Cartesian coordinate systems:

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

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

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

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:

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

with 10 independent piezoelectric coefficients.

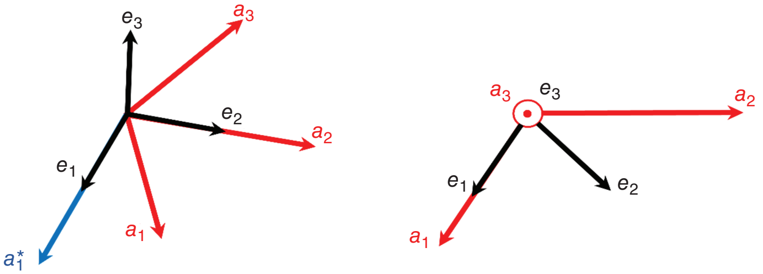
1.5.2 The Choice of the Cartesian Coordinate System

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 $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$ to the axes of the crystallographic, $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ and the reciprocal crystallographic coordinate systems $\boldsymbol{a}_1^*, \boldsymbol{a}_2^*, \boldsymbol{a}_3^*$. The basis vectors of the reciprocal coordinate system are related to that of the crystallographic coordinate system by the scalar products $\boldsymbol{a}_i \boldsymbol{a}_j^* = \delta_{ij}$. 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 $\boldsymbol{e}_2 // \boldsymbol{a}_2$, $\boldsymbol{e}_1 // \boldsymbol{a}_1^*$, and $\boldsymbol{e}_3 = [\boldsymbol{e}_1 \times \boldsymbol{e}_2]$. Nonetheless, for the hexagonal cell setting case, it is more common to define the crystal physical coordinate system as $\boldsymbol{e}_3 // \boldsymbol{a}_3$, $\boldsymbol{e}_1 // \boldsymbol{a}_1$, and $\boldsymbol{e}_1 = [\boldsymbol{e}_2 \times \boldsymbol{e}_3]$. 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 $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ itself has two "standard" cell settings: primitive ($\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3$ is parallel to the threefold axis) or *R*-centered ($\boldsymbol{a}_3$ 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	$\boldsymbol{a},\boldsymbol{b},\boldsymbol{c}$ or $\boldsymbol{a}_1,\boldsymbol{a}_2,\boldsymbol{a}_3$	$\boldsymbol{a}^*,\boldsymbol{b}^*,\boldsymbol{c}^*$ or $\boldsymbol{a}_1^*, \boldsymbol{a}_2^*, \boldsymbol{a}_3^*$	$\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{z}$ or $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3$
Metric	Depends on the crystal system	Depends on the crystal system	Cartesian $\boldsymbol{e}_i\boldsymbol{e}_j = \delta_{ij}$
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



(a) General convention

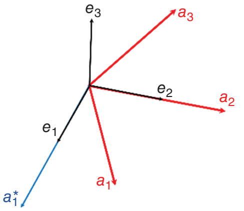
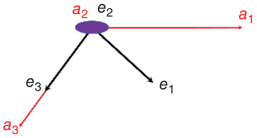
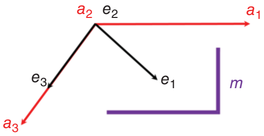
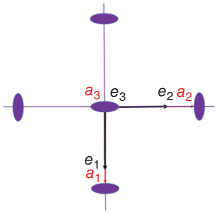
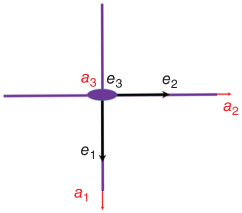
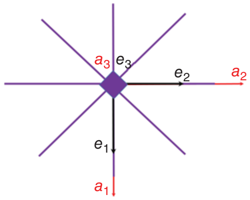
(a) Used for hexagonal cell setting

Figure 1.3 Two conventional choices of crystal physical Cartesian coordinate system $\boldsymbol{e}_1$, $\boldsymbol{e}_2$, $\boldsymbol{e}_3$ relative to the crystallographic $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$: (a) general three-dimensional case where $\boldsymbol{e}_2 \parallel \boldsymbol{a}_2$ and $\boldsymbol{e}_1 \parallel \boldsymbol{a}_1^*$, (b) special convention, which is frequently used for hexagonal lattice setting (in hexagonal and trigonal crystal classes), where $\boldsymbol{e}_1 \parallel \boldsymbol{a}_1$ and $\boldsymbol{e}_3 \parallel \boldsymbol{a}_3$. Note that special attention should be paid to the trigonal crystal classes 32 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

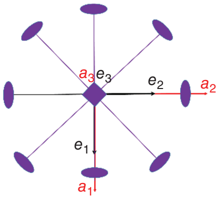
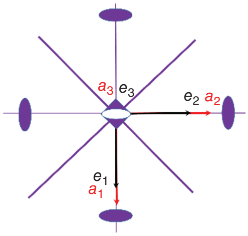
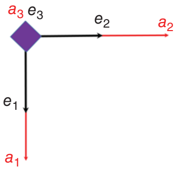
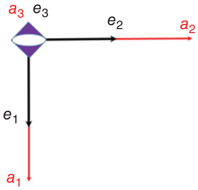
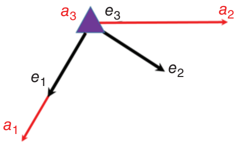
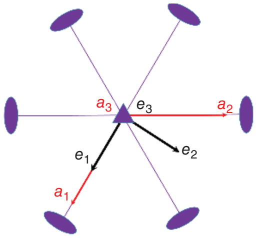
The transformation of the coordinate systems, keeping the crystal structure invariant, is contained in the information regarding the type of a space symmetry group. There are 230 types of space symmetry groups describing *three-dimensional periodic crystal structures*, all of which are listed in the 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	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix}$ (18)	
Monoclinic	2	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix}$ (8)	
	m	$\begin{pmatrix} d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & d_{26} \\ d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0 \end{pmatrix}$ (10)	
Orthorhombic	222	$\begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}$ (3)	
	*mm*2	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}$ (5)	
Tetragonal	4*mm*	$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$ (3)	

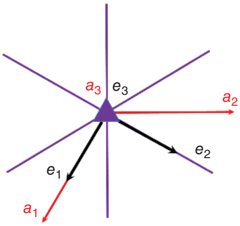
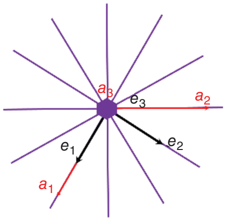
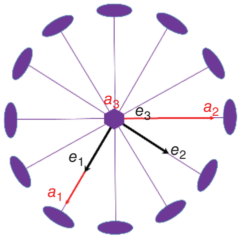
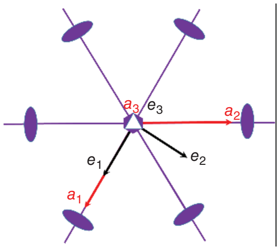
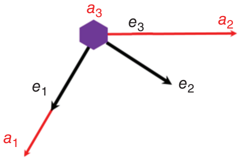
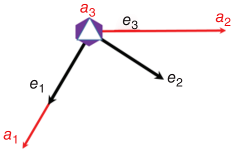
(Continued)

Table 1.4 (Continued)

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

(Continued)

Table 1.4 (Continued)

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

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, $\overline{4}$, 6, $\overline{6}$, 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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