines a crystallographic point group in which it and the identity are the only elements. The other 23 crystallographic point groups are groups of higher symmetry that are formed by combining two or more of these basic elements. The combination of symmetry elements generally reduces the number of independent properties. Combining symmetry elements can never add properties, since the property tensors must satisfy the restrictions of each symmetry element independently.

We shall discuss two examples for illustration.

The first is the case we just studied: the point group $C_{3h}$ ($\bar{6}$ in the international notation) which is the group of a 6-fold axis of improper rotations. This group belongs to the hexagonal system, that is, it is compatible with a hexagonal Bravais lattice (Table 15.1). As we have seen (Fig. 15.5), a 6-fold axis of improper rotations is equivalent to a 3-fold rotation axis and a perpendicular mirror plane. It follows that the tensor properties of a material with this symmetry group must simultaneously satisfy the restriction imposed by the mirror plane (section 15.5.2), and those imposed by the 3-fold rotation axis (section 15.5.6). Comparing the two, we find that the material cannot have a vector property, and cannot have more than two independent third-order tensor properties. Had we wished, we could have used the same rule to obtain the tensors $\beta$ and $\lambda$, but we already knew these from the solution for the group $C_6$ (section 15.5.8).
As a second example, consider the cubic group, \( O_h \) (m3m in the international notation) which is the point group of the FCC and BCC structures. This symmetry group has a great many symmetry elements. A simple and sufficient set for our purposes are its three perpendicular 4-fold axes. Let the three coordinate axes \( (\mathbf{e}_i) \) be chosen so that they parallel these four-fold axes.

First consider the vector property, \( \alpha \). By eq. 15.163, the 4-fold axis along \( \mathbf{e}_3 \) requires that \( \alpha_1 = \alpha_2 = 0 \), while the 4-fold axis along \( \mathbf{e}_2 \) requires that \( \alpha_1 = \alpha_3 = 0 \). It follows that

\[
\alpha = 0
\]

and the material cannot have a vector property.

The second-order tensor property also follows immediately from a comparison of those associated with the four-fold axes along \( \mathbf{e}_3 \) and \( \mathbf{e}_2 \). From eq. 15.164, and the similar form that pertains when the 4-fold axis parallels \( \mathbf{e}_2 \),

\[
\beta = \begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{11} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix}
= \begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{22} & 0 \\
0 & 0 & \beta_{11}
\end{bmatrix}
\]

It follows that

\[
\beta = \beta \delta
\]

where \( \beta \) is a scalar and \( \delta \) is the unit tensor. The second-order tensor properties of a material with the symmetry group \( O_h \) are isotropic.

We treat the third-order tensor properties in the same way. From eq. 15.165, and the similar equation obtained by placing the 4-fold axis along \( \mathbf{e}_2 \), we obtain

\[
\gamma = 
\begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{41} & \gamma_{42} & 0 \\
\gamma_{42} & -\gamma_{41} & 0 \\
0 & 0 & 0
\end{bmatrix}
= 
\begin{bmatrix}
0 & \gamma_{12} & 0 \\
0 & \gamma_{12} & 0 \\
0 & \gamma_{22} & 0 \\
\gamma_{41} & 0 & \gamma_{43} \\
0 & 0 & 0 \\
\gamma_{43} & 0 & -\gamma_{41}
\end{bmatrix}
\]

A comparison between the two shows that all elements of \( \gamma \) must vanish. Hence

\[
\gamma = 0
\]
A material with symmetry \( O_h \) does not have third-order tensor properties.

Finally, consider the fourth-order tensor properties. Eq. 15.166 gives the form of this tensor that is compatible with a 4-fold axis along \( e_3 \). The 4-fold axis along \( e_2 \) adds the restrictions, \( \lambda_{11} = \lambda_{33}, \lambda_{12} = \lambda_{13}, \lambda_{66} = \lambda_{44} \) and \( \lambda_{16} = 0 \), all of which come from the interchangeability of the \( e_1 \) and \( e_3 \) axes under 4-fold rotation about \( e_2 \). Adding these constraints to eq. 15.166 yields

\[
\lambda = \begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{12} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{12} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{12} & \lambda_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & \lambda_{44}
\end{bmatrix}
\]

15.198

The other symmetry elements of \( O_h \) add no new restrictions; eq. 15.198 is the most general form of the fourth-order property tensor for this symmetry.

