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Piezoelectric Coefficients and Crystallographic Symmetry

Semën Gorfman¹ and Nan Zhang²

¹Tel Aviv University, The Department of Materials Science and Engineering, Ramat Aviv, Tel Aviv 6997801, Israel

²Xi'an Jiaotong University, School of Electronic Science and Engineering, Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, 28 West Xianning Road, Xi'an 710049, China

1.1 Introduction

Piezoelectricity is the ability of some crystals to convert mechanical and electrical energy into each other. The direct piezoelectric effect describes the linear dependence of electric polarization in a crystal on applied external mechanical stress. The converse piezoelectric effect then describes the linear dependence of the mechanical deformation in a crystal on an applied external electric field. Piezoelectricity possesses many useful applications, such as pressure sensors/actuators [1], transducers [2], piezoelectric motors [3], sonars, and microelectromechanical systems (MEMs) [4]. The market for piezoelectric devices is projected to reach US\$41.0 billion by 2027. Over the last few decades, piezoelectricity has been the subject of considerable academic research, review papers, and monographs [5, 6]. In this chapter, we introduce the anisotropy of piezoelectric coefficients and their relationship with the crystallographic symmetry of materials.

1.2 On the Anisotropy of Piezoelectricity and Its Role in the Understanding of Structures of Crystalline Materials

Incidentally, the discovery of piezoelectricity played a key role in the evolution of ideas concerning the periodic atomic structures of crystals. Notably, such periodicity was only a hypothesis at that time and was experimentally proven later in 1912 by Max von Laue [7]. Piezoelectricity presented one of those first physical properties that highlighted the anisotropy (directional dependence) of single crystals. Indeed, an isotropic material cannot be piezoelectric: the development of polarization under applied stress means that at least the opposite ends of the polarization

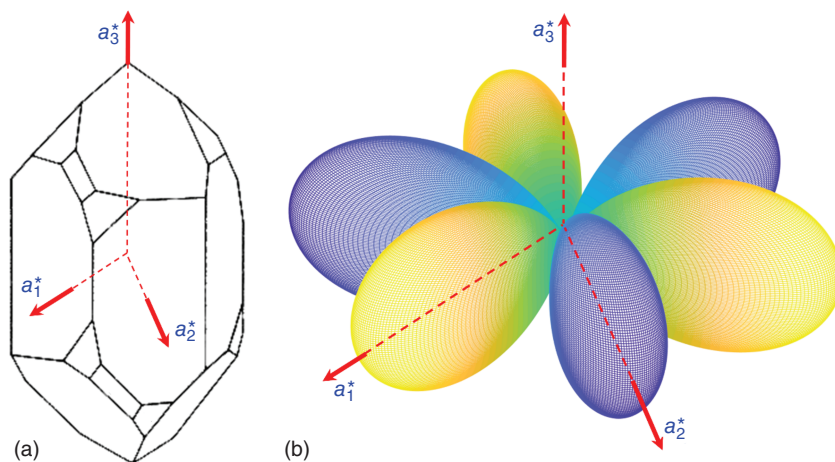


Figure 1.1 Schematic illustration of the anisotropy of piezoelectric effect in α -quartz: (a) typical natural shape of quartz crystal with three non-coplanar directions along the basis vectors of the reciprocal lattice \mathbf{a}_1^* , \mathbf{a}_2^* , \mathbf{a}_3^* , (b) the directional dependence of the magnitude of longitudinal piezoelectric coefficient (see the definition in the next paragraph). Remarkably, α -quartz develops no polarization under uniaxial strain along $\mathbf{a}_3/\mathbf{a}_3^*$ axis (parallel to the threefold symmetry axis) and does not deform under electric field parallel to $\mathbf{a}_3/\mathbf{a}_3^*$ axis. Source: Semën Gorfman.

vector are different; hence, a crystal must be anisotropic in order to be piezoelectric. The performance of a piezoelectric device strongly depends on its orientation relative to the lattice basis vectors. Figure 1.1 presents one particular example of the anisotropic longitudinal piezoelectricity in α -quartz.

