PIEZOELECTRIC RESPONSE OF BONE AND TENDON
SUBJECTED TO INHOMOGENEOUS STRESS

(Chapters I through IV)

Lance Harris Breger

Department of Physics and Materials Research Laboratory

University of Illinois, Urbana, Illinois 61801

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(Chapters I through IV)

BY

LANCE HARRIS BREGER

B.A., Lake Forest College, 1962
M.S., Northwestern University, 1967
M.S., University of Illinois, 1969

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THESIS

Submitted in partial fulfillment of the requirements
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MASTER

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Lance Harris Breger, Ph.D.
Department of Physics
University of Illinois, 1974

Bone and tendon are piezoelectric materials. When they are homogeneously stressed, they obey the classical or standard theory of piezoelectricity. However, this thesis shows that when bone and tendon are subjected to inhomogeneous stress, as in cantilever bending, they do not obey the classical piezoelectric theory, although the piezoelectric minerals quartz and tourmaline do. This thesis shows that an adequate, extended theory of piezoelectricity can be developed by including in addition to the usual independent variable, stress, a new independent variable, the gradient of stress. The extended theory includes the classical, piezoelectric theory as a special case. To test the predictions of the extended theory in cantilever bending, a new, null-balancing circuit was developed. This circuit detects piezoelectric voltages directly by obviating the difficulties caused by shunt capacitance between lead wires to the piezoelectric sample. Using this circuit, the magnitude of the piezoelectric voltage from the convex to the concave surface of a cantilever-bent bar (approximately 2 mm thick and 1 cm wide) of tendon or bone was measured to be in the order of 1 volt when the free end of the sample is depressed by the weight of 100 gms. This voltage is about 100 times larger than previously reported values. Our measurements also confirm the predictions of the extended theory of piezoelectricity for samples in cantilever bending. In addition, this thesis develops the predictions of the extended theory of piezoelectricity for samples subjected to pure bending.

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1974

Dedicated to the memory
of my beloved mother,
Sylvia Goldman Breger

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TABLE OF CONTENTS

I.	INTRODUCTION.....	1
II.	CONCEPTUAL BACKGROUND.....	6
	A. Introduction.....	6
	B. Intensive and Extensive Macroscopic Variables.....	7
	C. Structure of Matter from a Macroscopic Point of View.....	8
	D. Cartesian Tensors.....	18
	E. Relation of Cartesian Tensors and Point Symmetry Operations.....	28
	F. Stress.....	34
	G. Strain.....	38
	H. Relation of Stress and Strain.....	41
	Uniqueness Theorem.....	41
	Hooke's Law.....	43
	I. Electric Charge.....	44
	J. Polarization of Dielectrics and the Related Concepts of Displacement and Dielectric Constant.....	47
	K. Piezoelectric, Pyroelectric, and Ferroelectric Materials.....	57
	L. Tendon and Bone.....	67
	M. Quartz and Tourmaline.....	75
	N. Summary.....	82
III.	FAILURE OF STANDARD PIEZOELECTRIC THEORY FOR BENT BONE.....	83
	A. Introduction.....	83
	B. True Shape of the Bone Signal.....	84
	C. Changes in Voltage Polarity Upon Rotation of Specimen...	90
	D. Sign of ΔV_0 Across a Cantilever-Bent Bar According to the Classical Piezoelectric Theory.....	93

1.	Derivation of the Basic Equation.....	93
2.	Prediction of Sign Changes of ΔV_0 According to the Standard Theory.....	109
3.	Answering Possible Objections.....	113
E.	Summary.....	116
IV.	THE EXTENDED THEORY OF PIEZOELECTRICITY AND ITS APPLICATION TO CANTILEVER BENDING.....	118
A.	Introduction.....	118
B.	Derivation of the General Equation for the Electric Field According to the Extended Theory of Piezoelectri- city.....	120
C.	Applying General Equation for E_1 to Piezoelectric Bars in Cantilever Bending.....	125
D.	Sign Changes of ΔV_0 According to Extended Theory Following Rotation of the Sample.....	130
1.	That f_{2332} is a Component of a Fourth-Rank Tensor...	130
2.	That f_{2332} Does Not Change Sign Following 180° - Rotations of Bar.....	132
3.	That f_{2332} is Non-Zero.....	134
E.	Further Tests of the Extended Theory.....	137
F.	Summary.....	139
V.	EXPERIMENTAL VERIFICATION OF EXTENDED THEORY OF PIEZO- ELECTRICITY FOR CANTILEVER BENDING.....	140
A.	Introduction.....	140
B.	General Theory of Our Method for Measuring Piezoelectric Voltages.....	141
1.	Introduction.....	141
	Theory of the Piezoelectric Capacitor.....	141
	The Effect of Shunt Capacitance on Piezo- electric Voltages.....	144
	How to Measure Voltage from a Piezoelectric Source..	151

C. Details of the Construction and Operation of the Apparatus.....	163
Introduction.....	163
Circuit Measuring the Piezoelectric Voltage.....	164
Piezoelectric Samples.....	171
Devices for Applying and Measuring Mechanical Forces to Sample.....	173
Electrodes.....	181
D. Testing the Operation of the Apparatus.....	188
Introduction.....	188
Effect of Shunt Capacitance on Measured Voltage.....	188
Effect of Gain in the Feedback Circuit on ΔV_{IA}	190
Effect of Shielding Wires on ΔV_{IA}	190
Effect of Cable Length on ΔV_{IA}	192
Non-Piezoelectric Samples.....	194
Anomalous Effects.....	194
Conclusion.....	195
E. Experiments on Quartz.....	195
Introduction.....	195
Samples.....	196
Measurement Technique.....	196
Results.....	196
Conclusion.....	203
F. Experiments on Tourmaline.....	204
Introduction.....	204
Samples.....	204

	3. Measurement Technique.....	204
	4. Results.....	204
	5. Conclusion.....	207
G.	Experiments on Bone and Tendon.....	208
1.	Introduction.....	208
2.	Preparation of Samples of Bone and Tendon.....	208
3.	Voltage Decay.....	212
4.	Bone Experiments.....	217
5.	Tendon Experiments.....	230
H.	Conclusion and Summary.....	237
VI.	PREDICTIONS OF STANDARD AND EXTENDED THEORIES OF PIEZO- ELECTRICITY FOR PURE BENDING.....	238
A.	Introduction.....	238
B.	Exact Stress Distribution In a Bar of Rectangular Cross Section Subject to Pure Bending.....	240
C.	Equation for ΔV_0 Across the Thickness of the Bar in Pure Bending.....	243
D.	Effects on ΔV_0 of Misaligning Forces According to Standard Theory of Piezoelectricity.....	248
E.	Conclusion.....	253
VII.	DISCUSSION AND CONCLUSION.....	254
A.	Introduction.....	254
B.	Other Possible Causes of Piezoelectric Effect in Bone...	254
C.	Difference Between Piezoelectric Properties of Bone and Quartz.....	257
D.	Improvements in the Experiment.....	258
E.	New Experiments.....	259
F.	Original Contributions.....	260

BIBLIOGRAPHY.....	262
APPENDIX A--A Theorem Concerning Contraction of Two Tensors to Produce a Third Tensor.....	266
APPENDIX B--Hydrostatic-Pressure Test for Pyroelectricity.....	269
APPENDIX C--An Order-of-Magnitude Calculation to Show that Externally Applied Forces Are Much More Important in Determining Stress and Strain in Our Piezo- electric Bars Than is the Electric Field That is Caused by Bending.....	274
APPENDIX D--Attempt to Amend the Standard Theory of Piezo- electricity by Including Non-Linear Effects.....	277
APPENDIX E--Finding an Approximation for the Stress Distribu- tion in Bone and Tendon During Cantilever Bending.....	284
APPENDIX F--Theory of the Piezoelectric Capacitor and Related Concepts.....	299
APPENDIX G--Mathematical Treatment of Voltage Decay in Bone and Tendon.....	316
VITA.....	324

I. INTRODUCTION

This thesis is about a physical property of biological materials and how that property can be explained in physical terms. Specifically, the property is the ability of a specimen of bone or tendon to develop differences in electrical potential between different points in the specimen when it is stressed; this behavior is, in a general sense, piezoelectricity. Our explanation for it extends the classical theory of piezoelectricity to treat features of the electrical response of these materials that cannot be accounted for by the classical or standard theory.

Before describing the present work, let us review briefly the salient events in the discovery and investigation of piezoelectricity in bone and tendon. (For a complete review, see the review article by Williams.)¹

Fukada was the first to discover and investigate the piezoelectric effect in bone and tendon.² Using dry samples, he showed that when bone and tendon were subjected to a homogeneous stress, they would develop a potential difference between opposite surfaces of the bone or tendon (the direct piezoelectric effect) and when they were exposed to a uniform electric field, they would become homogeneously strained (the converse piezoelectric effect). He also noted that the electrical effect was a

¹Wendell S. Williams, "Sources of Piezoelectricity in Tendon and Bone," CRC Critical Reviews in Bioengineering, February, 1974, pp. 95-118.

