Piezoelectricity: Old Effect, New Thrusts

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Abstract—A tutorial synopsis of the piezoelectric effect is presented in the context of its history, traditional uses, and relation to crystal symmetry. Associated effects are briefly noted. Future prospects, particularly in the area of microelectromechanical systems/structures (MEMS) are discussed.

I. INTRODUCTION

PIEZOELECTRICITY was discovered by the brothers Curie in 1880. They found that, in certain materials such as zincblende, tourmaline, cane sugar, topaz, and quartz, mechanical stresses were accompanied by the production of electric surface charges. The following year, Lippmann, from thermodynamic considerations, predicted the converse effect: an imposed voltage produces mechanical deformations. The name "piezo" derives from the Greek, meaning "to press;" in more modern terminology, we say that the effect couples electric and elastic phenomena, as discussed below[1] [1].

The piezoelectric effect remained a curiosity until the early 1920's when its presence in quartz was utilized to realize crystal resonators for the stabilization of oscillators, thereby launching the field of frequency control [2]. With the introduction of quartz control, timekeeping moved from the sun and stars to small, man-made sources that exceeded astronomy-based references in stability. Since then, devices based on piezoelectricity have expanded dramatically in application. The quartz resonator has continued to evolve to become a device capable today of precision one million times greater than the original and serves as well as the "flywheel" in atomic frequency standards, which make frequency the most accurate entity known [3].

Piezoelectric devices are additionally used as transducers in applications from telephone speakers to sonar arrays; a newer and rapidly burgeoning area of utilization is the integral incorporation of mechanical actuation and sensing microstructures into electronic chips. These microelectromechanical structures/systems (MEMS) promise signal sensing, processing, and outputting features unattainable by exclusively electronic/photonic means. In many traditional applications, applied voltages conform to the norms for electronic circuits; accompanying mechanical displacements are then usually nanometers or less. Newer configurations available today

[1] It is interesting to note that, in the 19th century, when mechanics reigned supreme, luminaries like Kelvin and Maxwell "explained" light phenomena in terms of mechanical models such as coupled gyroscopes. Today, electromagnetism and electronics reign, and the art of mechanics seems in many respects an all-but-forgotten discipline. To present the workings of modern mechanical structures such as microactuators to the "real world," we now make use of equivalent electrical circuits!

for actuators often have much larger amplitudes at comparable voltages. Key to MEMS exploitation is the piezoelectric cantilever bimorph, consisting of a two-layer laminate, fashioned like a subminiature diving board [4]–[6]. Usually the bimorph substrate is silicon, with thin patches of piezoelectrically active films of materials such as aluminum nitride or zinc oxide to drive the structure into flexural motion. This bending mode delivers the greatest possible displacement for a given driving voltage, so, for example, a proof mass located at the "diver's" position provides the greatest sensitivity to accelerations; lenses/mirrors so situated yield maximal photonic excursions[2] [7], while FET gates or optical waveguides at the support end experience mechanical stress maxima for modulating the electronic or optical variables. The bimorph MEMS devices provide otherwise unavailable capabilities and require piezoelectricity as the transduction mechanism. An alternative configuration is the laminated plate, where aluminum nitride or zinc oxide thin-film layers drive silicon plates in resonant thickness modes for integrated frequency control devices [8].

One of the most appealing aspects of piezoelectricity for modern applications is the compelling immediacy and simplicity of the transduction mechanism. Micro and nanoelectronics are built upon the behavior of charged species subjected to electric fields; the extreme miniaturization of these structures is owed in large measure to their ability to take on a capacitor-like form [9]. Bulky inductors are banished and done without, and thin, planar electrodes introduce the electric fields to operate the circuits. These fields also provide the forces required to drive mechanical motions in a piezoelectric device. Elastic field/mechanical considerations are therefore incorporated into the operations of modern electronic components in a clean, efficient, and very direct manner, by making use of the voltages resident on the chips, via the piezo-effect.

II. MATERIAL CONSTITUTIVE EQUATIONS

Formally stated, piezoelectricity couples the mechanical stress (T) and strain (S) fields with the electric intensity (E) and displacement (D) fields. Depending on variable choice, four sets of material constitutive relations are defined for the linear case of insulating dielectric materials; these are, in compressed matrix form [10]–[12]