In homogeneous single crystals, the anisotropy of properties must originate from the intrinsic asymmetry of atomic structures maintained over macroscopically long distances. This can only be possible if the structure is long-range-ordered. This is why anisotropy of crystals in general and piezoelectricity of crystals in particular are the key ingredients for the idea of periodicity/long-range order of crystals.

1.3 Simplified Definitions of Piezoelectric Coefficients

As for any anisotropic physical property, the description of piezoelectricity requires handling several property coefficients. There are very few classes of piezoelectric crystals where only one independent coefficient is sufficient (e.g. $\text{Bi}_{12}\text{SiO}_{20}$ [8]). However, prior to introducing the proper tensor description of the piezoelectricity, we will inspect the simplified didactical definitions and understand the *physical meaning* of piezoelectric coefficients. Specifically, we will assume that a piezoelectric device has been prepared as a parallel plate capacitor, whereas mechanical stress, electric field, polarization, and deformation appear along the plate normally only (Figure 1.2).

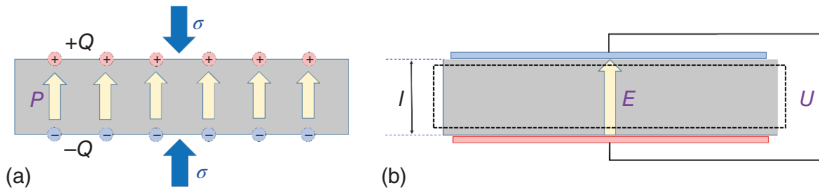


Figure 1.2 Simplified definitions of direct and converse piezoelectric effect: (a) the uniaxial stress σ is applied normally to the piezoelectric plate and causes polarization $\Delta P = d \cdot \sigma$ with the positive and negative charges emerging outside the plate face, (b) electric field is applied normally to the piezoelectric plate with the change of the plate thickness so that $x = d \cdot E$. Here, $x = \Delta l/l$. The shape of the deformed plate is shown by the dashed rectangle. Source: Semën Gorfman.

1.3.1 Direct Piezoelectric Effect

The simplified definition of direct piezoelectric effect is:

$$\Delta P = d \cdot \sigma \quad (1.1)$$

here, ΔP is the projection of the change in the polarization vector to the plate normal and σ is the pressure of the uniaxial forces normally applied to the plate. σ is positive/negative for extending/compressing forces. d is the direct piezoelectric coefficient. The units of polarization and stress are $[P] = \frac{C}{m^2}$ and $[\sigma] = \frac{N}{m^2}$; therefore, the units of the piezoelectric coefficient are $[d] = \frac{C}{N}$ or (practically used) $\frac{pC}{N} = 10^{-12} \frac{C}{N}$. This magnitude becomes more intuitive if we rewrite (1.1) as:

$$Q = d \cdot F \quad (1.2)$$

Here, $F = \sigma \cdot S$ is the magnitude of the force applied to the plate, $Q = \Delta P \cdot S$ is the electric charge outside the plate due to the increment of the polarization. S is the area of each face. According to (1.2), direct piezoelectric coefficient is the amount of electric charges accumulated outside the crystal plate per force applied to the plate. Thus, 1 N applied to a 1 pC/N piezoelectric plate will release 1 pC on the plate faces (positive on one side and negative on the opposite side).

1.3.2 Converse Piezoelectric Effect

Similarly, the simplified definition of the converse piezoelectric effect is:

$$x = d \cdot E \quad (1.3)$$

Here, E is the projection of the electric field vector to the plate normal, $x = \Delta l/l$ is the relative expansion of the plate. x is positive/negative for expansion/contraction. l is the thickness of the crystal plate. d is the converse piezoelectric coefficient. The units of converse piezoelectric coefficient are $[d] = \frac{m}{V}$ or, in practical terms, $\frac{pm}{V} = 10^{-12} \frac{m}{V}$. To get an impression about this unit, we can reformulate (1.3) as:

$$\Delta l = d \cdot U \quad (1.4)$$

Here, $U = E \cdot l$ is the voltage falling between the faces of the plate. Thus, converse piezoelectric coefficient is the elongation of the plate per applied voltage. For

example, the application of 1000 V to a 1 pm/V piezoelectric crystal plate expands or shrinks by 1 nm.