²Eiichi Fukada, "On the Piezoelectric Effect of Bone," Journal of the Physical Society of Japan, October 1957, pp. 1158-1162; Eiichi Fukada, "Piezoelectric Effect in Collagen," Japanese Journal of Applied Physics, February, 1964, pp. 117-121.

property of the non-living part of bone and tendon. and that its magnitude decreased as the bone or tendon became more moist. Classical piezoelectric theory was totally adequate to account for all of the results Fukada obtained using homogeneous stress and homogeneous electric fields.

Later Bassett, Pawluk, and Cochran performed experiments to determine the character of the piezoelectric response of bones kept moist by physiological solutions.¹ They cut long parallelepiped-shaped samples so that each sample's long axis was parallel to the length of the bone. Clamping one end of the sample in a vise, they bent the other end down in cantilever bending and measured a difference of potential between the convex and concave surfaces of the bone as shown in figure(1:1). (Wick electrodes were used to eliminate spurious signals from the wet bone.) The signals were small, only 1/2 to 5 mV at their peak, and decayed quickly within a period of from 1/2 sec to 5 sec.. Bassett also reported that during the initial pulse, when force was applied to the sample, the convex surface was always positive with respect to the concave.

It is extremely important to note that Bassett and Cochran's work differs fundamentally from Fukada's in that Bassett and Cochran applied inhomogeneous stresses to the sample, whereas Fukada applied only homogeneous stresses. Bassett and Cochran did not attempt to interpret their results by using the classical piezoelectric theory. (In fact, this theory is insufficient, as we will show later.)

¹G. V. B. Cochran, R. J. Pawluk, and C. A. L. Bassett, "Electromechanical Characteristics of Bone Under Physiologic Moisture Conditions," Clinical Orthopaedics and Related Research, May-June 1968, pp. 249-270.

Figure (1:1)

Bassett and Cochran's Experiments on Cantilever Bending in Bone

Bassett was interested in what physiological effects might be produced by the piezoelectric response of bone. He postulated that the piezoelectric effect in bone might be the mechanism by which a long-known law of bone growth, Wolff's Law, was mediated. Wolff's Law states, "The form of (living) bone being given, the bone elements place or displace themselves in the direction of functional pressure and increase or decrease their mass to reflect the amount of functional pressure."¹ Bassett thought that the positive piezoelectric charges developed in bone might stimulate destruction of bone and, conversely, that negative charges might stimulate bone growth. For Bassett, bars of bone bent in cantilever fashion became models with which to explain bone remodeling in real legs and arms.

Our work in this thesis began as an attempt to see if the classical laws of physics could predict the electrical results of cantilever bending of bars of bone.

This introduction now concludes with a synopsis of the rest of the thesis. The reader will need to become acquainted with many concepts, some of which are frequently spoken of and frequently misunderstood. These concepts are explained in Chapter II. Chapter III discusses some of our early qualitative experiments on cantilever bending of bone and shows that even qualitatively the classical theory of piezoelectricity cannot explain the piezoelectric effect in bone. An extended theory of

¹Andrew Bassett, "Electrical Effects in Bone," Scientific American, 1965, p. 18.

piezoelectricity is presented in Chapter IV. and applied to cantilever bending. (The theory is called "extended" because the classical theory is a special case of it.) The experiments performed to test this extended theory in the case of cantilever bending are described in Chapter V. Chapter VI presents the predictions of the extended theory for pure bending of bars of bone and tendon. Chapter VII presents a summary and list of conclusions from this work. Several appendices follow Chapter VII. They contain detailed proofs, etc., that would probably distract the reader from following the main path of the argument during an initial reading. However, they do contain much useful information, which could profitably be read subsequently. Some of the information in the appendices is original, but not all of it.

II. CONCEPTUAL BACKGROUND

A. Introduction

Following is a summary of the concepts basic to an understanding of piezoelectricity in bone. It should be especially helpful for those whose field is not physics, e.g., biologists, to acquire the background necessary to understand the rest of this thesis. This summary is also useful because it collects into one place the many and diverse facts that pertain to piezoelectricity.

Little in this summary is proved. These well-known results are most often merely stated and reference made to texts where a more complete treatment can be found.

All the concepts are presented from a continuum or macroscopic point of view, i.e., details of the atomic organization of matter never enter the discussion. In fact, the whole thesis adopts a macroscopic point of view.

These concepts apply to all three states of matter, solid, liquid, and gaseous, unless one or more states is explicitly excluded.

MKS units are used exclusively throughout the rest of the thesis.

B. Intensive and Extensive Macroscopic Variables¹

The macroscopic properties of anybody are of two types: intensive and extensive. These macroscopic properties can be differentiated by the following experiment. First, measure the macroscopic properties of a system; then divide the system into two parts and measure these properties in each part. If a property has the same value in the undivided system as in the subsystem it is called an "intensive" property; an example is temperature. If the property has a different value in the undivided system than in the subsystem, it is called an "extensive" property; an example is volume.

Intensive and extensive properties may be joined together in pairs (or conjugated) according to this rule: if the product of an intensive property and an extensive property has the units of energy or energy per unit volume, the two variables are said to be conjugate. This concept will become important later on when we develop the equations that relate the electric field to stress, temperature, etc., in a piezoelectric body.

¹F. Reif, Fundamentals of Statistical and Thermal Physics, pp. 148-150.

C. Structure of Matter from a Macroscopic Point of View¹

We assume that all bodies in this discussion have three macroscopic structural properties:

1. Continuity

Not only does this imply that there are no macroscopic holes in the solid, but, even more importantly, that the fluctuations in properties caused by the real atomic constitution of the material can be averaged out in a unique way at each point to define the macroscopic properties there.

2. Possible anisotropy

This means that the macroscopic properties at each point may vary with direction at the point ²

3. Homogeneity

Whatever macroscopic properties the body has at one point, it has exactly the same properties at all other points in the solid.

The internal order of the arrangement of atoms in a body can be discovered by observing the diffraction pattern the body causes when it is placed in a beam of x-rays. On this basis, matter can be classified on a spectrum according to the amount of internal order in the arrangement of its atoms, as shown in figure (2C:1). At one extreme are the crystals, solids

¹John Nye, Physical Properties of Crystals, pp. 276-283.

²The name "anisotropic" is aptly chosen, since it means that the properties are not ("an-") the same ("-iso") in different directions or turnings ("-tropic").

Figure (2C:1)

Spectrum of Materials on the Basis of Internal Order

increasing order

crystals

(perfect order in
all 3 directions)

textures

(order in only
1 or 2 directions)isotropic
amorphous
materials(order in no
direction)

which are perfectly ordered in all three dimensions. At the other extreme is isotropic, amorphous matter, like air or liquid water, which has no regularity in any direction. In between are materials that are sometimes called textures, those arranged like a bundle of twigs: they show order in some direction (e.g., along the length of the twigs) but not in all directions, (e.g., perpendicular to the twig's length). Bones and tendons have this type of internal organization.

To describe the order or arrangement of atoms in a body, we state which "symmetry operations" the arrangement possesses. Roughly speaking, a symmetry operation is a way to superimpose, or map, the body onto itself. However, before we can define precisely what a symmetry operation is, we need to define a prerequisite concept, an orthogonal transformation.

A transformation in 3-dimensional space is a mapping, or pairing, that associates every point in space with one and only one other point, that is, a transformation is a one-to-one and onto mapping of Euclidean space onto itself. An orthogonal transformation is a transformation that keeps the distance between every two image points equal to the distance between the points from which they came. That is the precise definition of an orthogonal transformation. However, the intuitive idea is this. We can think of "mapping" as moving each atom of any body in 3-dimensional space from some initial position to a final one according to some plan. That the mapping is "one-to-one and onto" means no atoms are created or destroyed during the movement. That the movement is also "orthogonal" means this displacement of the atoms does not distort the basic shape of the body

they compose.¹ Some simple examples of orthogonal transformations are translations, rotations about a line, reflections in a plane, inversions through a point, or any combination of these.

Mathematicians have shown that all orthogonal transformations have all of the following basic properties:²

1. All "atoms" that lie in straight line before orthogonal transformation will lie on a straight line afterward, but not necessarily the same line. The word "atom" here denotes any point, or particle, of the body itself, rather than a point fixed in space.
2. The magnitude of the angle between any two straight lines of atoms before orthogonal transformation is the same as the magnitude afterward, but the sign may be different.
3. All atoms lying in a plane before transformation will lie in a plane afterwards, but not necessarily the same plane.