It follows that a material with symmetry \( O_h \) has no vector or third-order tensor properties. This has the consequence, among many others, that a cubic material with symmetry \( O_h \) cannot be pyroelectric or piezoelectric. Its second-order tensor properties are spherical. Hence, for example, a cubic material is an isotropic conductor.

15.6 TENSOR PROPERTIES FOR THE 32 POINT GROUPS

We shall finish this chapter by completing the list of allowable tensor properties for the 32 crystallographic point groups, organized by Bravais lattice.

15.6.1 Monoclinic and triclinic symmetry

The triclinic Bravais lattice has two point groups: \( C_1 \) (1) and \( S_2 \) (\( \bar{I} \)).

The group \( C_1 \) contains only the identity, so there are no tensor restrictions on the tensor properties in this case. Each tensor property has the most general form, and the maximum number of elements, allowed by the rules set out in sections 15.4.1 and 15.4.2. The group \( S_2 \) (\( \bar{I} \)) is the simple inversion groups described in sec. 15.5.1.

The monoclinic Bravais lattice has the point groups \( C_2 \) (2), \( C_{1h}(m) \) and \( C_{2h} \) (2/m). The group \( C_2 \) contains a single two-fold rotation axis, and is described in sec. 15.5.3. The group \( C_{1h} \) contains a single mirror plane, and is described in sec. 15.5.2.
The group $C_{2h}$ contains a two-fold rotation axis and a perpendicular mirror plane. It must, therefore, satisfy the restrictions imposed by both $C_2$ and $C_{1h}$. A comparison of the odd-order properties for $C_2$ and $C_{1h}$ shows that they are completely incompatible. Hence

$$\alpha = \gamma = 0$$

A comparison of the even-order properties for $C_2$ and $C_{1h}$ shows that they are the same. It follows that

$$\beta[C_{2h}] = \beta[C_{1h}] = \beta[C_2] = \beta[\text{monoclinic}]$$

$$= \begin{bmatrix}
\beta_{11} & \beta_{12} & 0 \\
\beta_{12} & \beta_{22} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix}$$

(4 elements) 15.200

$$\lambda[C_{2h}] = \lambda[C_{1h}] = \lambda[C_2] = \lambda[\text{monoclinic}]$$

$$= \begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & \lambda_{16} \\
\lambda_{12} & \lambda_{22} & \lambda_{23} & 0 & 0 & \lambda_{26} \\
\lambda_{13} & \lambda_{23} & \lambda_{33} & 0 & 0 & \lambda_{36} \\
0 & 0 & 0 & \lambda_{44} & \lambda_{45} & 0 \\
0 & 0 & 0 & \lambda_{45} & \lambda_{55} & 0 \\
\lambda_{61} & \lambda_{26} & \lambda_{36} & 0 & 0 & \lambda_{66}
\end{bmatrix}$$

(13 elements) 15.201

### 15.6.2 Orthorhombic symmetry

The orthorhombic Bravais lattice has the point groups $D_2$ (222), which has three perpendicular 2-fold axes, the group $C_{2v}$ (mm2), which has a 2-fold axis, $e_3$, and mirror planes perpendicular to $e_1$ and $e_2$, and $D_{2h}$ (mmm), which has three perpendicular mirror planes. Two-fold axes and mirror planes impose the same restrictions on $\beta$ and $\lambda$. Hence these properties have the same form for all orthorhombic groups. The three perpendicular axes eliminate all non-diagonal elements. The property matrices are:

$$\beta[D_2] = \beta[C_{2v}] = \beta[D_{2h}] = \beta(\text{orthorhombic}) =$$

$$= \begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{22} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix}$$