$$[T] = [c^E][S] - [e]'[E] \tag{1a}$$

$$[D] = [e][S] + [\varepsilon^S][E] \tag{1b}$$

$$[T] = [c^D][S] - [h]'[D] \tag{2a}$$

[2] The mode shape of the resonant bimorph cantilever may be altered by frequency adjustments; two states are particularly useful in photonic applications: pure translation of the tip, without rotation, and pure rotation of the tip, without translation.
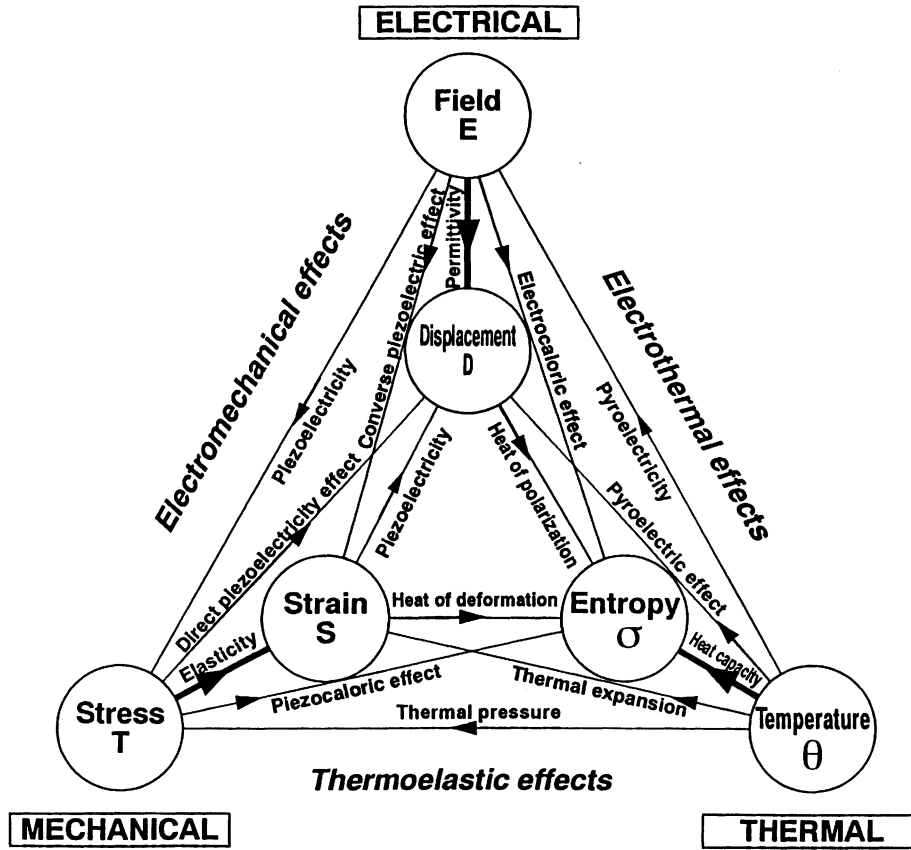
Fig. 1. Couplings between electrical, mechanical, and thermal fields.

$$[E] = -[h][S] + [\beta^S][D] \tag{2b}$$
$$[S] = [s^E][T] + [d]'[E] \tag{3a}$$
$$[D] = [d][T] + [\varepsilon^T][E] \tag{3b}$$
$$[S] = [s^D][T] + [g]'[D] \tag{4a}$$
$$[E] = -[g][T] + [\beta^T][D]. \tag{4b}$$

Because the electric variables $[E]$ and $[D]$ are tensors of rank one (i.e., 3-D vectors), and the mechanical variables $[T]$ and $[S]$ are tensors of rank two which have been converted to six-dimensional vectors, $[c^E], [c^D]$ and $[s^E], [s^D]$ are (6 × 6) symmetric matrices representing the elastic stiffnesses and compliances at constant E and D; $[\varepsilon^S], [\varepsilon^T]$ and $[\beta^S], [\beta^T]$ are symmetric (3 × 3) dielectric permittivity and impermeability matrices at constant S and T, while $[e], [h], [d]$, and $[g]$ are (3 × 6) piezoelectric matrices. A prime denotes transpose. Alternative formulations, using the electric polarization vector $[P]$ in place of $[D]$, are sometimes used, particularly in electrooptic applications; the piezoelectric polarization $[a]$ and $[b]$ matrices are then used [13]–[16].

The four equivalent pairs of material constitutive equations (1)–(4) differ in their combinations of independent and dependent variables; the material constants used in the sets are interrelated. The relations are derived in Appendix I. Appendix II provides the units of the field and matter variables.

The material constitutive relations given may be further broadened to include couplings to thermal, magnetic, and other fields in what may be called a Heckmann diagram [17]. Fig. 1 depicts the phenomenology arising from the mutual couplings among the electric, elastic, and thermal fields. The outer quantities are the thermodynamic intensive variables (generalized forces); the inner quantities are the extensive variables (generalized displacements) [2], [17]–[19].

Thurston has extended the Heckmann diagram to cover relations between mechanical, electrical (microwave) and optical variables [20]. These are indicated in Fig. 2.

Piezoelectricity is a linear effect; reversal of the electric field reverses the mechanical deformation. Conditions for its existence in crystals are given below. Electrostriction, on the other hand, exists in all dielectric solids. It is a deformation quadratic in the polarization field [21], [22]. Biased electrostriction, where small field variations are superimposed on a constant component, is phenomenologically equivalent to linear piezoelectricity; this artifice may be used with nonpiezoelectric crystals such as silicon, but the coupling depends upon the bias and is often not large.

Resonance measurements on thickness mode plate vibrators and pulse-echo (transit-time) measurements determine values for the matrix elements $[c^E]$, $[e]$, and $[\varepsilon^S]$ from which the other material parameter sets may be computed if desired. Resonance measurements on low frequency bar and rod specimens lead alternatively to determination of the $[s^E]$, $[d]$, and $[\varepsilon^T]$ set [23]–[25]. These dynamic techniques are both more accurate and more precise than static measurements.
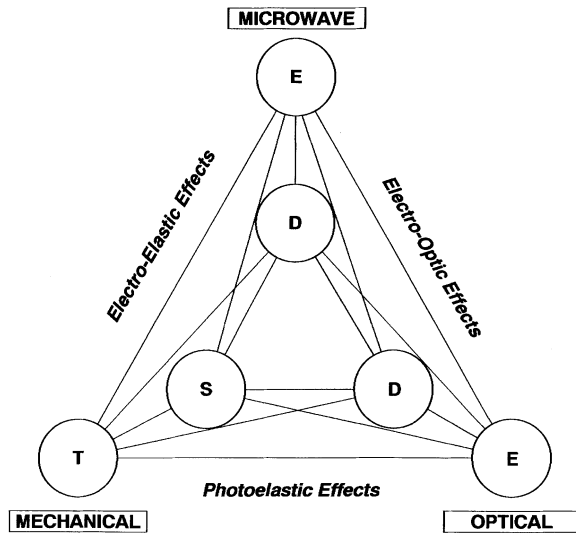
Fig. 2. Couplings between mechanical, electrical (microwave), and optical fields [20].