All orthogonal transformations, no matter how complicated, can always be resolved into two unique motions: a unique "point operation" about the origin of the standard laboratory frame (i.e., a Cartesian frame whose

¹There is another equivalent way to think of an orthogonal transformation because what is ultimately important in any transformation is the relative change between the standard Cartesian frame and the material. The same relative change that was obtained by preserving distances between atoms during the movement of material can also be obtained by leaving the material still and undisturbed and moving the standard orthogonal frame to a different position and orientation. We will not adopt this latter viewpoint here, since in practice the material is moved, not the standard laboratory frame.

²P. S. Modenov and A. S. Parkhomenko, Geometric Transformations, Volume 1, pp. 17-76.

position is fixed in the laboratory and relative to which we describe the events in our experiment) followed by a unique rigid-body translation of the material. By a "point operation" we mean a particular kind of orthogonal transformation of the material that leaves at least one point, or atom, unmoved after the transformation, e.g., rigid-body rotation about a point. By saying that the point operation is "about the origin," we mean that this unmoved point is at the origin of the standard laboratory frame. These point operations can in turn always be resolved into a unique combination of rotations about a line through the origin and reflections in a plane through the origin.

Imagine a local Cartesian frame centered at and moving with a particular atom during an orthogonal transformation with its axes always remaining parallel to those of the standard Cartesian, laboratory frame. (See figure (2C:2).) During the transformation, other surrounding atoms appear to an observer in this frame to move about him, i.e., to undergo a point operation about him because he thinks he is stationary. The point operation this local observer sees occurring about him during the orthogonal transformation of the whole body is exactly the same as the unique point-operation component of the orthogonal transformation of the whole body about the origin of the standard laboratory frame. In fact, every single atom sees its neighboring atoms undergoing this same point operation during an orthogonal transformation. During non-orthogonal transformations, observers on different atoms see their neighboring atoms undergoing different point operations. It is an important characteristic of orthogonal transformations that observers on all atoms see their surrounding atoms undergoing the same point operation.

Figure (2C:2)

Diagram Showing that During an Orthogonal Transformation the Local Point Operation is the Same at All Points in the Body

bar after rotation

← = fixed direction in the material itself

Having discussed orthogonal transformation we can return to our original purpose, to discuss symmetry transformations, transformations which move every atom of the body into a location occupied by an identical atom before the transformation. Thus, the body looks the same before and after a symmetry transformation as seen from the standard Cartesian frame or from the local Cartesian frames centered on each atom with axes parallel to those of the standard frame.¹ For discussing piezoelectricity, the test of "sameness" before and after transformation is this: two arrangements use the "same" if they diffract x-ray beams in the "same" way. (For magnetic properties, this is not a sufficient test of "sameness," since the nuclear spins could be different in the two cases, but the x-ray diffraction patterns could be the same).

Which transformations can be symmetry transformations depends on the structure of the material. For materials that are the same at all points (homogeneous), the kind we hypothesize, only those transformations that perform the same point operation at each point in the material can possibly be symmetry transformations. Only orthogonal transformations can do this. Therefore, in discussing symmetry transformations in homogeneous material, we will only consider transformations that are also orthogonal.

For simplicity in describing the symmetry transformation of a material, we will ignore its boundaries and assume it extends infinitely in all directions. Assuming all bodies to be infinite permits translation to be

¹Arthur Cracknell, Crystals and Their Structures, Pergamon Press, pp. 180-208.

a symmetry transformation, since no non-zero, rigid-body translation can move every atom on the boundary of a finite body to a position occupied by another atom before translation. This assumption or approximation is excellent in any macroscopic-sized piece of material when considered from an atomic viewpoint.

Suppose a certain orthogonal transformation is also a symmetry transformation in a particular homogeneous material. Then we say that the point-operational part of the orthogonal symmetry transformation is a point symmetry operation of the material.¹ For present purposes we ignore the translational part of the symmetry transformation, since only the point-operational part affects the material's physical properties.²

Some point symmetry operations, like rotations, can be easily done in the laboratory. Others, like inversions through a point, cannot really be done in the laboratory, since they would require ripping the material apart and reassembling it atom-by-atom.

¹Even if the point operation when acting alone is not a symmetry transformation of the material, we still say the material has it as a point symmetry because its physical properties have the same form as a material which has this point operation acting alone as a symmetry operation. Thus, e.g., if a material has a 4-fold, screw axis as a symmetry transformation, we say it has a 4-fold, rotational axis as a point symmetry operation.

²Nye, p. 278.

The point symmetry operation can be further divided into two types. Those point symmetry operations that are consistent with regularity in all three dimensions are called the "crystallographic point symmetry operations," e.g., rotation by $(\frac{360^\circ}{2})$ about an axis. These are the only point symmetry operations crystals may have. Those point symmetry operations that are inconsistent with complete order in all three dimensions are the "non-crystallographic point symmetry operations." An example is an ∞ -fold axis of rotation, meaning that every rotation about that axis, no matter what the angle of rotation, is a symmetry operation for the material in question. Textures may have either type of point symmetry operations. Isotropic, amorphous materials not only may, but do in fact have all possible point symmetry operations; for them, every orthogonal transformation is a symmetry transformation, since they were completely disorganized before the transformation and they are completely disorganized afterwards.

Several sets of co-ordinate axes are defined at each point in a solid in order to facilitate the description of its various properties. First, there are what we will call the natural axes. (If we were discussing only crystals, and not also textures, the natural axes would be called the "natural crystallographic axes.") These are defined to coincide with the various planes and axes of the symmetry operations of the material at the point. The natural axes simplify the description of the Miller indices of a crystal's natural planes and plane faces.

Unfortunately the natural axes are often not perpendicular or even three in number. Thus, they are not well-suited to describe macroscopic

physical properties at a point. For describing macroscopic physical properties, we define a new co-ordinate system at the point called the physical axes (OX_1, OX_2, OX_3), which are three in number, mutually perpendicular, right-handed, and have a fixed orientation relative to the natural axes at the point. The exact relation of the physical to the natural axes depends on the point symmetry properties of the material and ~~is~~ described in detail in several texts.¹

The local laboratory axes (X, Y, Z) are the final set of axes centered at each point that we will discuss. The axes are defined not relative to the material's planes and axes of symmetry, but are defined to be parallel to the corresponding axes in the standard, laboratory frame, which is fixed in the laboratory. These axes are also three in number, perpendicular, and right-handed; but they may be rotated relative to the physical axes. Equations describing physical processes in a material are written using the local and standard laboratory axes, since they remain fixed relative to the laboratory itself, even if the sample is rotated; however, the natural and physical axes move relative to the laboratory every time we rotate the sample.

¹Nye, pp. 280-1.

D. Cartesian Tensors¹

A "Cartesian tensor at point $\vec{r}$ " is, in a rough sense, an array of numbers that measures some physical property at a particular point or atom of the material, whose location relative to the Cartesian, standard, laboratory frame is given by position vector $\vec{r}$. The term "atom" in this context merely means a point of the material itself, which moves during a transformation, in distinction to a point in space which remains stationary. (We will refer to "Cartesian tensors" simply as "tensors" for brevity.) The numbers in the tensor array are measured relative to the local Cartesian laboratory frame centered on the atom in question and with axes parallel to the co-ordinate axes of the Cartesian standard laboratory frame centered elsewhere. (See figure(2D:1).) All tensor properties, e.g., stress, electric field, etc., are measured in this way at each point.

In contrast to other methods of describing these properties, tensor representation has the advantage that it easily predicts how the elements of the tensor will change after an orthogonal transformation is performed on the material. As we will see later, the elements of a tensor do not change due to mere translation; only the point operation of the orthogonal transformation affects their value. Obviously, then, there must be some relation between tensors and point symmetry operations, since both involve point operations. We will return to this subject in the next section.

Up to now we have only described tensors in a rough way; but before we can define precisely what a Cartesian tensor is, we need to define a

¹Nye, pp. 3-30.

Figure (2D:1)
How Cartesian Tensors are Defined

related concept, the "transformation matrix" ($A_{i'i}$) or Jacobian of an orthogonal transformation at an atom whose position before transformation is $\vec{r}$. Before transformation, we define a local laboratory frame at point $\vec{r}$ in the usual way, with axes parallel to those of the standard laboratory frame. (See figure (2D:2).) To facilitate the definition, we imagine that this original local laboratory frame is painted on the surrounding atoms and then moves with the material during the orthogonal transformation.

Because the transformation is orthogonal and preserves straight lines and the angles between them, the painted lines remain straight and mutually perpendicular after the transformation.¹ However, the painted lines are not necessarily parallel to the axes of the standard laboratory frame after transformation. Since, by definition, Cartesian tensors must always be measured at each point in a Cartesian laboratory frame with axes parallel to those of the standard laboratory frame, a new Cartesian laboratory frame must be defined at the atom in question after transformation.