1.3.3 On the Equivalence of Direct and Converse Piezoelectric Coefficients

It can be easily shown that the units of $\frac{C}{N}$ are equivalent to $\frac{m}{V}$. This equivalence raises the question of whether there exists any relationship between the direct and converse piezoelectric coefficients. Indeed, these coefficients are not just related; if defined exactly as in Eqs. (1.1) and (1.3), they are *numerically equal to each other*. This is the reason why the same symbol d for the direct and converse piezoelectric coefficients can be retained. However, only for this paragraph, we will temporarily introduce the notations $d^{(d)}$ and $d^{(c)}$ for the direct and converse piezoelectric coefficients, correspondingly.

Here, we will look back at Lippmann's original theory [9] for the longitudinal direct Eq. (1.1) and converse Eq. (1.3) effects only. The interested reader may refer to Nye's book [10] for a comprehensive description of the matter. We assume that a small variation of external mechanical stress, $d\sigma$, and electric field, dE , results in the increments of mechanical strain, dx , and polarization, dP . The first law of thermodynamics expresses the conservation of energy during the electric polarization and mechanical deformation of the material as:

$$dU = \delta A + \delta Q \quad (1.5)$$

Here, dU is the change in the internal energy of the crystal, δQ is the amount of energy received by the crystal in the form of *heat*, δA is the amount of energy received by the crystal in the form of *work* by the external electric ($\delta A_E = E \cdot dP$) and mechanical ($\delta A_M = \sigma \cdot dx$) forces [10]. All the quantities are expressed per unit volume of the material. Assuming no heat exchange with the environment ($\delta Q = 0$ otherwise, further caloric physical properties would be involved), we can rewrite (1.5) as:

$$dU = E \cdot dP + \sigma \cdot dx \quad (1.6)$$

Introducing $\Phi = U - E \cdot P - \sigma \cdot x$, we can rewrite (1.6)

$$d\Phi = -P \cdot dE - x \cdot d\sigma \quad (1.7)$$

Because Φ is a full differential, the polarization and strain can be expressed as partial derivatives:

$$P = -\frac{\partial \Phi}{\partial E}, x = -\frac{\partial \Phi}{\partial \sigma} \quad (1.8)$$

On the other hand, equations (1.1) and (1.3) can also be rewritten in the form of partial derivatives, where $d^{(d)} = \frac{\partial P}{\partial \sigma}$ represents the direct piezoelectric effect and $d^{(c)} = \frac{\partial x}{\partial E}$ represents the converse piezoelectric effect. The equivalence between $d^{(d)}$ and $d^{(c)}$ follows immediately as:

$$d^{(d)} = -\frac{\partial^2 \Phi}{\partial \sigma \partial E} \text{ and } d^{(c)} = -\frac{\partial^2 \Phi}{\partial E \partial \sigma} \quad (1.9)$$

Table 1.1 Typical orders of magnitude of piezoelectric coefficients.

Material	d (pC/N)	Refs.	Material	d (pC/N)	References
α -quartz (SiO ₂)	2	[11]	BaTiO ₃	150	[12]
PVDF	20	[13]	PbZr _{0.52} Ti _{0.48} O ₃ (PZT ceramics)	200–400	[14]
Al _{0.67} Sc _{0.33} N	26	[15]	PMN–PT single crystals	2000	[16]
Bi ₁₂ SiO ₂₀	40	[8]	Sm-doped PMN–PT single crystals	3400–4100	[17]

This is because the second derivative does not depend on the order of variables.