III. ELECTROMECHANICAL COUPLING FACTORS

Electromechanical coupling factors k $(0 \leq k \leq 1)$ are dimensionless measures of efficacy of piezoelectric transduction and are far more important than the piezoelectric constants taken by themselves. They appear in considerations of bandwidth and insertion loss in transducers and signal processing devices, in location and spacing of critical frequencies of resonators, and in electrical/mechanical energy conversion efficiency in actuators. For high frequency plate resonators, coupling factors have the generic form $k = e/\sqrt{(\varepsilon c)}$; for low frequency bar and rod vibrators, the form becomes $k = d/\sqrt{(\varepsilon s)}$; alternative forms using the "h" and "g" piezoparameters are used as well [19], [25]. These quantities are also called piezo-coupling factors; representative values are listed in Table I. Additional material values are contained in [26]–[33].

IV. THE PIEZOELECTRIC EFFECT AND CRYSTAL SYMMETRY [34]–[38]

Crystallographers have, over the centuries, cataloged the various geometrical arrangements of atoms that can exist in crystal structures. The starting point is the unit cell, which normally contains the smallest grouping of atoms representing the chemical formula of the substance. In a crystal, this cell, with its particular size, shape, and arrangement within it of atoms, is repeated over and over in three dimensions. The result is an orderly stacking of cells that has translational invariance, meaning that moving one's observation point by an integral number of cells in any direction yields a completely equivalent view. The shapes of the unit cells suitable for such stacking fall into seven general types or systems. These are: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic (also called isometric). When the actual arrangements of atomic species possible within the unit cell are compounded with the possible shapes of unit cells, the total number of independent geometrical arrangements available in three dimensions is 230. These are the space groups.

TABLE I
REPRESENTATIVE VALUES OF PIEZOCOUPLING FACTORS

Material Type	Crystal Class	Substance	Orientation	Coupling Factor (%)
Dielectrics				
	3m	lithium niobate (LiNbO$_3$)	X-cut 36° rotated-Y-cut	k_{15} = 68.9 k_{22} = 48.7
	32	quartz	AT-cut BT-cut	k'_{26} = 8.8 k'_{26} = 5.0
Ceramics				
(solid solutions)	∞mm	lead titanate zirconate	Z-cut	k_{33} = 30 to 60
Piezoelectric polymers				
	mm2	PVDF	Z-normal sheet	k_{31} = 16
Binary semiconductors				
	$\bar{4}$3m	gallium arsenide	(110) cut (111) cut	k'_{26} = 6.1 k'_{11} = 4.3
	6mm	α- silicon carbide	X- or Y-cut Z-cut	k_{15} = 2.5 k_{33} = 3.5
	$\bar{4}$3m	β- silicon carbide	(110) cut (111) cut	k'_{26} = ?* k'_{11} = ?* * Estimated ≈ α form

k' is a rotated (off-axis) value.

In most practical situations, one deals with a continuum approximation, where considerations of the exact placement of atoms in the cells are not important, and the situation simplifies considerably. For example, elasticity is described by the few phenomenological stiffness and compliance constants used in the equations above. These numbers arise from a "smearing-out" of the effects of the individual interatomic potentials; only important are the directional aspects stemming from the atomic arrangements, not the arrangements themselves. Variation with direction of continuum properties such as acoustic wave speed is known as anisotropy. All the requisite geometric information specifying the varieties of anisotropy reside in the classification that the crystallographers call the point groups. These are only 32 in number and arise simply from three types of symmetry elements: pure rotation axes (1-, 2-, 3-, 4-, or 6-fold), planes of reflection (mirror) symmetry, and axes of rotatory inversion (rotation followed by inversion through a center). The point groups are described by their Hermann-Mauguin symbols; these are shorthand listings of the symmetries. The names "point group" and "crystal class" are used synonymously. The classes are arranged in Table II according to the seven crystal systems, labeled "I"–"VII." Systems IV–VII are further subdivided into "a" and "b" categories; these are discussed briefly below.

The crystallographic point-group symmetry elements completely determine the form and symmetries of the elastic,

TABLE II
THE SEVEN CRYSTAL SYSTEMS AND THIRTY-TWO POINT GROUPS [62]

CRYSTAL SYSTEM	CENTRIC POINT GROUPS		ACENTRIC POINT GROUPS					OPTIC AXES
			POLAR $\underline{p}$		NONPOLAR p			
TRICLINIC I	$\bar{1}$ h		1 e		NONE			B I A X I A L
MONOCLINIC II	2/m h		2 e	m o	NONE			
ORTHORHOMBIC III	mmm h		mm2 o		222 e			
TETRAGONAL IV	4/m a	4/m mm b h	4 e a	4mm b	$\bar{4}$ o a	$\bar{4}2m$ o b	422 e b	U N I A X I A L
TRIGONAL V	$\bar{3}$ a	$\bar{3}$ m b h	3 e a	3m b	32 e b			
HEXAGONAL VI	6/m a	6/m mm b h	6 e a	6mm b	$\bar{6}$ a	$\bar{6}2m$ b	622 e b	
CUBIC VII	m3 a	m3m b h	NONE		23 e a	$\bar{4}$ 3m b	432 e $\bar{p}$ b	ISO-TROPIC
	11 GROUPS		10 GROUPS		11 GROUPS			

piezoelectric, and dielectric matrices that appear in the constitutive relations given earlier. The specific values of the individual components result, of course, from the particular substance considered. The piezoelectric $[e]$ and $[h]$ matrix forms for each point group are identical; the $[d]$ and $[g]$ are likewise the same but differ from the $[e], [h]$ sets by factors of 2 for certain matrix elements in classes 3, 32, 3m, $\bar{6}$, and $\bar{6}m2$ because of the conversion between the tensor and matrix formulations.

That the material tensor term schemes are determined by the point group symmetry is a manifestation of Neumann's Principle, which may be stated in several equivalent ways [35]

- The symmetry elements of any physical property of a crystal must include all the symmetry elements of the point group of the crystal.
- Every physical property of a crystal must possess at least the symmetry of the point group of the crystal.
- Any kind of symmetry that is possessed by the crystallographic form of a material is possessed by the material in respect of every physical property.