For clarity we will denote with unprimed numbers the painted lines that were parallel to the axes of the standard laboratory frame before the material was transformed, and we denote with primed numbers the axes of the laboratory frame at the same atom after the orthogonal transformation of the material. Since the standard laboratory axes stayed fixed during the transformation, the relation of the primed and unprimed axes must somehow tell what the transformation did to the material. The

¹Even if the transformation were not orthogonal, the painted lines would still be straight in the immediate neighborhood of the atom,⁰ but they would not, in general, be perpendicular. However, a transformation matrix could be defined for this non-orthogonal transformation in a manner analogous to the one for the orthogonal transformation discussed in the text.

Figure (2D:2)

Diagram Defining the Transformation Matrix of an Orthogonal Transformation

transformation matrix $(A_{i',i})$, or Jacobian, embodies this information. $(A_{i',i})$ is defined by the following expression:

$$(A_{i',i}) = \begin{pmatrix} \cos \angle(X',X) & \cos \angle(X',Y) & \cos \angle(X',Z) \\ \cos \angle(Y',X) & \cos \angle(Y',Y) & \cos \angle(Y',Z) \\ \cos \angle(Z',X) & \cos \angle(Z',Y) & \cos \angle(Z',Z) \end{pmatrix}$$

where $\angle(i',i)$ is the angle from the i' th axis in the primed frame to the i th axis in the unprimed frame. The symbols i' and i , which stand for any axis in the primed and unprimed frames, respectively, need not have the same numerical value (1, 2, or 3) at any one time.

Because we define $(A_{i',i})$ for an orthogonal transformation of the material, $(A_{i',i})$ is the same at each atom. This follows because at each atom $(A_{i',i})$ is completely determined by the angles between the axes of two different cartesian frames centered at that atom after transformation. One frame is the laboratory frame defined after transformation at that atom, and the other frame is the "painted lines" which label those atoms that originally lay on the axes of the laboratory frame before transformation at the atom in question. The laboratory frames defined after transformation at all atoms are mutually parallel, and the painted-line frames at all atoms are also mutually parallel after transformation. Therefore, the angles between the axes of these two types of frames must be the same at each point.

The reason the laboratory frames after transformation are mutually parallel at all atoms is that each is constructed parallel to the axes of the standard laboratory, and lines parallel to the same line are parallel.

to each other. The "painted line" frames are mutually parallel after transformation because they were constructed before transformation to be mutually parallel and the orthogonal transformation rotated the atoms surrounding each atom in the same way so they remain mutually parallel afterwards, too. Only orthogonal transformations do this.

With this definition of the transformation matrix in hand, we can proceed to define precisely a Cartesian tensor of rank N at a point located by position vector $\vec{r}$. It is an array of numbers or elements, $T_{i_1 i_2 \dots i_N}$ (where $i_1, i_2, \dots, i_N$ take on values 1, 2, or 3) which describes some physical property at point $\vec{r}$ measured relative to the local laboratory frame centered at the point $\vec{r}$ and which must satisfy both of these two criteria:

1. Criterion 1: The number of elements in the array must be 3^N .

This result follows because the number of subscripts is N and each can take on any one of three values, 1, 2, or 3, giving 3^N different possible subscripts. Thus, we see, the rank of the tensor is the same as the number of its subscripts, providing these subscripts can only assume the values 1, 2, or 3.

2. Criterion 2: The elements, $T'_{i'j' \dots}$, of the tensor defined at a certain atom after an orthogonal transformation are related to the elements, $T_{ij \dots}$, of the same tensor property before transformation according to the following pattern. Both measurements are performed in a local, Cartesian laboratory frame centered on the same atom with axes parallel to those of the standard laboratory frame at the time of measurement.

<u>Rank of Tensor</u>	<u>Relation of New and Old Values</u>
1	$T'_{i'_1 1} = \sum_{i_1} A_{i'_1 i_1} T_{i_1 1}$
2	$T'_{i'_1 i'_2 1 2} = \sum_{i_1 i_2} \sum_{i'_1 i'_2} A_{i'_1 i_1} A_{i'_2 i_2} T_{i_1 i_2 1 2}$
$\vdots$	$\vdots$
N	$T'_{i'_1 i'_2 \dots i'_N} = \sum_{i_1 i_2} \dots \sum_{i_N} A_{i'_1 i_1} A_{i'_2 i_2} \dots A_{i'_N i_N} T_{i_1 i_2 \dots i_N}$

By this scheme we can calculate the elements of the new array in terms of the known elements of the old one. Summing over a dummy index, like i_1 , is called contraction.

Mere translation does not change the value of the elements of a tensor at a given atom. We can verify this statement analytically by noting that if there is only translation, the local laboratory axes of each atom before and after orthogonal transformation must be parallel. Therefore,

$$(A_{ij}) = \begin{bmatrix} \cos 0^\circ & \cos 90^\circ & \cos 90^\circ \\ \cos 90^\circ & \cos 0^\circ & \cos 90^\circ \\ \cos 90^\circ & \cos 90^\circ & \cos 0^\circ \end{bmatrix}$$

$$(A_{ij}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Or in terms of elements, rather than whole arrays, this says

$$A_{ij} = \delta_{ij}$$

where δ_{ij} = Kronecker delta. This implies that the elements of the tensor at the atom must change as follows:

$$T'_{i'j'k'} = \delta_{i'i} \delta_{j'j} \delta_{k'k} T_{ijk}$$

or

$$T'_{i'j'k'} = 1 \cdot 1 \cdot 1 T_{i'j'k'}$$

That is, each element of the tensor measured after transformation is exactly the same as the corresponding element measured before transformation.

Since the elements of the tensor at a given atom do in general change following an orthogonal transformation, it must be that they are only sensitive to the point operation part of the orthogonal transformation, because they are insensitive to the only other part of the transformation, viz., the translation.

There is a relation between tensors and matrices. Both are arrays of numbers; but matrices are those that can be tabulated in two or less dimensions, i.e., they have at most two subscripts, and also follow the usual rules for adding or multiplying together such two-dimensional arrays.¹ Tensors of rank two or less are matrices; and, therefore, matrix algebra applies to them. Tensors of rank over two are not matrices; and, therefore, matrix algebra does not apply directly to them. Sometimes it is possible to express a rank three tensor in matrix form, i.e., using only two subscripts. When we can do this, we acquire the big advantage of being able to apply the proven theorems of matrix algebra to our newly formed matrix. Later on we will use this technique to develop our equations of piezoelectricity.

Some important "do's" and don't's" govern the writing of tensor equations, such as the following²

$$D_i = d_{ijk} T_{jk}$$

¹Mary Boas, Mathematical Methods in the Physical Sciences, pp. 96-104.

²Nye, pp. 7-8.

1. Subscripts may only have the values 1, 2, or 3, unless otherwise stated.
2. A subscript that is repeated two or more times in two different factors of one term should be summed even if the summation sign does not appear (Einstein convention). Such a subscript is called a dummy or umbral index.
3. Indices that are not summed (free indices) should be the same on both sides of the equation.
4. The order of subscripts in any one factor of a term is important, i.e., a different order means something else.
5. The order of factors in a term is not important, i.e., a different order means the same thing.
6. Parentheses around a term or factor, e.g., (σ_{ij}) , indicate we are thinking of the whole array, not just one element in it.

We know $(A_{i'j})$ is the matrix that allows us to predict the primed elements of a tensor after orthogonal transformation of the material if we know what the unprimed elements were before transformation. For example, in the case of a second-rank tensor,

$$T_{i'j'} = A_{i'i} A_{j'j} T_{ij} .$$

There must be another matrix $(b_{ii'})$ that will allow us to go backward and calculate what the unprimed elements before transformation were by knowing what the primed elements are afterwards, e.g., in the case of second-rank tensors:

$$T_{ij} = b_{ii'} b_{jj'} T_{i'j'} .$$

The relation between $(b_{ii'})$ and $(A_{i'i})$ is simply¹

$$b_{ii'} = A_{i'i}.$$

Therefore, in the case of our example, a second-rank tensor,

$$T_{ij} = A_{i'i} A_{j'j} T_{i'j'}.$$

This fact will be used later on.

There is a very important theorem that we will use over and over about a tensor A of rank α which is produced by contracting another tensor B of rank β with an array C . Schematically we write

$$A = CB.$$

The theorem states that

1. Array C is also a tensor
2. The rank of C is $(\alpha + \beta)$.

The proof is found in Appendix A.

¹Nye, p. 10.

E. Relation of Cartesian Tensors and Point Symmetry Operations¹

Tensors and point symmetry operations must be related, since both deal with point operations. Tensors are concerned with all possible orthogonal point transformations, some of which may also be symmetry operations for the particular material concerned, i.e., they also leave the apparent arrangement of the material unchanged. As we shall see next, the relation of tensors and point symmetry is that once the point symmetry operations of a homogeneous material are known, it is possible, using a principle known as Neumann's Principle, to predict the form of tensors measuring the intrinsic properties of that material at each atom. That is, we can predict which elements of the tensor are zero and what the relationship of the non-zero elements is.