(3 elements) 15.202

$$\lambda[D_2] = \lambda[C_{2v}] = \lambda[D_{2h}] = \lambda(\text{orthorhombic}) =$$
\[
\begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{22} & \lambda_{23} & 0 & 0 & 0 \\
\lambda_{13} & \lambda_{23} & \lambda_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_{55} & 0 \\
0 & 0 & 0 & 0 & 0 & \lambda_{66}
\end{bmatrix}
\]

(9 elements) 15.203

The odd-order properties are more specific. Only the group \( C_{2v} \) has a unique direction, and, hence, a vector property:

\[
\alpha[D_2] = \alpha[D_{2h}] = 0
\]

15.204

\[
\alpha[C_{2v}] = \alpha_3 e_3
\]

15.205

The group \( C_{2v} \) also permits third-order tensor properties with five independent elements.

\[
\gamma[C_{2v}] = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{23} \\
0 & 0 & \gamma_{33} \\
0 & \gamma_{42} & 0 \\
\gamma_{51} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

(5 elements) 15.206

The group \( D_2 \) permits third-order tensor properties with 3 elements, while the higher symmetry of \( D_{2h} \) forbids third-order tensor properties.

\[
\gamma[D_2] = \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & \gamma_{41} \\
\gamma_{41} & 0 & 0 \\
0 & \gamma_{52} & 0 \\
0 & 0 & \gamma_{63}
\end{bmatrix}
\]

(3 elements) 15.207

\[
\gamma[D_{2h}] = 0
\]

15.208
15.6.3 Tetragonal symmetry

The tetragonal Bravais lattice has seven point groups, each of which contains a single 4-fold axis. As listed in Table 15.1 they are C₄ (4), S₄ (4̅), C₄ᵥ (4/m), D₄ (422), C₄ᵥ (422), D₂d (42m) and D₄h (4/mmm). The common feature of a 4-fold axis has the consequence that all of the tetragonal property matrices are the same or reductions of the properties of C₄ discussed in sec. 15.5.4.

The second-order tensor properties are the same for all tetragonal groups, and are determined by the 4-fold axis:

\[ \mathbf{\beta}[C₄] = \mathbf{\beta}[S₄] = \mathbf{\beta}[C₄ᵥ] = \mathbf{\beta}[D₄] = \mathbf{\beta}[D₂d] = \mathbf{\beta}[D₄h] = \]

\[
\begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{11} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix}
\] (2 elements) 15.209

For the fourth order tensor properties, the tetragonal groups fall into two sets. The groups C₄, S₄ and C₄ᵥ have a single symmetry axis (e₃), and have the fourth-order tensor properties of C₄:

\[ \mathbf{\lambda}[C₄] = \mathbf{\lambda}[S₄] = \mathbf{\lambda}[C₄ᵥ] = \]

\[
\begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & \lambda_{16} \\
\lambda_{12} & \lambda_{11} & \lambda_{13} & 0 & 0 & -\lambda_{16} \\
\lambda_{31} & \lambda_{31} & \lambda_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_{44} & 0 \\
\lambda_{61} & -\lambda_{61} & 0 & 0 & 0 & \lambda_{66}
\end{bmatrix}
\] (7 elements) 15.210

The groups D₄, C₄ᵥ, D₂d and D₄h have more than one symmetry axis. This has the consequence that \( \lambda_{16} = 0 \) in 15.215. The other elements are the same:

\[ \mathbf{\lambda}[D₄] = \mathbf{\lambda}[C₄ᵥ] = \mathbf{\lambda}[D₂d] = \mathbf{\lambda}[D₄h] = \]
Regarding the odd-order tensor properties of the tetragonal groups, only the groups \( C_4 \) and \( C_{4v} \) have a unique direction. Hence,

\[
\alpha[S_4] = \alpha[C_{4h}] = \alpha[D_4] = \alpha[D_{2d}] = \alpha[D_{4h}] = 0
\]

\[
\alpha[C_4] = \alpha[C_{4v}] = \alpha_3 e_3
\]