Of the 32 point groups, 11 have centers of symmetry (these are referred to as the Laue groups) and therefore cannot be piezoelectric because piezoelectricity is a polar effect; see the column of Table II labeled "centric." The division of crystal systems IV, V, VI, and VII into "a" and "b" categories is based upon X-ray patterns. Classical X-ray diffraction has the effect of adding a center of symmetry to the intrinsic symmetry of the crystal under study; each acentric point group appears as one of the eleven centric Laue groups. The groups that appear as holohedral under X-ray examination are assigned to the "b" category; the remainder are put in the "a" category. The structure in each of the seven systems that possesses the highest point group symmetry compatible with that system is the holohedral class; these are denoted by the letter "h." Class 432 lacks a center of symmetry but has other symmetries that,

TABLE III
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS 1

POINT GROUP 1 {Triclinic, I,1}

e_{11}	e_{12}	e_{13}	e_{14}	e_{15}	e_{16}
e_{21}	e_{22}	e_{23}	e_{24}	e_{25}	e_{26}
e_{31}	e_{32}	e_{33}	e_{34}	e_{35}	e_{36}

taken together, preclude the existence of piezoelectricity. The 20 piezo-classes are: triclinic class 1; monoclinic classes 2 and m; orthorhombic classes 222 and mm2; tetragonal classes 4, $\bar{4}$, 422, 4mm, and $\bar{4}2m$; trigonal classes 3, 32, and 3m; hexagonal classes 6, $\bar{6}$, 622, 6mm, and $\bar{6}m2$; and cubic classes 23 and $\bar{4}3m$. See the columns of Table II labeled "acentric."

Tables III–XVIII give the $[e]$ forms of the piezoelectric matrices (also called "term schemes") for the twenty piezoclasses; four pairs share the same schemes, so that there are but sixteen independent matrices. Tables XV, XIV, XI, and XVIII are, respectively, the piezo-schemes of four popular crystal classes: 3m, (the strong piezoelectrics, lithium niobate, and lithium tantalate), 32 (quartz and langasite), 6mm (AlN and ZnO, used in thin-film form on Si for MEMS devices and transversely isotropic, poled polycrystalline ceramics such as lead zirconate titanate), and $\bar{4}3m$. Nearly all compound semiconductors, such as gallium arsenide, indium phosphide, and silicon carbide, are members either of class 6mm or of class $\bar{4}3m$. Class 4mm, which includes the popular piezoelectric transducer and filter material lithium tetraborate, has an $[e]$ matrix identical in form to that of class 6mm.

The matrices are to be read in conjunction with (1)–(4) as follows. An applied electric field E_i directed along the X_i axis produces, according to the constitutive relations given earlier,

TABLE IV
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS 2

POINT GROUP 2 [IEEE axial convention] {Monoclinic, II, 3}

0	0	0	e_{14}	0	e_{16}
e_{21}	e_{22}	e_{23}	0	e_{25}	0
0	0	0	e_{34}	0	e_{36}

TABLE V
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS m

POINT GROUP m [IEEE axial convention] {Monoclinic, II, 4}

e_{11}	e_{12}	e_{13}	0	e_{15}	0
0	0	0	e_{24}	0	e_{26}
e_{31}	e_{32}	e_{33}	0	e_{35}	0

TABLE VI
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS 222

POINT GROUP 222 {Orthorhombic, III, 6}

0	0	0	e_{14}	0	0
0	0	0	0	e_{25}	0
0	0	0	0	0	e_{36}

TABLE VII
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS mm2

POINT GROUP mm2 {Orthorhombic, III, 7}

0	0	0	0	e_{15}	0
0	0	0	e_{24}	0	0
e_{31}	e_{32}	e_{33}	0	0	0

TABLE VIII
PIEZOELECTRIC $[e]$ MATRIX FOR CLASSES 4 AND 6

POINT GROUPS 4 {Tetragonal, IVa, 9} AND 6 {Hexagonal, VIa, 21}

0	0	0	e_{14}	e_{15}	0
0	0	0	e_{15}	$-e_{14}$	0
e_{31}	e_{31}	e_{33}	0	0	0

TABLE IX
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS $\overline{4}$

POINT GROUP $\overline{4}$ {Tetragonal, IVa, 10}

0	0	0	e_{14}	e_{15}	0
0	0	0	$-e_{15}$	e_{14}	0
e_{31}	$-e_{31}$	0	0	0	e_{36}

TABLE X
PIEZOELECTRIC $[e]$ MATRIX FOR CLASSES 422 AND 622

POINT GROUPS 422 {Tetragonal, IVb, 12} AND
622 {Hexagonal, VIb, 24}

0	0	0	e_{14}	0	0
0	0	0	0	$-e_{14}$	0
0	0	0	0	0	0

TABLE XI
PIEZOELECTRIC $[e]$ MATRIX FOR CLASSES 4mm AND 6mm

POINT GROUPS 4mm {Tetragonal, IVb, 13} AND
6mm {Hexagonal, VIb, 25}; TRANSVERSE ISOTROPY

0	0	0	0	e_{15}	0
0	0	0	e_{15}	0	0
e_{31}	e_{31}	e_{33}	0	0	0

TABLE XII
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS $\overline{4}2m$

POINT GROUP $\overline{4}2m$ {Tetragonal, IVb, 14}

0	0	0	e_{14}	0	0
0	0	0	0	e_{14}	0
0	0	0	0	0	e_{36}

mechanical stresses T_λ equal to $(-e_{i\lambda}E_i)$. The axis index "i" takes the values 1, 2, 3; these correspond to orthogonal X, Y, Z axes assigned to each crystal class by standard convention. The index "λ" takes on values 1, 2, $\cdots$, 6; these represent the tensor indexes according to the scheme: $1 \rightarrow 11; 2 \rightarrow 22; 3 \rightarrow 33; 4 \rightarrow 23$ or $32; 5 \rightarrow 13$ or $31; 6 \rightarrow 12$ or 21. Each of the three rows of the $[e]$ matrix is "driven" by a different electric field component, and each will produce up to six stress components. For example, in class 3m materials (Table XV), an electric field along the Y axis (E_2) will produce, according to (1a), compressive or tensile stresses along both the X and Y axes but not along the Z axis. Moreover, the X- and Y-directed stresses are equal and opposite in sign