Neumann's Principle says that if an orthogonal transformation which is also a symmetry operation is performed on a body, then every element of each intrinsic tensor measured at any particular atom of the body will have exactly the same value after transformation as it did before transformation. The principle assumes the intrinsic tensors at each point are measured relative to a local laboratory frame centered at the particular atom in question and with axes parallel to those of the standard laboratory frame at the time of measurement. This invariance is reasonable because as far as an observer using x-ray diffraction in the laboratory frame can tell, the body is the same now, after transformation, as it was before transformation.

Let us take an example to see how the form of a tensor is determined by the point symmetry properties of a material. We will show if a material

¹Nye, pp. 3-30.

has inversion point symmetry at each point in it, then all the elements of any third-rank tensor are zero. This theorem nicely illustrates the method of determining the form of tensor properties, but it is an important result in its own right: since the piezoelectric coefficients are--as we shall see later--a third-rank tensor, this theorem shows the piezoelectric coefficients must be zero in all materials that have point inversion symmetry, like crystals of NaCl. No matter what the point transformation of the material is, all third-rank tensors at each atom change in the following way, when the body is orthogonally transformed:

$$T'_{i'j'k'} = A_{i'i} A_{j'j} A_{k'k} T_{ijk} \quad (2E:1)$$

If that point transformation is also a symmetry operation, then according to Neumann's principle we cannot detect any change in tensors measured relative to the laboratory axes, i.e.,

$$T'_{i'j'k'} = T_{i'j'k'} \quad (2E:2)$$

Substituting this expression in the previous equation, we see that for point symmetry operations

$$T'_{i'j'k'} = T_{i'j'k'} = A_{i'i} A_{j'j} A_{k'k} T_{ijk} \quad (2E:3)$$

To solve this equation, we next need to find $(A_{i'i})$ for point inversion; from figure (2E:1) we see

$$(A_{i'i}) = \begin{pmatrix} \cos (X',X) & \cos (X',Y) & \cos (X',Z) \\ \cos (Y',X) & \cos (Y',Y) & \cos (Y',Z) \\ \cos (Z',X) & \cos (Z',Y) & \cos (Z',Z) \end{pmatrix}$$

$$(A_{i'i}) = \begin{pmatrix} \cos 180^\circ & \cos 90^\circ & \cos 90^\circ \\ \cos 90^\circ & \cos 180^\circ & \cos 90^\circ \\ \cos 90^\circ & \cos 90^\circ & \cos 180^\circ \end{pmatrix}$$

Figure (2E:1)

Calculating the Transformation Matrix for the
Point Inversion Transformation

$$(A_{i,i}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$(A_{i,i}) = -(\delta_{i,i}) .$$

Thus, the individual elements of $(A_{i,i})$ are:

$$A_{i,i} = -\delta_{i,i} \quad (2E-4)$$

Next, let us use the expression for $(A_{i,i})$ to find one of the elements of tensor, e.g., T'_{123} , after transformation. Using equation (2E-4)

$$T_{123} = T'_{123} = A_{1i}A_{2j}A_{3k}T_{ijk}$$

Doing the summation first over k, we obtain,

$$T_{123} = A_{1i}A_{2j}(A_{31}T_{ij1} + A_{32}T_{ij2} + A_{33}T_{ij3})$$

$$T_{123} = A_{1i}A_{2j}(0T_{ij1} + 0T_{ij2} + (-1)T_{ij3})$$

$$T_{123} = A_{1i}A_{2j}(-1)T_{ij3}$$

Performing the summation over j gives us

$$T_{123} = A_{1i}(-1)(A_{21}T_{i13} + A_{22}T_{i23} + A_{23}T_{i33})$$

$$T_{123} = A_{1i}(-1)(0T_{i13} + (-1)T_{i23} + 0T_{i33})$$

$$T_{123} = A_{1i}(-1)^2T_{i23}$$

Finally, the summation over i is carried out and yields:

$$T_{123} = (+1)(A_{11}T_{123} + A_{12}T_{223} + A_{13}T_{323})$$

$$T_{123} = (+1)(-1T_{123} + 0T_{223} + 0T_{323})$$

$$T_{123} = -T_{123}$$

Thus,

$$2T_{123} = 0$$

or

$$T_{123} = 0$$

This result holds true for all elements of T_{ijk} . However, we can obtain that result in a much faster way than by solving for each individual element of $(T'_{i'j'k'})$ as we have done above. Instead let us make use of the equation

$$A_{i'i} = -\delta_{i'i} \dots$$

Using this relation in equation (2E:3), we obtain

$$T_{i'j'k'} = (-\delta_{i'i})(-\delta_{j'j})(-\delta_{k'k})T_{ijk}$$

$$T_{i'j'k'} = (-1)T_{i'j'k'}$$

$$2 T_{i'j'k'} = 0$$

$$T_{i'j'k'} = 0 \dots$$

Thus, all elements of any third-rank tensor in a material with inversion point symmetry must be zero. Q.E.D.

There is one common confusion about Neumann's principle which we wish to avoid. Neumann's principle does not say that the point symmetry operations of matter determine the form of all possible tensor properties that can exist in that material but only those properties which are intrinsic, i.e., are determined solely by the material itself. Thus, point symmetry operations would indeed determine the form of a material's electrical conductivity tensor (a second-rank tensor) which is an intrinsic property of the material. However, symmetry properties would not determine what form the electric field (a first-rank tensor) might have, since the electric field is applied from outside the material by means of capacitors, batteries, etc., and, thus, depends on factors other than the material itself.

If a material is homogeneous and Neumann's principle is used to determine the form of intrinsic tensor properties of the material at one point, then these tensor properties must have the same form at all other points in the body, too.

To record the form of tensors determined by applying Neumann's principle, we use a method illustrated in this example

$$\begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix} = \begin{pmatrix} T_{11} & T_{11} \\ 0 & T_{22} \end{pmatrix}.$$

Normally only the expression on the right would be written. If an element is recorded in a position other than its original one, that element is equal to the original one, e.g., T_{11} in the (1, 2) position means $T_{12} = T_{11}$. A zero in a certain place means the element naturally occurring there is zero, e.g., in our illustration $T_{21} = 0$.

In this section we have seen that if we know the x-ray diffraction pattern of a certain material, i.e., its point symmetry operations, we can predict the form of all its intrinsic tensor properties by using Neumann's principle.

F. Stress¹

Stress at a point is an important concept in piezoelectricity and is also a good example of a second-rank tensor quantity.

When is a body in a state of stress? When one section of the body exerts contact forces on adjacent parts. Forces acting on the surface of the body or non-uniform heating can put a body in a state of stress.

Stress at a point $\vec{r}$ is described mathematically by a second-rank tensor defined as follows: Imagine a local Cartesian frame centered at $\vec{r}$ and the body then divided in two in your imagination by one of the co-ordinate planes of this local frame as in figure (2F:1). Each half of the body exerts equal and opposite contact forces on the other half across the dividing plane according to Newton's third law. Calculate the force per unit area one-half of the body exerts on the other half at point $\vec{r}$. Now select either half as the reference half of the body and resolve the force per unit area exerted on the reference half at $\vec{r}$ into three components along each of the three co-ordinate axes of local Cartesian frame at $\vec{r}$. The component perpendicular to the dividing plane is the "normal" component of the force per unit area. The other two components lying in the dividing plane are the "shear" components. If this procedure is repeated for each of the three co-ordinate planes at point $\vec{r}$, a total of nine numbers is generated, three components for each of the three co-ordinate planes. These nine numbers measure the stress at point $\vec{r}$ and are the stress tensor (σ_{ij}) .

The components of the tensor are named this way. The first subscript, i , names the co-ordinate plane along which the imaginary cut is made; this

¹Nye, p. 82; Arthur Boresi, Elasticity in Engineering Mechanics, pp. 35-62.

Figure (2F:1)

How Stress is Defined at a Point in a Body

plane is identified by telling the axis "i" to which it is perpendicular. The second subscript, j, names the direction "j" along which the component of the force per unit area points.

Positive and negative signs are assigned to the components of (σ_{ij}) according to this convention. The normal component of stress is always positive in the direction of the outward normal to the dividing plane, but the positive directions of the shear components are a little complicated. If the reference half of the body is chosen so that the outward normal at $\vec{r}$ is along the positive direction of the co-ordinate axis perpendicular to the dividing plane, then the shear components are positive along the positive directions of the co-ordinate axes lying in the dividing plane. However, if the reference half of the body is chosen so that the outward normal at $\vec{r}$ is along the negative direction of the co-ordinate axis perpendicular to the dividing plane, then the shear components are positive along the negative directions of the co-ordinate axes lying in the dividing plane.

The stress at a point in a body is not a vector quantity, like force; instead it is a new type of quantity, a second-rank, symmetric tensor.