This remarkable feature, appearing in the form of “conjugated” pairs, also holds for many other properties. For example, pyroelectricity is conjugated with the electrocaloric effect and thermal expansion is conjugated with the piezocaloric effect.

1.3.4 Typical Values of Piezoelectric Coefficients

Following our understanding of the piezoelectric coefficient units, it is worth observing their typical values. Table 1.1 lists the piezoelectric coefficients of a few selected materials. Notably, the table here is merely for the purpose of obtaining an impression regarding the typical magnitude of piezoelectric coefficients. As will be discussed in the following chapters, piezoelectric coefficients are described by tensors, and each material may have few coefficients that may differ from one another by an order of magnitude. Still, it is clear from the table that piezoelectric coefficients of most known materials are below 2000 pC/N. Only in so-called relaxor ferroelectric single crystals of PbMg_{1/3}Nb_{2/3}O₃–PbTiO₃ (PMN–PT) [16, 18] and their derivatives [17], piezoelectric coefficients may exceed such high values.

1.4 Description of Piezoelectricity by Third-rank Tensor

1.4.1 Tensor of Piezoelectric Coefficients

Piezoelectricity of single crystals must be described by tensors. For the direct piezoelectric effect:

$$\Delta P_k = d_{kij} \sigma_{ij} \quad (1.10)$$

Here, ΔP_k represents the components of the change in the polarization vector, σ_{ij} represents the components of the second-rank stress tensor, and d_{kij} represents the components of the third-rank tensor of direct piezoelectric coefficients. More information about the meaning of the stress and strain tensors can be found in [10, 19, 20]. The indices i, j, k run between 1 and 3, and the Einstein summation rule applies to

every repeated index (i and j in this case). The vector and tensor components are expressed as relative to a Cartesian coordinate system $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$. Later, we will elaborate on the crucial role of this Cartesian system.

According to Eq. (1.10), d_{kij} describes the polarization increment along the Cartesian \mathbf{e}_k axis due to the force applied along the \mathbf{e}_i to the surface, which is normal to \mathbf{e}_j . For example, if the piezoelectric coefficient d_{233} is nonzero, then the polarization along the \mathbf{e}_2 axis will develop in response to the *tensile* mechanical stress on the face, normal to \mathbf{e}_3 . If, for example, the piezoelectric coefficient d_{123} is nonzero, then the polarization along the \mathbf{e}_1 will develop due to the *shearing* stress on the face normal to the \mathbf{e}_3 but in the direction of \mathbf{e}_2 .

For the converse piezoelectric effect:

$$x_{ij} = d_{kij}E_k \quad (1.11)$$

Here, x_{ij} represents the components of the second-rank strain tensor and E_k represents the components of the electric field vector. In this case, the Einstein summation applies over the repeated index k . According to (1.11), the converse piezoelectric coefficient, d_{kij} , describes the strain component, x_{ij} , in response to the electric field along the Cartesian \mathbf{e}_k axis. For example, the converse piezoelectric coefficient d_{233} stands for the *elongation* along the \mathbf{e}_3 in response to an electric field applied along \mathbf{e}_2 . The converse piezoelectric coefficient d_{123} describes the *shear* strain in the $\mathbf{e}_2\mathbf{e}_3$ plane due to electric field along \mathbf{e}_1 .

The thermodynamics of the piezoelectric effect remains similar to the simplified case considered earlier in this chapter. Specifically, if expressed in the same Cartesian coordinate system, *all* the components of the direct piezoelectric tensor are numerically equal to those for the converse piezoelectric tensor. However, it is crucial that the tensor components are defined exactly as in (1.10) and (1.11), i.e. the first index is “electric,” while the second and the third indices are “mechanical.”