TABLE XIII
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS 3

POINT GROUP 3 {Trigonal, Va, 16}

e_{11}	$-e_{11}$	0	e_{14}	e_{15}	$-e_{22}$
$-e_{22}$	e_{22}	0	e_{15}	$-e_{14}$	$-e_{11}$
e_{31}	e_{31}	e_{33}	0	0	0

TABLE XIV
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS 32

POINT GROUP 32 {Trigonal, Vb, 18}

e_{11}	$-e_{11}$	0	e_{14}	0	0
0	0	0	0	$-e_{14}$	$-e_{11}$
0	0	0	0	0	0

TABLE XV
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS 3m

POINT GROUP 3m {Trigonal, Vb, 19}

0	0	0	0	e_{15}	$-e_{22}$
$-e_{22}$	e_{22}	0	e_{15}	0	0
e_{31}	e_{31}	e_{33}	0	0	0

TABLE XVI
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS $\bar{6}$

POINT GROUP $\bar{6}$ {Hexagonal, VIa, 22}

e_{11}	$-e_{11}$	0	0	0	$-e_{22}$
$-e_{22}$	e_{22}	0	0	0	$-e_{11}$
0	0	0	0	0	0

TABLE XVII
PIEZOELECTRIC $[e]$ MATRIX FOR CLASS $\bar{6}$m2

POINT GROUP $\bar{6}$m2 {Hexagonal, VIb, 26}

e_{11}	$-e_{11}$	0	0	0	0
0	0	0	0	0	$-e_{11}$
0	0	0	0	0	0

TABLE XVIII
PIEZOELECTRIC $[e]$ MATRIX FOR CLASSES 23 AND $\bar{4}$3m

POINT GROUPS 23 {Cubic, VIIa, 28} AND $\bar{4}$3m {Cubic, VIIb, 31}

0	0	0	e_{14}	0	0
0	0	0	0	e_{14}	0
0	0	0	0	0	e_{14}

Alternatively, an applied strain S_μ produces a dielectric displacement D_j via the $D_j = e_{j\mu} S_\mu$ portion of constitutive (1b). Continuing the example of a class 3m material, it will be seen that a shear strain $S_4 = S_{23} = S_{32}$ leads, because of the presence of the piezo-coefficient e_{24}, to a component of dielectric displacement D_2, and consequent polarization charge accumulation on free surfaces having normals in the $X_2(Y)$ direction.

V. PIEZOELECTRIC FORCES

The volumetric force density is given by

$$F_j = \partial T_{ij}/\partial X_i.$$

Piezoelectric force density components may be found from (1a) as

$$-\partial(e_{k\lambda} E_k)/\partial X_i.$$

This means that piezoelectric forces may arise either from spatial gradients of the piezoelectric constant or from spatial gradients of the electric field. In single crystal materials such as quartz, it is not usual that the piezoelectric "constant" will vary from place to place, although the presence of microtwins, etc., makes this a possibility. In polycrystalline materials such as ceramics and in ferroelectric single crystal materials such as lithium niobate and lithium tantalate (see below), this situation arises in practice, sometimes by design.

Usually, piezoelectric forces arise because of spatial gradients in the applied electric field. An excellent example of this is the use of interdigital transducer (IDT) electrode arrays to produce surface acoustic waves (SAW's) and related acoustic wave types. From the electrode array placement and the crystal term scheme (rotated, if necessary, to the orientation of the crystal surface), one may find the force components and infer qualitatively if a particular type of wave motion may be driven piezoelectrically by the electrode array [39].

VI. ENANTIOMORPHISM

Eleven crystal classes are devoid of a plane of symmetry. These are 1, 2, 222, 4, 422, 3, 32, 6, 622, 23, and 432. In these classes, two structures of the same kind can exist; each is the mirror image of the other. These are known as enantiomorphic pairs; quartz (class 32) is probably the most famous example, with "left-" and "right-handed" varieties. The handedness arises at the atomic level from the spiral

because $e_{21} = -e_{22}$. The longitudinal stress along Z vanishes because $e_{23} = 0$. In addition, E_2 produces a shear stress $T_4 = T_{23} = T_{32}$, via the constant e_{24}, which, for this class, equals e_{15}.

arrangement of the SiO_2 molecules in the crystal, but from Neumann's Principle, the external appearances of the facets in completely developed specimen-pairs exhibit the mirror-symmetric aspect macroscopically. The enantiomorphic groups are indicated in Table II by the symbol "e."

VII. OPTICAL BEHAVIOR

The first-order optical behavior of materials is governed by the dielectric permittivity tensor. In crystals, three cases are distinguished, depending on whether the principal dielectric constants are all equal (isotropic medium), two are equal, and one is unequal (uniaxial medium), or all are unequal (biaxial medium); the corresponding crystal class distributions are indicated in Table II in the last column.

One second-order optical effect of importance is that of optical activity or gyration [19]. In optically active substances, the passage of plane polarized light is accompanied by a rotation of the direction of the polarization vector. The effect comes about from the chiral nature of the molecules comprising the material. A common example is a sugar-water solution. Molecules of sugar (dextrose or levulose) are chiral in nature; a solution comprised of sugar of either handedness rotates a light beam accordingly, despite the fact that the molecules are randomly oriented in the solution. This is because reversal of the axis of a spiral does not reverse its handedness, so no cancellation of the effect takes place. Optical activity is characterized phenomenologically by an axial second rank tensor called the gyration tensor. Only crystals that lack a center of symmetry can be optically active (gyrotropic). Crystals that are enantiomorphic are necessarily gyrotropic; in these eleven classes, the gyration tensor determinant is nonvanishing. Optical activity also exists in four nonenantiomorphic classes: m, mm2, $\overline{4}$, and $\overline{4}$2m; in these classes, the gyration tensor determinant vanishes. The symbol "o" denotes these groups in Table II.