"Symmetric" means that

$$\sigma_{ij} = \sigma_{ji}$$

and this is true even if the body is not in equilibrium, even if the stress is non-homogeneous, and even if body forces act, providing only that no body torques act.¹

¹Boresi, p. 35.

Stress is not a vector quantity because if it were, then by knowing the components of the force/unit area with respect to one co-ordinate plane at point $\vec{r}$, we would be able to calculate, as we can for a vector, what the components would be with respect to all planes passing through $\vec{r}$. We cannot do this, since there could be equal and opposite forces acting in the reference half body parallel to the first co-ordinate plane that would make no contribution to the force/unit area measured relative to that particular co-ordinate plane, but would make contributions to the force/unit area acting on other co-ordinate planes at the same point $\vec{r}$.

One particularly important, special kind of stress at a point $\vec{r}$ is plane stress. This means that at the point $\vec{r}$ it is possible to find a plane so that all components of the force/unit area, relative to this plane are zero, as they would be, for example, relative to the free surface of a metal in vacuum. If all points in a body are in plane stress and all the reference planes for plane stress at all points are parallel to each other, the body as a whole is said to be in a state of plane stress. In our later experiments, we will be able to make the approximation that our samples bars are in plane stress.

The main point to remember is that stress at a point is always a second-rank tensor and almost always it is symmetric, too.

G. Strain¹

Strain at a point in a body is another symmetric, second-rank tensor that is important in piezoelectricity.

A body is said to be in a "state of strain" when it is deformed, i.e., when its shape is changed. Deformation could be caused by externally applied forces or by heating the body either uniformly or non-uniformly. In this discussion we will assume all deformations are small because although the discussion could be carried through for arbitrarily big deformations, only in the case of small deformations can a simple, physical picture be presented. Besides, this was the type of deformation that actually occurred in our experiments.

The strain tensor, (ϵ_{ij}) , is the means we use to describe the state of strain at each point $\vec{r}$ in a body. The strain tensor ignores any rigid body motion and considers only true deformations of the body. It is defined as follows. Imagine a local Cartesian frame centered at atom "A" located at point $\vec{r}$ before deformation. After deformation, the atoms that originally lay on the axes of the local Cartesian frame before deformation still lie on straight lines, emanating from the transposed atom A, at least in the immediate neighborhood of that atom. However, these lines are no longer necessarily perpendicular. To understand the meaning of the off-diagonal elements of the strain tensor, consider one typical element, ϵ_{xy} . ϵ_{xy} is one-half the angle, γ_{xy} , by which the lines of atoms originally lying along the X- and Y-axes, the axes mentioned in

¹Boresi, pp. 63-101.

Figure (2G:1)
How Strain is Defined in a Body

original local
Cartesian frame

the subscript, before deformation are no longer perpendicular after transformation. That is

$$\epsilon_{xy} = (1/2)\gamma_{xy}$$

Analogous definitions apply to all other off-diagonal elements. Each element lying on the principal diagonal of the strain tensor (e.g., ϵ_{xx}) is the linear stretch/unit length of the line of atoms that originally lay on the axis mentioned in the subscript (e.g., the X-axis) before deformation.

Thus, the strain tensor, (ϵ_{ij}) , can also be written

$$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{pmatrix} = \begin{pmatrix} \epsilon_{11} & (1/2)\gamma_{12} & (1/2)\gamma_{13} \\ (1/2)\gamma_{21} & \epsilon_{22} & (1/2)\gamma_{23} \\ (1/2)\gamma_{31} & (1/2)\gamma_{32} & \epsilon_{33} \end{pmatrix}$$

and it is also symmetric, i.e.,

$$\epsilon_{ij} = \epsilon_{ji}$$

To avoid confusion, it is worthwhile to remember that there is another similar array of numbers--sometimes used in engineering work--which also describes the strain at point $\vec{r}$, but is not a second-rank tensor, viz.,

$$\begin{pmatrix} \epsilon_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{21} & \epsilon_{22} & \gamma_{23} \\ \gamma_{31} & \gamma_{32} & \epsilon_{33} \end{pmatrix}$$

This array is not a tensor because it doesn't obey the tensor transformation rules. The difference between this array and the strain tensor is that each of its off-diagonal terms is the total angle γ_{ij} rather than $(1/2)\gamma_{ij}$.

Thus both the stress and the strain at a point $\vec{r}$ are symmetric second-rank tensors.

H. Relation of Stress and Strain¹

In general both stress and strain tensors may exist simultaneously at a point $\vec{r}$ in a body. (However, it is possible to have a non-zero stress while the strain at the same point is zero, and vice versa, by heating the body in various ways.) Since both these tensors coexist at each point, there should be some relations between them, and this is what we will discuss in this section. We assume throughout this section that the deformations are small.

Uniqueness Theorem: Often there is no step-by-step method for finding the stress and strain at each point in a body; a certain amount of scientific guesswork is needed. Having guessed an answer and checked that it meets all the boundary conditions, how do we know it is the solution the body actually obeys? How do we know there isn't some other solution for stress and strain at each point which also meets all the boundary conditions and which is the one that the body really obeys? The uniqueness theorem tells us how to decide: if the proposed solution for stress and strain meets the following three conditions, it is the unique and correct solution for stress and strain. We do not have to worry about there being any other "good" solutions; there aren't any.

The three necessary and sufficient conditions are these:

1. The components of the proposed stress tensor at each point must satisfy the equations of motion, which are nothing more than Newton's second law rewritten in terms of stresses and body forces. They say²

¹Boresi, pp. 102-126, pp. 90-91.

²Boresi, p. 57.

$$\frac{\partial \sigma_{XX}}{\partial X} + \frac{\partial \sigma_{XY}}{\partial Y} + \frac{\partial \sigma_{XZ}}{\partial Z} + B_X = \rho \frac{\partial^2 U}{\partial t^2}$$

$$\frac{\partial \sigma_{YX}}{\partial X} + \frac{\partial \sigma_{YY}}{\partial Y} + \frac{\partial \sigma_{YZ}}{\partial Z} + B_Y = \rho \frac{\partial^2 V}{\partial t^2}$$

$$\frac{\partial \sigma_{ZX}}{\partial X} + \frac{\partial \sigma_{ZY}}{\partial Y} + \frac{\partial \sigma_{ZZ}}{\partial Z} + B_Z = \rho \frac{\partial^2 W}{\partial t^2}$$

where:

(B_X, B_Y, B_Z) = components of the body forces/unit volume acting at point $\vec{r}$.

(U, V, W) = components of the displacement of the atom initially at point $\vec{r}$ caused by the deformation.

Usually we can neglect the body forces/unit volume in relation to (σ_{ij}) , and also usually the body does not accelerate, making U, V , and W all equal to zero. The equations thus simply reduce to

$$\frac{\partial \sigma_{XX}}{\partial X} + \frac{\partial \sigma_{XY}}{\partial Y} + \frac{\partial \sigma_{XZ}}{\partial Z} = 0$$

$$\frac{\partial \sigma_{YX}}{\partial X} + \frac{\partial \sigma_{YY}}{\partial Y} + \frac{\partial \sigma_{YZ}}{\partial Z} = 0$$

$$\frac{\partial \sigma_{ZX}}{\partial X} + \frac{\partial \sigma_{ZY}}{\partial Y} + \frac{\partial \sigma_{ZZ}}{\partial Z} = 0$$

and now they are called the equilibrium equations.

2. The components of the proposed strain tensor must satisfy these equations (called the compatibility equations) at each point in the body, viz.

$$\begin{aligned} \frac{\partial^2 \epsilon_{XX}}{\partial Y^2} + \frac{\partial^2 \epsilon_{YY}}{\partial X^2} &= \frac{\partial^2 \epsilon_{XY}}{\partial X \partial Y} \\ \frac{\partial^2 \epsilon_{YY}}{\partial Z^2} + \frac{\partial^2 \epsilon_{ZZ}}{\partial Y^2} &= \frac{\partial^2 \epsilon_{YZ}}{\partial Y \partial Z} \\ \frac{\partial^2 \epsilon_{ZZ}}{\partial X^2} + \frac{\partial^2 \epsilon_{XX}}{\partial Z^2} &= \frac{\partial^2 \epsilon_{ZX}}{\partial Z \partial X} \end{aligned}$$

$$\begin{aligned}
2 \frac{\partial^2 \epsilon_{XX}}{\partial Y \partial Z} &= \frac{\partial}{\partial X} \left(- \frac{\partial \gamma_{YZ}}{\partial X} + \frac{\partial \gamma_{XZ}}{\partial Y} + \frac{\partial \gamma_{XY}}{\partial Z} \right) \\
2 \frac{\partial^2 \epsilon_{YY}}{\partial Z \partial X} &= \frac{\partial}{\partial Y} \left(- \frac{\partial \gamma_{ZX}}{\partial Y} + \frac{\partial \gamma_{YX}}{\partial Z} + \frac{\partial \gamma_{YZ}}{\partial X} \right) \\
2 \frac{\partial^2 \epsilon_{ZZ}}{\partial X \partial Y} &= \frac{\partial}{\partial Z} \left(- \frac{\partial \gamma_{XY}}{\partial Z} + \frac{\partial \gamma_{ZY}}{\partial X} + \frac{\partial \gamma_{ZX}}{\partial Y} \right)
\end{aligned}$$

The physical significance of the compatibility equation is this. The displacement of each point, which can be calculated by integrating (ϵ_{ij}), is a unique quantity. Thus, it should not depend on whether integration is done with respect to X first, or Y first, or Z first. If (ϵ_{ij}) satisfies the compatibility equations, the independence of the displacement to the order of integration, and, hence, also its uniqueness, are guaranteed. Remembering these equations will be much easier if we keep in mind that the last two equations in each set of equations are just cyclic permutations of the first one.