1.4.2 Voigt/Matrix Notation for Piezoelectric Coefficient

Any third-rank tensor has a maximum of $27 = 3^3$ independent components. However, their real number is smaller because of the symmetry. There are two types of symmetries: the first is *physical* and appears as a consequence of energy, charge, and momentum conservation laws. The second is *crystallographic*, which is inherited from the geometrical symmetry of crystal structures and expressed in the form of the Neumann principle. For piezoelectricity, the *physical* symmetry results in the invariance with respect to the interchange of “mechanical” indices:

$$d_{kij} = d_{kji} \quad (1.12)$$

Equation (1.12) is valid for any piezoelectric material, regardless of which atomic structure it contains. This property is intuitively related to similar symmetry properties of the strain and stress tensors $x_{ij} = x_{ji}$, $\sigma_{ij} = \sigma_{ji}$. This symmetry means that the pair ij may cover six different variants: 11, 22, 33, 23 \equiv 32, 13 \equiv 31, 12 \equiv 21. For writing compactness reasons, a special indexing scheme is commonly used (first introduced

Table 1.2 The substitution of “mechanical” indices using Voigt notation.

ij (tensor)	11	22	33	23 \equiv 32	13 \equiv 31	12 \equiv 21
m (Voigt)	1	2	3	4	5	6
Strain, $x_m =$	x_{11}	x_{22}	x_{33}	$2x_{23}$	$2x_{13}$	$2x_{12}$
Stress, $\sigma_m =$	σ_{11}	σ_{22}	σ_{33}	σ_{23}	σ_{13}	σ_{12}
Piezo, $d_{km} =$	d_{k11}	d_{k22}	d_{k33}	$2d_{k23}$	$2d_{k13}$	$2d_{k12}$

The first row of the table shows six different pairs of indices ij . The second row shows the Voigt index m , corresponding to each pair. The third, fourth, and fifth rows show the relationship between the components of the strain, stress, and piezoelectric tensors in Voigt and index notations.

by Voigt [21]). The pair ij can be replaced by a single index $m = 1 \dots 6$, according to Table 1.2.

Such substitution is used for strain and stress tensors too $x_m \leftarrow x_{ij}$ and $\sigma_m \leftarrow \sigma_{ij}$, and is shown in the next two rows of Table 1.2. The Voigt substitution of indices for the piezoelectric coefficients follows as $d_{km} \leftarrow d_{kij}$, where $ij = 1 \dots 3$ and $m = 1 \dots 6$, and is shown in the last row of the same table. Then, equations (1.10) and (1.11) can be rewritten in a shorter form:

$$P_k = d_{km} \sigma_m \quad (1.13)$$

$$x_m = d_{km} E_k \quad (1.14)$$

The piezoelectric coefficients are written in the form of 3×6 matrix:

$$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} = \begin{pmatrix} d_{111} & d_{122} & d_{133} & 2d_{123} & 2d_{113} & 2d_{112} \\ d_{211} & d_{222} & d_{233} & 2d_{223} & 2d_{213} & 2d_{212} \\ d_{311} & d_{322} & d_{333} & 2d_{323} & 2d_{313} & 2d_{312} \end{pmatrix} \quad (1.15)$$

The maximum number of independent piezoelectric coefficients is 18. This number can be reduced if we consider the geometrical symmetry of the crystal or medium.

1.5 Symmetry Considerations

1.5.1 Neumann Principle for the Piezoelectric Effect

As for any physical property, the Neumann principle [22] holds for the piezoelectricity as well. This principle states that: “if a crystal is invariant with respect to certain symmetry operations any of its physical properties must also be invariant with respect to the same symmetry operations.” In other words, the components of the piezoelectric tensor should be invariant with respect to the transformation between two symmetry-equivalent Cartesian coordinate systems:

$$d'_{ijk} = d_{ijk} \quad (1.16)$$

Here, d'_{ijk} represents the components of the piezoelectric coefficient tensor relative to the new Cartesian coordinate system $\mathbf{e}'_1, \mathbf{e}'_2, \mathbf{e}'_3$, which is symmetry-equivalent to the original Cartesian coordinate system $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$. Allow us to introduce the matrix $[T]$, which enables the transformation between these coordinate systems using the following formal matrix equation:

$$(\mathbf{e}_1 \ \mathbf{e}_2 \ \mathbf{e}_3) = (\mathbf{e}'_1 \ \mathbf{e}'_2 \ \mathbf{e}'_3) \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix}, \text{ or } \mathbf{e}_i = \mathbf{e}'_k T_{ki} \quad (1.17)$$