The third-order tensor properties are a more complicated set. The groups \( C_{4h} \) and \( D_{4h} \) have mirror planes perpendicular to the 4-fold axis, and, hence, have no third-order tensor properties. Each of the remaining groups has non-zero third-order tensor properties of its own peculiar form:

\[
\gamma[C_{4h}] = \gamma[D_{4h}] = 0
\]

\[
\gamma[C_4] = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{41} & \gamma_{42} & 0 \\
\gamma_{42} & -\gamma_{41} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

\[
\gamma[S_4] = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & -\gamma_{13} \\
0 & 0 & 0 \\
\gamma_{41} & \gamma_{42} & 0 \\
-\gamma_{42} & \gamma_{41} & 0 \\
0 & 0 & \gamma_{63}
\end{bmatrix}
\]

\[
\gamma[C_{4v}] = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
0 & \gamma_{42} & 0 \\
\gamma_{42} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]
\[ \gamma[D_{2d}] = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \gamma_{41} & 0 & 0 \\ 0 & \gamma_{41} & 0 \\ 0 & 0 & \gamma_{63} \end{bmatrix} \text{ (2 elements)} \]

\[ \gamma[D_4] = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ \gamma_{41} & 0 & 0 \\ 0 & -\gamma_{41} & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ (1 element)} \]

15.6.4 Rhombohedral (trigonal)

The rhombohedral (or trigonal) Bravais lattice has five point groups, each of which has a single 3-fold axis. From Table 15.1, these are: \( C_3 \) (3), \( S_6 \) (3), \( D_3 \) (32), \( C_{3v} \) (3m), \( D_{3d} \) (3m). The common 3-fold axis has the consequence that all property matrices are contained in those for \( C_3 \) (sec. 15.5.6).

The second-order tensor properties are the same for all rhombohedral groups, and are determined by the 4-fold axis:

\[ \beta[C_3] = \beta[S_6] = \beta[D_3] = \beta[C_{3v}] = \beta[D_{3d}] = \begin{bmatrix} \beta_{11} & 0 & 0 \\ 0 & \beta_{11} & 0 \\ 0 & 0 & \beta_{33} \end{bmatrix} \text{ (2 elements)} \]

Like the tetragonal groups, the rhombohedral groups have either of two fourth-order property matrices. The groups \( C_3 \) and \( S_6 \) have a single symmetry axis (\( e_3 \)), and have the fourth-order tensor properties of \( C_3 \):
\( \lambda[C_3] = \lambda[S_6] = \)

\[
\begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & \lambda_{14} & -\lambda_{25} & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{13} & -\lambda_{14} & \lambda_{25} & 0 \\
\lambda_{13} & \lambda_{13} & \lambda_{33} & 0 & 0 & 0 \\
\lambda_{14} & -\lambda_{14} & 0 & \lambda_{44} & 0 & \lambda_{25} \\
-\lambda_{25} & \lambda_{25} & 0 & 0 & \lambda_{44} & \lambda_{14} \\
0 & 0 & 0 & \lambda_{25} & \lambda_{14} & \frac{1}{2}(\lambda_{11} - \lambda_{12})
\end{bmatrix}
\]

(7 elements) \(15.221\)

The groups \(D_3, C_{3v}\) and \(D_{4d}\) have more than one symmetry axis. This has the consequence that \(\lambda_{25} = 0\) in \(15.221\). The other elements are the same:

\( \lambda[D_3] = \lambda[C_{3v}] = \lambda[D_{3d}] = \)

\[
\begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & \lambda_{14} & 0 & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{13} & -\lambda_{14} & 0 & 0 \\
\lambda_{13} & \lambda_{13} & \lambda_{33} & 0 & 0 & 0 \\
\lambda_{14} & -\lambda_{14} & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & \lambda_{14} & 0 \\
0 & 0 & 0 & 0 & \lambda_{14} & \frac{1}{2}(\lambda_{11} - \lambda_{12})
\end{bmatrix}
\]

(6 elements) \(15.222\)

Regarding the odd-order tensor properties, of the rhombohedral groups, only the groups \(C_3\) and \(C_{3v}\) have a unique direction. Hence,

\[\alpha[S_6] = \alpha[D_3] = \alpha[D_{3d}] = 0\]