3. The proposed stresses and strains must satisfy the boundary conditions at the surface of the body.

Hooke's Law: Let us further restrict our problem by assuming that the strain is caused wholly by the stress, not by temperature changes. Also let us assume that our material is perfectly elastic, i.e., if it is deformed slightly by sufficiently small stresses, as soon as the stresses are removed the body will immediately return to its original shape. Under these conditions there is a simple relation between strain and stress at each point in the body known as Hooke's Law, i.e.¹

$$\epsilon_{ij} = S_{ijkl} \sigma_{kl}$$

¹Nye, p. 132.

Since (ϵ_{ij}) and (σ_{kl}) are known to be second-rank tensors, the theorem we proved in appendix A tells us that (S_{ijkl}) is a fourth-rank tensor.

I. Electric Charge

Up to this point, we have not discussed the electrical properties of matter, which are, of course, of prime importance in piezoelectricity. In this and several following sections, this defect will be remedied. However, the description will be, as before, from a macroscopic point of view; i.e., one not making any assumptions about the detailed structure of the particles that constitute the bodies, which may be either gaseous, liquid, or solid.

We distinguish between two kinds of charged particles in material of all kinds; viz., bound charged particles (also called

"bound charges") and free charged particles (also called "free charges"). Free charges are those that are free to move relative to other particles in the body over macroscopic distances. On the other hand, bound charges are tightly incorporated or bound into the molecules of the body. These bound charges may be displaced relative to the other particles in the body only a small distance on the atomic scale, since strong restoring forces soon develop, which halt any further relative displacement. All matter contains bound charge--with the rare exception of some kinds of plasmas. However, not all matter contains free charge, which, when it occurs, usually dominates over the bound charge in determining the electrical behavior of the material.

There is a simple test to determine if a body has free charge in it or not. Place electrodes on the body and with them maintain a uniform and constant electric field in the material. If current continuously flows in the wires leading to the electrodes, free charge must exist and be flowing inside the body. If only a pulse of current, but no steady flow, occurs,

the body contains only bound charge. The greater the current flow during this test, the greater the concentration of free charge in the body.

Matter can be classified according to the kind of charge it contains. If a body contains only bound charge, it is a perfect non-conductor. If it contains an appreciable concentration of free charge, it is a conductor. Our main concern in piezoelectricity is with perfect or nearly-perfect non-conductors, since, as we will see later on, free charge would annihilate the interesting piezoelectric effects these materials possess.

Non-conductors are themselves often classified according to their function. For example, a stone may be called a "paperweight" if it is used to hold down a stack of loose papers in a breezy office; and this same stone may be called a "door stop" if it is used to keep the office door from slamming shut. In the same manner, when a non-conductor is used to prevent free charge from entering or leaving an electrical system, it is called an "insulator." When this same non-conductive material is used to affect the internal functioning of the electrical system, it is called a "dielectric."¹ This is the sense in which Maxwell used these words.² For example, consider the material teflon. If it is wrapped around a 60 Hz power cable, it is an insulator; if it is between the plates of a capacitor, thereby changing the capacitance of the circuit itself and its behavior, it is a dielectric.

¹A. Zaky and R. Hawley, Dielectric Solids, p. 2.

²James Clark Maxwell, A Treatise On Electricity and Magnetism, Volume 1, pp. 34-35.

When we speak of the "density" of various kinds of charge at a point in the body, we refer to the excess of positive over negative charges of the same kind per unit volume at that point--not to the absolute amount of both positive and negative charges per unit volume. For example, the density of bound charge at a point means the density of excess positive bound charge to negative bound (not free and bound) charge at that point.

J. Polarization of Dielectrics and the Related Concepts of Displacement and Dielectric Constant

If the total positive charge is not equal to the total negative charge in a body, the body is said to be "electrically charged," and it will, in general, produce a macroscopic, static electric field. Therefore, if electrodes are placed on its surface, a difference of potential will exist between them.

However, charging a body is not the only way to cause it to produce a macroscopic, static electric field. For example, imagine a neutral body; i.e., one with equal total

positive and negative charge, and also imagine that initially the charges are distributed so that in every small volume of the body there are equal amounts of positive and negative charge. This body does not produce a macroscopic electric field. Now, without adding or removing any charge, rearrange the charges so that some small volumes have excess positive charge and, of course, others have excess negative charge. This rearrangement of charges now causes this neutral body to produce a static, macroscopic electric field although it has no excess charge as a whole. Redistributing charges in a neutral body in this way, so that various small regions contain excess positive or negative charge, is called "induction." If free charge is the kind that is redistributed, the process is named "induction by conduction;" and if bound charge is redistributed, the process is known as "induction by polarization" or just "polarization."¹ In a perfect non-conductor the only kind of induction

¹R. G. Fowler, Introduction to Electric Theory, pp. 56-61.

that can occur is "induction by polarization" because the only kind of charge that exists in it is bound charge.

To measure the amount of polarization that has occurred at each point in a conductor or non-conductor, we define a vector quantity, the polarization vector, in this way. During the induction, a current, $\vec{j}_B(\vec{r}, t)$, of bound charge flows, in general, for a brief while at each point. Just as in the concept of charge density, currents are the difference between positive charge moving in a certain direction and negative charges moving in the same direction, of course, per unit time per unit area. The polarization vector, $\vec{P}$, at point $\vec{r}$ at time t , is¹

$$\vec{P}(\vec{r}, t) = \int_0^t \vec{j}_B(\vec{r}, t') dt', \quad (2J:1)$$

We assume here that prior to $t = 0$ no bound charges had flowed. If some had flowed previously, the integral on the right-hand side is the change in the polarization vector from time 0 to time t rather than the total polarization vector. In other words, the polarization vector at point $\vec{r}$ at time t is the total, net-positive, bound charge per unit area that has passed that point up to time t , where the unit area is taken perpendicular to the direction of charge flow. $\vec{P}$ is also a rank-one tensor.

There is another well-known definition of the polarization vector at point $\vec{r}$, i.e., the total dipole moment per unit volume. This definition focuses on the details of the atomic structure in mentioning dipoles and so is better suited to an atomic or microscopic description of polarization than the macroscopic description given in this thesis. Therefore,

¹Maxwell, p. 65.

this microscopic definition will not be used subsequently in this thesis. Abraham and Becker show that the microscopic definition of $\vec{P}$ and the macroscopic definition are entirely equivalent.¹

Parenthetically, it is worthwhile to note that if a little free charge also existed in the polarized dielectric, the free charge would tend to flow toward the regions of excess positive and negative bound charge and neutralize them. This result would destroy the macroscopic electric field of the polarized dielectric. Possible effects of this kind justify the statement above, that free charge will in general mask or dominate the effects of bound charge in a body.

How can a dielectric be polarized? From reading the usual textbooks on electrodynamics, one would think that the only method is by placing the dielectric in a pre-existing electric field. Actually any agency or "force" that is capable of moving bound charge can cause polarization, e.g., mechanical stress and temperature changes. Symbolically we can state the same idea in this way $\vec{P}(\vec{r}, t) = \vec{P}^E(\vec{r}, t) + \vec{P}^\sigma(\vec{r}, t) + \vec{P}^t(\vec{r}, t) + \vec{P}^{etc}(\vec{r}, t)$ i.e., the total polarization, $\vec{P}$, is the sum of many contributions. $\vec{P}^E$ is the contribution of just the externally-applied electric field, $\vec{E}$; $\vec{P}^\sigma$ is the contribution of just mechanical stresses (σ_{ij}), etc.