Two effects that are closely associated with piezoelectric materials are pyroelectricity and ferroelectricity.

VIII. PYROELECTRICITY

Of the twenty piezoelectric point groups, ten contain a unique polar axis. In Table II, the symbol "p̲" appears in the polar column to indicate that the classes therein are both piezoelectric and pyroelectric, while the symbol "p" in the nonpolar column indicates piezoelectric classes only [2]. The entry "p" with an overbar, appearing with class 432, indicates that this class is nonpiezoelectric. Crystals in the polar classes possess electric dipole moments along their polar axes. When the crystals are subjected to a uniform change of temperature, electric charges accumulate on the ends of the polar axes. This phenomenon is known as pyroelectricity; because a temperature change (a scalar) produces a charge separation, and consequently, an electric field (a vector), the pyroelectric coefficients form a tensor of rank one, i.e., a vector, and would be represented as a (3×1) matrix if we were to extend the constitutive equations given earlier to include this effect.

The pyroelectric classes are: 1, 2, m, mm2, 4, 4mm, 3, 3m, 6, and 6mm. Thus, α-SiC and lithium niobate are

pyroelectric, while β-SiC, quartz, and gallium arsenide are not. The presence of piezoelectricity is necessary but not sufficient for a crystal to be pyroelectric.

IX. FERROELECTRICITY [40], [41]

The name ferroelectricity is given to those polar crystals capable of having the spontaneous polarization along the polar axis reversed, usually in response to an applied electric field. The name is derived by analogy with ferromagnetism, but in the magnetic case, the very atoms themselves possess permanent magnetic moments [42]; in the electric case, the permanent electric moment is a property of the placement of the atoms within the unit cells of the structure. The orientations of the intrinsic atomic magnetic moments permitted in ferromagnetic crystals, in addition to the spatial atomic arrangements allowed, produce additional complexity with regard to crystal symmetry. When the spin orientations are taken in combination with the thirty-two conventional point groups, the result is ninety crystallographic magnetic point groups [43], [44]. Coupling to the magnetic field variables is not considered further here.

The presence of the ferroelectric state requires that the crystal be of a pyroelectric class; the converse is, however, not true. One cannot conclude *a priori* that a pyroelectric crystal is ferroelectric; one must settle this issue experimentally or by numerical simulation. The ferroelectric state usually exists only below a certain critical temperature called the Curie temperature or Curie point[3] [45]. Above this point, the material may belong to a class that is not pyroelectric or even piezoelectric. Upon cooling through the Curie point, the crystal undergoes a phase transition (which may be either first- or second-order)[4] [46], where the atoms of the structure shift their positions slightly, and the crystal changes its symmetry, usually from a nonpolar form to the symmetry of a pyroelectric class.

Since the ferroelectric state has reversible dipoles, upon cooling, it is a matter of chance which polarity will be assumed; near the Curie point, the structure is very susceptible to disturbance. Because the lattice is relatively unstable around this point, small forces can produce large effects; this is the case with the dielectric constant. This quantity is the measure of dielectric displacement produced in response to an applied electric field. Near the Curie point, dielectric constants assume very large values; this behavior ("dielectric anomaly") led to the initial discovery of this class of materials. Very often ferroelectrics have large piezoelectric coupling values.

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[3] Strictly speaking, the Curie point and Curie temperature are conceptually different, although we use the terms synonymously. The Curie point is the actual temperature of a crystallographic phase change, while the Curie temperature is associated with the formula variable in the Curie-Weiss Law [42], [46]. For materials undergoing first-order transitions [46], the two definitions can differ by 10 or more kelvins; for second-order transitions, the two are virtually the same.

[4] In a first-order phase transition, energy, volume, and crystal structure change discontinuously as function of temperature (or, e.g., pressure); when these change more or less continuously, but their derivatives are discontinuous, the phase transition is said to be of second order. Since, e.g., specific heat is the temperature derivative of energy, then at the temperature of a second-order phase transition, its variation with temperature would experience a discontinuity.

The archetypical ferroelectric is Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$). This crystal is unusual in that it possesses two Curie points. When cooled into the ferroelectric phase, it passes from class 222 to class 2. Its piezoeffect was established by the Curie brothers in 1880. Pockels found the dielectric anomaly in 1894. It was used for ultrasonics applications in the early 20th century, but because of its solubility in water, it is not considered any longer to be a practical material for these uses.

Barium titanate, another historically important material, exists in the nonpiezoelectric perovskite class m3m above its upper Curie point and undergoes a succession of structural phase transformations, passing through 4mm and mm2 classes before reaching 3m symmetry as the temperature is reduced.

Piezoelectric ceramics, such as lead zirconate titanate ($Pb(Ti, Zr)O_3$), are solid solutions comprised of microscopic crystallites, each of which is ferroelectric; the material originally is macroscopically isotropic at all temperatures because of the random orientations of the crystallites. When cooled through the Curie point in the presence of a static electric field, (a process called "poling") the domains are preferentially oriented and frozen into a configuration where the body is macroscopically piezoelectric. It remains isotropic perpendicular to the field axis, but the isotropy is destroyed in the parallel direction. The result is cylindrical polar symmetry (transverse isotropy), represented by the symbol ∞mm; as far as the elastic, piezoelectric, and dielectric matrices are concerned, the schemes of coefficients are identical to those for the class 6mm. In fact, for all tensors up to and including rank five, the schemes of coefficients are identical to the corresponding class 6mm schemes [37]; one may, therefore, differentiate transversely isotropic substances from 6mm crystals by measuring higher-order effects, e.g., third-order elastic constants (tensor of rank six).