Here, the columns of the transformation matrix represent the vectors' coordinates of the old coordinate system \mathbf{e}_i relative to the new coordinate system \mathbf{e}'_i . It can be shown [10, 20] that the transformation of the tensor components from the coordinate system \mathbf{e}_i to the coordinate system \mathbf{e}'_i is:

$$d'_{ijk} = T_{ii_1} T_{jj_1} T_{kk_1} d_{i_1 j_1 k_1} \quad (1.18)$$

If $[T]$ describes the symmetry operation, then

$$d_{ijk} = T_{ii_1} T_{jj_1} T_{kk_1} d_{i_1 j_1 k_1} \quad (1.19)$$

It is important to note that equations (1.18) and (1.19) can be applied only to the full tensor form. Obviously, the Voigt 3×6 matrix cannot be directly used here. In the following, we will consider how the presence of one or another symmetry operation in the structure of a crystal reduces the number of piezoelectric coefficients.

Example 1.1 Center of Inversion

Let us assume that a crystal structure is centrosymmetric. The following transformation matrix relates two symmetry-equivalent Cartesian coordinate systems:

$$[T] = \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \text{ or } T_{ij} = -\delta_{ij} \quad (1.20)$$

Substituting (1.20) into (1.19) and using the property of the Kronecker symbol, $\delta_{ij} x_j = x_i$, we obtain

$$d_{ijk} = (-1)^3 d_{ijk} \text{ or equivalently } d_{ijk} = 0 \quad (1.21)$$

In other words, all piezoelectric coefficients are zero, so that centrosymmetric material cannot be piezoelectric. This property instantly removes the crystals of 11 centrosymmetric (Laue) classes from the list of potential piezoelectric materials. Conversely, observing piezoelectricity in a given material indicates that it is non-centrosymmetric. This ability to identify the absence of the inversion center is useful in X-ray structure analysis [23, 24].

Example 1.2 Mirror Plane

Let us assume that the structure of a crystal has a mirror plane perpendicular to \mathbf{e}_3 . Thus, the following transformation matrix relates two symmetry-equivalent

Cartesian coordinate systems:

$$[T] = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix} \quad (1.22)$$

Substituting (1.22) in (1.19), we can rewrite (1.19) as:

$$d_{ijk} = (-1)^n d_{ijk} \quad (1.23)$$

Here, $n \leq 3$ is the number of cases where any of the three indices is equal 3 (e.g. $n = 0$ for d_{122} , $n = 1$ for d_{123} , or $n = 2$ for d_{323}). Accordingly, the tensor of piezoelectric coefficients in the matrix (Voigt notation) will take the form:

$$[d] = \begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & 0 & d_{26} \\ 0 & 0 & 0 & d_{34} & d_{35} & 0 \end{pmatrix} \quad (1.24)$$

with 10 independent piezoelectric coefficients.

1.5.2 The Choice of the Cartesian Coordinate System

According to (1.18), the values of piezoelectric coefficients depend on the choice of the coordinate system. Therefore, every time when piezoelectric coefficients of a material are reported or retrieved from a literature, it is crucial to know how the coordinate system is chosen. All physical properties are described in Cartesian coordinate systems and are commonly referred to as the crystal physical coordinate system. It is imperative to understand that this system is not related to the experimental setup but rather to the basis vectors of the crystal itself.