\(15.223\)

\[\alpha[C_3] = \alpha[C_{3v}] = \alpha_3 e_3\]

\(15.224\)

The groups \(S_6\) and \(D_{3d}\) have inversion symmetry, and, hence, have no third-order tensor properties (sec. 15.5.7). Each of the remaining groups has non-zero third-order tensor properties of its own peculiar form:

\[\gamma[S_6] = \gamma[D_{3d}] = 0\]

\(15.225\)
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$$\gamma[C_3] = \begin{bmatrix}
\gamma_{11} & -\gamma_{22} & \gamma_{13} \\
-\gamma_{11} & \gamma_{22} & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{41} & \gamma_{51} & 0 \\
\gamma_{51} & -\gamma_{41} & 0 \\
-2\gamma_{22} & -2\gamma_{11} & 0
\end{bmatrix} \quad (6 \text{ elements}) \quad 15.226$$

$$\gamma[C_{3v}] = \begin{bmatrix}
0 & -\gamma_{22} & \gamma_{13} \\
0 & \gamma_{22} & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
0 & \gamma_{51} & 0 \\
\gamma_{51} & 0 & 0 \\
-2\gamma_{22} & 0 & 0
\end{bmatrix} \quad (4 \text{ elements}) \quad 15.227$$

$$\gamma[D_3] = \begin{bmatrix}
\gamma_{11} & 0 & 0 \\
-\gamma_{11} & 0 & 0 \\
0 & 0 & 0 \\
\gamma_{41} & 0 & 0 \\
0 & -\gamma_{41} & 0 \\
0 & 0 & -2\gamma_{11}
\end{bmatrix} \quad (2 \text{ elements}) \quad 15.228$$

15.6.5 Hexagonal

The hexagonal Bravais lattice has seven point groups, each of which has a single 6-fold axis. From Table 15.1, these are: $C_6$ (6), $C_{3h}$ (6), $C_{6h}$ (6/m), $D_6$ (622), $C_{6v}$ (6mm), $D_{3h}$ (6m2) and $D_{6h}$ (6/mmm). The common 6-fold axis has the consequence that all property matrices are contained in those for $C_6$ (sec. 15.5.6).

The second- and fourth-order tensor properties are the same for all hexagonal groups, and are determined by the 6-fold axis (sec. 15.5.8):

$$\beta[C_6] = \beta[C_{3h}] = \beta[C_{6h}] = \beta[D_6] = \beta[C_{6v}] = \beta[D_{3h}] = \beta[D_{6h}] =$$

$$= \begin{bmatrix}
\beta_{11} & 0 & 0 \\
0 & \beta_{11} & 0 \\
0 & 0 & \beta_{33}
\end{bmatrix} \quad (2 \text{ elements}) \quad 15.229$$
The hexagonal groups have a common matrix of fourth-order properties, which is just the matrix determined by \( C_6 \) (sec. 15.5.6):

\[
\lambda[C_6] = \lambda[C_{3h}] = \lambda[C_{6h}] = \lambda[D_6] = \lambda[C_{6v}] = \lambda[D_{3h}] = \lambda[D_{6h}] = \lambda(\text{hex}) =
\]

\[
\begin{bmatrix}
\lambda_{11} & \lambda_{12} & \lambda_{13} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{13} & 0 & 0 & 0 \\
\lambda_{13} & \lambda_{13} & \lambda_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{2}(\lambda_{11}-\lambda_{12})
\end{bmatrix}
\]

(5 elements) \hspace{1cm} 15.230

Regarding the odd-order tensor properties, of the hexagonal groups, only the groups \( C_6 \) and \( C_{6v} \) have a unique direction. Hence,

\[
\alpha[C_{3h}] = \alpha[C_{6h}] = \alpha[D_6] = \alpha[D_{3h}] = \alpha[D_{6h}] = 0
\]

\[
\alpha[C_6] = \alpha[C_{6v}] = \alpha_3 e_3
\]