Above the Curie point, most (but not all) ferroelectrics belong to one of three classes: 222 (e.g., Rochelle salt), $\overline{4}2m$ (e.g., potassium dihydrogen phosphate, KDP), and m3m (e.g., $BaTiO_3$). In the ferroelectric state, most of the practically important compounds likewise fall into three classes: 4mm, 3m, and mm2.

Unpoled single crystal ferroelectrics such as lithium niobate are comprised of domain regions where the directions of polarization are collinear but oppositely directed. The presence of domains can alter various macroscopic properties (e.g., piezoelectric voltage) and not change others (e.g., index of refraction).

X. Piezoelectric Polymers [26]

Certain polymers, such as polyvinyl chloride (PVC), polyvinyl fluoride (PVF), and polyvinylidene fluoride (PVF_2 or PVDF) can be made piezoelectric by a combination of mechanical stretching and electric field poling at elevated temperatures. The induced anisotropy varies with the polymer and the subsequent treatment; polymethyl glutamate, for example, has symmetry ∞22, which is equivalent to class 622 for the properties discussed here. PVDF sheet, poled along the thickness, belongs to class ∞mm (equivalent to 6mm);

3-5	N	P	As	Sb
B	c	c	c	
Al	h	c	c	c
Ga	h	c	c	c
In	h	c	c	c

2-6	O	S	Se	Te
Be	h	c	c	c
Zn	h	(α-h / β-c)	c	c
Cd		h	h	c

1-7	Br	Cl	I
Cu	c	c	c
Ag			h

4-4	C
Si	(α-h / β-c)

h = hexagonal, 6mm (wurtzite)
c = cubic, $\overline{4}$3m (sphalerite; zinc blende)

Fig. 3. Piezoelectric binary semiconductors.

uniaxial stretching or rolling converts it to orthorhombic class mm2, while a biaxial stretching again produces class ∞mm.

XI. Piezoelectric Semiconductors [47]–[49]

In the case of semiconductors, the piezoelectric equations are broadened to incorporate the further coupling to charge transport mechanisms. It is apparently not well appreciated how wide-spread is the phenomenon of piezoelectricity in semiconductors. The single-element semiconductors silicon and germanium have, of course, no piezo-effect because of the inherent symmetry by which the atoms are arrayed in their crystals; they share with diamond the perovskite structure of point group m3m. Binary semiconductors, however, because of the dissymmetry of the two atomic species, are generally piezoelectric. Fig. 3 provides a partial listing of these materials, grouped according to the columns of the periodic table; it is seen that the compounds fall into two categories: those marked "c" belong to the cubic point group $\overline{4}$3m, the sphalerite or zincblende structure, while those indicated with "h" belong to the hexagonal point group 6mm, the wurtzite structure.

Piezosemiconductors have an encouraging future because of the appealing promise of monolithic, integrated, mixed-effect devices; for example, electronic drivers that modulate photonic processors via submicroscopic mechanical actuators containing optical components.

XII. Quantum Effects in Piezosemiconductors

References [50]–[54] discuss new acoustic wave anomalies in experiments with surface acoustic waves on GaAs/AlGaAs heterostructures driven by their piezoeffect. These current experiments are carried out at low temperatures; the electron confinement in the heterostructures alters the density of states profile, leading potentially to the realization of custom designed, high-performance, hybrid, piezoelectronic devices. One may anticipate future areas of application such as ultrahigh speed signal processing.

XIII. Wide Bandgap Semiconductors [55]–[58]

A growing number of advanced applications, particularly those involving high power and high temperature devices
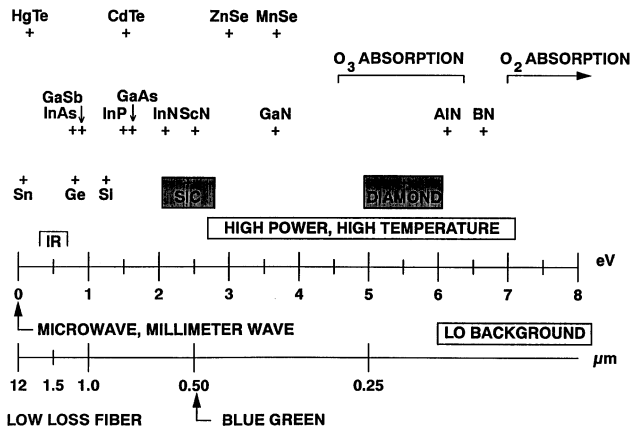
Fig. 4. Bandgap of important semiconductors [59].

require semiconductors with wide bandgaps. For a variety of reasons, silicon carbide and diamond are particularly apt candidates for these uses; see Fig. 4 [59]. Diamond is non-piezoelectric in both its crystalline (m3m) and amorphous forms, whereas both the cubic and hexagonal forms of silicon carbide are piezoelectric in nature. In those applications necessitating mixed-effect devices that incorporate traditional semiconductor ideas with mechanical forces and motions, the piezo-semiconductors are highly commended; where, in addition, these devices are required for high temperature operation, then silicon carbide is a material of choice. The cubic form β-SiC has a bandgap energy of 2.2 eV, while the hexagonal form α-SiC has a bandgap energy of 2.9 eV; these are significantly higher than that of GaAs, with a value of 1.43 eV. The piezocoupling values are comparable; see Table I. As material quality continues to improve with attainment of lower impurity and defect levels, and as semiconductor processing skills increase with silicon carbide, one may anticipate the extension of smart MEMS technology to a variety of hostile but environmentally important areas.