For single crystals, it is convenient to relate the axes of the crystal's physical coordinate system $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ to the axes of the crystallographic, $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and the reciprocal crystallographic coordinate systems $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$. The basis vectors of the reciprocal coordinate system are related to that of the crystallographic coordinate system by the scalar products $\mathbf{a}_i \mathbf{a}_j^* = \delta_{ij}$. Table 1.3 summarizes these three types of coordinate systems, including their metric (the lengths and the angles between the basis vectors), their usage, and their conventional choice. The standard relationships between the crystal physical and crystallographic coordinate systems are given, e.g. in [35]. Nowadays, it is common to define the crystal physical coordinate system as in Figure 1.3a, so that $\mathbf{e}_2 // \mathbf{a}_2$, $\mathbf{e}_1 // \mathbf{a}_1^*$, and $\mathbf{e}_3 = [\mathbf{e}_1 \times \mathbf{e}_2]$. Nonetheless, for the hexagonal cell setting case, it is more common to define the crystal physical coordinate system as $\mathbf{e}_3 // \mathbf{a}_3$, $\mathbf{e}_1 // \mathbf{a}_1$, and $\mathbf{e}_2 = [\mathbf{e}_1 \times \mathbf{e}_3]$. In any case, we discourage the reader from making a blind assumption of one or another convention used and recommend a critical inspection of every individual case. The cases of trigonal crystals are particularly difficult since the crystallographic coordinate system $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ itself has two "standard" cell settings: primitive ($\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$ is parallel to the threefold axis) or R -centered (\mathbf{a}_3 is parallel to the threefold axis).

Table 1.3 Coordinate systems used for the description of crystal structures and properties.

Coordinate system	Crystallographic	Reciprocal crystallographic	Crystal physical
Designation for the basis vectors	$\mathbf{a}, \mathbf{b}, \mathbf{c}$ or $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$	$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ or $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$	$\mathbf{x}, \mathbf{y}, \mathbf{z}$ or $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$
Metric	Depends on the crystal system	Depends on the crystal system	Cartesian $\mathbf{e}_i \mathbf{e}_j = \delta_{ij}$
Used for	Description of periodic structures of crystals	Description of diffraction pattern and natural shapes of crystalline polyhedrons	Physical properties
The conventional choice, orientation of basis vectors	Aligned to certain symmetry elements of the crystal lattice	Related to the crystallographic coordinate system	Attached to the crystallographic coordinate system

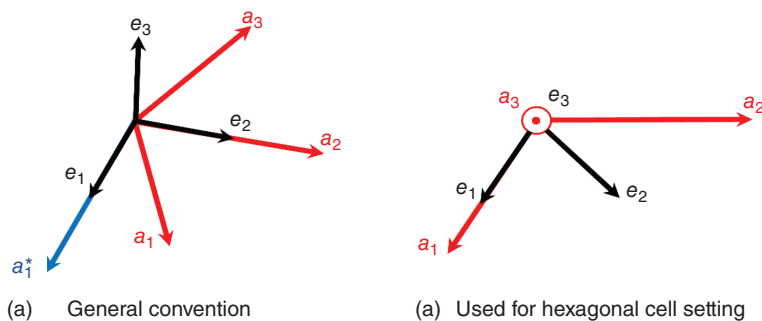


Figure 1.3 Two conventional choices of crystal physical Cartesian coordinate system $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ relative to the crystallographic $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$: (a) general three-dimensional case where $\mathbf{e}_2 \parallel \mathbf{a}_2$ and $\mathbf{e}_1 \parallel \mathbf{a}_1^*$, (b) special convention, which is frequently used for hexagonal lattice setting (in hexagonal and trigonal crystal classes), where $\mathbf{e}_1 \parallel \mathbf{a}_1$ and $\mathbf{e}_3 \parallel \mathbf{a}_3$. Note that special attention should be paid to the trigonal crystal classes $\bar{3}2$ and $3m$ (where the two standard orientations of the crystallographic coordinate system itself are possible). Source: Semën Gorfman.