15.231

15.232

The groups \( C_{6h} \) and \( D_{6h} \) have inversion symmetry, and, hence, have no third-order tensor properties (sec. 15.5.7). Each of the remaining groups has non-zero third-order tensor properties of its own peculiar form:

\[
\gamma[C_{6h}] = \gamma[D_{3h}] = 0
\]

\[
\gamma[C_6] = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{41} & \gamma_{51} & 0 \\
\gamma_{51} & -\gamma_{41} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

(4 elements) \hspace{1cm} 15.234

\[
\gamma[C_{6v}] = \begin{bmatrix}
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{13} \\
0 & 0 & \gamma_{33} \\
\gamma_{51} & 0 & 0 \\
\gamma_{51} & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

(3 elements) \hspace{1cm} 15.235
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\[ \gamma[C_3h] = \begin{bmatrix} 
\gamma_{11} & -\gamma_{22} & 0 \\
-\gamma_{11} & \gamma_{22} & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
-2\gamma_{22} & -2\gamma_{11} & 0 
\end{bmatrix} \quad (2 \text{ elements}) \quad 15.236 \\
\gamma[D_3h] = \begin{bmatrix} 
0 & -\gamma_{22} & 0 \\
0 & \gamma_{22} & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
-2\gamma_{22} & 0 & 0 
\end{bmatrix} \quad \gamma[D_6] = \begin{bmatrix} 
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & -\gamma_{41} & 0 
\end{bmatrix} \quad (1 \text{ element}) \quad 15.237 \\
\lambda[T] = \lambda[T_h] = \lambda[O] = \lambda[T_d] = \lambda[H] = \lambda[O_h] = \lambda(\text{cubic}) \\
= \begin{bmatrix} 
\lambda_{11} & \lambda_{12} & \lambda_{12} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{12} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{12} & \lambda_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & \lambda_{44} 
\end{bmatrix} \quad (3 \text{ elements}) \quad 15.221 \\

15.6.6 Cubic

The cubic Bravais lattice has five point groups, which are characterized by four 3-fold axes along each of the \(<111>\) directions of the unit cube. From Table 15.1, the cubic groups are: T (23), T_h (m\text{3}), O (432), T_d (43m), and O_h (m\text{3}m) (sec. 15.15.10).

The second- and fourth-order tensor properties are the same for all cubic groups, and are determined by the multiple 3-fold axes:

\[ \beta[T] = \beta[T_h] = \beta[O] = \beta[T_d] = \beta[H] = \beta(\text{cubic}) \]

\[ = \begin{bmatrix} 
\beta & 0 & 0 \\
0 & \beta & 0 \\
0 & 0 & \beta 
\end{bmatrix} \quad (1 \text{ element}) \quad 15.238 \\
\lambda[T] = \lambda[T_h] = \lambda[O] = \lambda[T_d] = \lambda[H] = \lambda(\text{cubic}) 

\[ = \begin{bmatrix} 
\lambda_{11} & \lambda_{12} & \lambda_{12} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{11} & \lambda_{12} & 0 & 0 & 0 \\
\lambda_{12} & \lambda_{12} & \lambda_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & \lambda_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \lambda_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & \lambda_{44} 
\end{bmatrix} \quad (3 \text{ elements}) \quad 15.221 \]
None of the cubic groups has a preferred direction. It follows that

$$\alpha[T] = \alpha[T_h] = \alpha[O] = \alpha[T_d] = \alpha[O_h] = \alpha(\text{cubic}) = 0$$  \hspace{1cm} (15.231)

The groups $T_h$, $O$ and $O_h$ do not permit third-order tensor properties. The groups $T$ and $T_d$ permit a third-order tensor property with a single element.

$$\gamma[T_h] = \gamma[O] = \gamma[O_h] = 0$$  \hspace{1cm} (15.232)

$$\gamma[T] = \gamma[T_d] = \begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\gamma_{41} & 0 & 0 \\
0 & \gamma_{41} & 0 \\
0 & 0 & \gamma_{41}
\end{bmatrix}$$  \hspace{1cm} (15.232)

The cubic crystals that exhibit piezoelectricity are members of the groups $T$ and $T_d$. 