XIV. POLYTYPISM IN SILICON CARBIDE [60]–[62]

Alpha-SiC, of symmetry 6mm, exhibits a curious variety of forms known as polytypes. Polytypism arises because the molecules may be stacked in an infinite variety of zig-zag sequences, while preserving the point group symmetry. Theoretically, the number of polytypes is unbounded; practically, hundreds are known, each with a different unit cell, and with a variety of space groups and X-ray diffraction patterns. Condensation under different growth conditions is thought to determine the polytype produced; the most common varieties are known as 6H and 4H. Each polytype can theoretically differ in its phenomenological constants because some bond angles and lengths vary; in most cases, the differences are imperceptible, but differences of several percent in the elastic constants of 6H and 4H material have been reported [56]. Beta-SiC, because of its $\overline{4}$3m symmetry, cannot have polytypes.

XV. HIGH POWER DEVICES

For applications such as acoustic resonators, the power level is usually low. Here, silicon carbide of either the alpha or beta

variety is an attractive choice for high temperature operation. The acoustic losses are at present not very high, so the quality factor (Q) is quite acceptable; as the material quality continues to improve with attainment of lower and lower impurity levels and defects, Q values will substantially increase in the future, leading to higher stability oscillators for "hot" environments.

For acoustic transducer operation, where power levels are a concern at any temperature, silicon carbide, in the beta (cubic) form, is a desirable material because of its structural stability and its nonferroelectric nature. Lithium niobate and lithium tantalate, strongly piezoelectric ferroelectrics commonly used as transducers, can experience depoling and consequent loss of efficiency at very high power and temperature levels.

XVI. CONCLUSION

The piezoelectric effect has been briefly reviewed, in tutorial fashion, from the standpoints of origin, traditional uses, connection with associated effects, and relation to crystal symmetry. Sample material coefficients are given, with ample references to the pertinent literature. Future prospects for use of the piezoeffect appear bright because it mediates directly between the elastic and electronic variables in the rapidly growing area of MEMS devices and technology.

APPENDIX I
RELATIONS AMONG THE CONSTITUTIVE COEFFICIENTS

The equations relating the constitutive material values may be determined by first pairing the equations sharing common variables

$$
\begin{aligned}
&\text{(1a) and (3a):} \quad T, S, E \\
&\text{(2a) and (4a):} \quad T, S, D \\
&\text{(1b) and (2b):} \quad E, D, S \\
&\text{(3b) and (4b):} \quad E, D, T.
\end{aligned}
$$

One variable is then eliminated from each pair, yielding the required results. For example, from (1a) and (3a), we have (dropping the matrix brackets for simplicity)

$$
\begin{aligned}
T &= c^E S - e'E = c^E(s^E T + d'E) - e'E \\
&= c^E s^E T + c^E d'E - e'E = T
\end{aligned}
$$

therefore

$$
c^E s^E = I \quad \text{and} \quad e = dc^E \quad \text{or} \quad d = es^E.
$$

The full set obtained in this manner is

$$
\varepsilon^+ \beta^+ = c^* s^* = I, \quad \text{where } + \text{ is } T \text{ or } S, * \text{ is } E \text{ or } D,
$$
$$
\text{and } I = \text{unit matrix}
$$

and

$$
e = \varepsilon^S h = dc^E; \quad d = \varepsilon^T g = es^E; \quad h = \beta^S e = gc^D;
$$
$$
g = \beta^T d = hs^D.
$$

In addition to these multiplicative identities, there exist difference relations divided between the dielectric quantities at constant stress and at constant strain and between the elastic constants at constant electric field and at constant

Field tensors:

Mechanical stress, S: pascal, $\mathrm{Pa} = \mathrm{newton/meter}^2 = \mathrm{N/m}^2$

Mechanical strain, T: meter/meter = m/m = dimensionless

Electric intensity, E: volt/meter = V/m

Displacement, D: coulomb/meter^2 = C/m^2

Matter tensors:

Permittivity, $\varepsilon^T, \varepsilon^S$: farad/meter = F/m = C/(m-V)

Impermeability, β^T, β^S: meter/farad = m/F = (m-V)/C

Piezo constants: e C/m^2 = N/(m-V)

d m/V = C/N

h V/m = N/C

g m^2/C = (m-V)/N

Elastic stiffness, c^E, c^D Pa = N/m^2 = J/m^3

Compliance, s^E, s^D (Pa)$^{-1}$ = m^2/N = m^3/J.

displacement. To obtain these, we equate the right hand sides of the following pairs of equations: (2b) = (4b); (1b) = (3b); (3a) = (4a); and (1a) = (2a). These are then compared respectively to $(-g)$ times (2a); (e) times (3a); (g') times (3b); and (h') times (1b). After some algebra, the following are found:

$$(c^D - c^E) = h'e = e'\beta^S e = h'\varepsilon^S h$$
$$(s^E - s^D) = g'd = d'\beta^T d = g'\varepsilon^T g$$
$$(\varepsilon^T - \varepsilon^S) = ed' = es^E e' = dc^E d'$$
$$(\beta^S - \beta^T) = gh' = hs^D h' = gc^D g'.$$

These relations show that the presence of piezoelectricity modifies the elastic and dielectric constants, that the mechanical (elastic) conditions must be specified for dielectric quantities, and that electric conditions must be specified for elastic quantities. To obtain an order of magnitude estimate of the size of the effect, we may neglect the matrix nature of the above equations and treat them as scalars. Then, using the symbol Δ to represent differences, we have, from the first difference relation

$$(\Delta c/c) = e\beta^S e/c = e^2/(\varepsilon c) = k^2,$$

and similarly for the other relations. Thus, the fractional differences are determined by dimensionless combinations of elastic, piezoelectric, and dielectric constants. We call each combination the square of a quantity k, known as a piezoelectric coupling factor.

APPENDIX II
UNITS OF THE VARIOUS QUANTITIES

See the top of the page.

ACKNOWLEDGMENT

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