1.5.3 How to Use the Space Symmetry Group Information to Find the List of Independent Piezoelectric Coefficients

The transformation of the coordinate systems, keeping the crystal structure invariant, is contained in the information regarding the type of a space symmetry group. There are 230 types of space symmetry groups describing *three-dimensional periodic crystal structures*, all of which are listed in the International Tables for Crystallography, Volume A [25]. Each symmetry operation includes the “rotation” and “translation” parts. The translation part is irrelevant for macroscopic physical properties: for example, a “screw” axis or “glide” plane acts as a simple rotation axis and a mirror

Table 1.4 The shapes of piezoelectric tensors for 20 piezoelectric crystal classes.

Crystal system	Crystal class	Piezoelectric tensor (Number of independent coefficients)	Conventional choice of Cartesian coordinate system
Triclinic	1	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \quad (18)$	
Monoclinic	2	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix} \quad (8)$	
	m	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{pmatrix} \quad (10)$	
Orthorhombic	222	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (3)$	
	mm2	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (5)$	
Tetragonal	4mm	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (3)$	

(Continued)

Table 1.4 (Continued)

Crystal system	Crystal class	Piezoelectric tensor (Number of independent coefficients)	Conventional choice of Cartesian coordinate system
	422	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (1)$	
	$\bar{4}2m$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (2)$	
	4	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (4)$	
	$\bar{4}$	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & -d_{15} & d_{14} & 0 \\ d_{31} & -d_{31} & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (4)$	
Trigonal	3	$\begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (6)$	
	32	$\begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (2)$	

(Continued)

Table 1.4 (Continued)

	$3m$	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (4)$	
Hexagonal	$6mm$	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (3)$	
	622	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (1)$	
	$\bar{6}m2$	$\begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (1)$	
	6	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \quad (4)$	
	$\bar{6}$	$\begin{pmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (2)$	
Cubic	$\bar{4}32$ 23	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{pmatrix} \quad (1)$	<p>The axes of Cartesian coordinate system are parallel to a_1, a_2, a_3</p>

plane for the physical properties. If all the “translation” components of the symmetry operations are removed, then the 230 types of space symmetry groups are reduced to 32 types of point symmetry groups. These types of groups are called crystal classes. 11 of 32 crystal classes, known as Laue classes, and are centrosymmetric, ruling out piezoelectricity straight away. For the remaining 21 non-centrosymmetric crystal classes, the piezoelectricity must be analyzed according to the algorithm outlined previously. Here, we restrict ourselves to the derivation of the piezoelectric coefficients for all possible non-centrosymmetric crystal classes. The interested reader may consult Nye’s dedicated book[12].

1.5.4 The Shapes of Piezoelectric Tensors for Different Crystal Classes

Table 1.4 shows the shapes of tensors of piezoelectric coefficients for 20 piezoelectric crystal classes. The only non-centrosymmetric crystal class where all the piezoelectric coefficients vanish is 432. The first column of Table 1.4 lists the crystal system (crystal system is the symmetry group of the infinite crystal lattice without the unit cell). The second column shows the International Hermann–Mauguin symbol for the crystal classes. The last column adds some information about the assumed orientation of the crystal’s physical coordinate system relative to the crystallographic axes. It involves the drawing of the symmetry diagram so that the orientation of the crystallographic and crystal physical coordinate axes can be related to the symmetry elements of the crystal.

Some additional comments are in place here regarding the choice of the crystal physical Cartesian coordinate system. The following transformation of the Cartesian coordinate system does affect the numerical values of the “independent” piezoelectric coefficients without changing the shape of the piezoelectric tensor itself.

- For the crystal class 1: any change of the coordinate system.
- For the crystal classes 2,3, 4, 4, 6, $\bar{6}$, $4mm$, $6mm$: rotation around the symmetry axis by an arbitrary angle.
- For the crystal class m : rotation around the normal to the mirror plane.
- For all crystal classes: inversion of the coordinate axes will invert all the piezoelectric coefficients.

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