In general, the relation between the various causes of polarization and the polarization components they produce is complicated in two ways. First the equations are not usually linear. Sometimes it is a reasonable

¹Max Abraham and Richard Becker, The Classical Theory of Electricity and Magnetism, p. 73.

approximation to say they are linearly related, for example; sometimes in the case of polarization caused by $\vec{E}$,

$$\vec{P}_i(\vec{r}) = \epsilon_0 \chi_{ij} E_j(\vec{r})$$

where $(\epsilon_0 \chi_{ij})$ is the constant or tensor of proportionality. However, even if cause and effect are linearly related, the second complication of the involved relationship still appears, viz., the time relations. Notice that in the above example equation, time is not specifically mentioned, only the position $\vec{r}$ is denoted. This is because as the equation stands with χ_{ij} assumed to be a real number, the equation only applies to equilibrium states; it is not true during the change from one equilibrium state to another. The reason is simply that a dielectric cannot in general change its polarization fast enough to keep up with changes in the various causes of polarization. It is necessary to wait for a while after suddenly changing a cause for the resulting polarization to reach a steady level. Thankfully, we will deal only with equilibrium states in our experiments and theories, i.e., d.c. conditions; and so we can ignore this perplexing problem of time relations. However, a further discussion of this problem is given in Appendix F. Although polarization caused by an electric field was taken as an example, the same considerations apply to all other causes of polarization.¹

To summarize, textbooks which give the equation

$$P_i = \epsilon_0 \chi_{ij} E_j$$

make the assumptions:

¹In fact, the same two complications exist in all the constitutive equations associated with Maxwell's four equations of electromagnetism. However, Maxwell's equations themselves do not suffer these complications, i.e., they are exact and the "effects" are always in phase with their "causes."

1. That the only significant cause of polarization is the externally applied electric field, although there are many other possible causes.
2. That for the particular material in question, it is possible to linearize the relation of $\vec{P}$ and $\vec{E}$. In general the relation is non-linear.
3. That equilibrium conditions prevail. This equation does not in general apply as written during transitions from one equilibrium state to another.

There are two very important theorems relating the density of bound charge at a point in a dielectric to the polarization vector at the point. If the point $\vec{r}$ is in the interior of the dielectric body, the relation is

$$\rho_B(\vec{r}, t) = -\vec{\nabla} \cdot \vec{P}(\vec{r}, t)$$

where

$$\rho_B(\vec{r}, t) = \text{volume density of bound charge at point } \vec{r} \text{ at time } t.$$

If the point $\vec{r}$ is on the surface of the dielectric body, the relation is

$$\sigma_B(\vec{r}, t) = + \vec{P}(\vec{r}, t) \cdot \hat{n}_{\text{out}}(\vec{r}, t)$$

where

$$\sigma_B(\vec{r}, t) = \text{surface density of bound charge at point } \vec{r} \text{ at time } t$$

$$\hat{n}_{\text{out}}(\vec{r}, t) = \text{outward-directed normal vector to the surface at point } \vec{r} \text{ at time } t.$$

Both these theorems can be proved by applying the principle of conservation of bound charge to a small Gaussian surface surrounding the point in question and by using the previous definition of polarization to calculate

the net positive bound charge flowing into the surface.¹

Related to the dielectric polarization vector is another concept, the displacement vector, $\vec{D}$. In most textbooks all that is said about the physical meaning of $\vec{D}$ is to state its definition,

$$\vec{D}(\vec{r}, t) = \epsilon_0 \vec{E}(\vec{r}, t) + \vec{P}(\vec{r}, t)$$

where

$\vec{E}(\vec{r}, t)$ = macroscopic electric field at point $\vec{r}$ at time t

ϵ_0 = permittivity of free space, a constant.

The reason more is not said is that to give $\vec{D}$ a physical interpretation one must assume the existence of the ether. The ether, according to Maxwell, was an unusual, non-conducting gas that transmitted light waves and that permeated all space, including solid bodies. Thus, Maxwell thought there were two kinds of dielectrics: the ordinary kind, which we call dielectrics today, and a special kind, the ether.¹ The displacement vector at a point $\vec{r}$ was, according to Maxwell, the total dielectric polarization at the point, which consisted of two contributions: $\vec{P}$ from the ordinary dielectric material at the point and $\epsilon_0 \vec{E}$, the polarization of the ether at the point.

Since today we do not believe in the existence of the ether, what can we say $\vec{D}$ means? No simple physical picture exists; it is not simply the part of the total, static electric field due only to free charge.² However $\vec{D}$ does have some very useful properties that are worth mentioning:

¹Abraham, pp. 74-75.

²This is true for several reasons: (1) $\vec{D}$ depends on bound charge, too, because its direction and magnitude can change at an interface between dielectrics where there is only bound charge, (2) if $\vec{D}$ were the electric field produced by static free charge, its curl would have to be zero always, as is true of all static electric fields. Curl $\vec{D}$ is not always zero in static cases, since curl $\vec{P}$ is not always zero in static cases.

1. Although we do not think the ether exists, $\vec{D}$ is a measurable quantity, since $\vec{E}$ and $\vec{P}$, in terms of which it is defined, are both measurable.
2. $\vec{D}$ is the macroscopic variable conjugate to $\vec{E}$. Multiplied together, $\vec{D}$ and $\vec{E}$ give the total energy per unit volume necessary to establish a static electric field at point $\vec{r}$, i.e.,

$$\text{Energy/unit volume} = \frac{1}{2} \vec{D} \cdot \vec{E} = \frac{1}{2} (\epsilon_0 \vec{E} + \vec{P}^{\text{total}}) \cdot \vec{E} = \frac{1}{2} \epsilon_0 E^2 + \frac{1}{2} \vec{P}^{\text{total}} \cdot \vec{E}$$

The first term, $\frac{1}{2} \epsilon_0 E^2$, is the amount of energy per unit volume that would be necessary to establish a static electric field, $\vec{E}$, at $\vec{r}$ if there were no matter present at $\vec{r}$. The second term, $\frac{1}{2} \vec{P}^{\text{total}} \cdot \vec{E}$, gives the extra amount of energy per unit volume that must be supplied to establish the field because of the presence of polarizable matter at $\vec{r}$.

3. There are processes whose description is simplified by using $\vec{D}$ as an independent variable, since it does not change during these processes. Later on in developing our equations for the electric field in piezoelectric samples, we will use $\vec{D}$ for this reason.

$$4. \quad \vec{\nabla} \cdot \vec{D} = \rho_{\text{free}}$$

This fact follows simply from the definition of $\vec{D}$,

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P},$$

Taking the divergence of both sides, we get

$$\vec{\nabla} \cdot \vec{D} = \epsilon_0 \vec{\nabla} \cdot \vec{E} + \vec{\nabla} \cdot \vec{P}.$$

But $\vec{\nabla} \cdot \vec{P}$ is $-\rho_B$. From Gauss' Law, $\epsilon_0 \vec{\nabla} \cdot \vec{E}$ is the total charge density, ρ_{total} , or $(\rho_{\text{free}} + \rho_{\text{bound}})$, at the point $\vec{r}$ in question.

Substituting these facts in the previous equation, we obtain

$$\vec{\nabla} \cdot \vec{D} = \rho_{\text{free}} + \rho_{\text{bound}} - \rho_{\text{bound}}$$

$$\vec{\nabla} \cdot \vec{D} = \rho_{\text{free}} \quad \text{Q.E.D.}$$

Later on we will use this theorem in developing an equation for the static electric field in a piezoelectric material.

A second and final concept related to $\vec{P}$ is the dielectric constant (K_{ij}) at a point $\vec{r}$ in a dielectric body. The dielectric constant is measured in an experiment in which the following assumptions are true:

1. All changes in $\vec{P}$ are caused by $\vec{E}$
2. The components of $\vec{P}$ are linearly related to the components of $\vec{E}$ over the range in which $\vec{E}$ changes
3. The material at $\vec{r}$ is possibly anisotropic so that P_i may depend on components of $\vec{E}$ other than E_i alone.

These three assumptions are expressed by this equation

$$P_i^{\text{total}}(\vec{r}, t) = P_i^E(\vec{r}, t) = \epsilon_0 \chi_{ij} E_j(\vec{r}, t).$$

The dielectric constant attempts to express $\vec{D}$ in terms of $\vec{E}$ in that experiment. The general relation of $\vec{D}$ and $\vec{E}$ is:

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

or in component form

$$D_i = \epsilon_0 E_i + P_i.$$

But in our experiment

$$P_i = P_i^E = \epsilon_0 \chi_{ij} E_j.$$

By substituting the last equation into the general one for D_i , we get:

$$D_i = \epsilon_0 E_i + \epsilon_0 \chi_{ij} E_j.$$

To allow us to factor out E_j , we rewrite the first term as:

$$\epsilon_0 E_i = \epsilon_0 \delta_{ij} E_j$$

where δ_{ij} = Kronecker delta. Using this later expression for $\epsilon_0 E_i$, the equation for D_i becomes

$$D_i = \epsilon_0 \delta_{ij} E_j + \epsilon_0 \chi_{ij} E_j$$

$$D_i = \epsilon_0 (\delta_{ij} + \chi_{ij}) E_j$$

and we define the constant relating D_i and E_j to be the "dielectric constant," i.e., $K_{ij} = \delta_{ij} + \chi_{ij}$. Therefore,

$$D_i = \epsilon_0 K_{ij} E_j$$

Often this is rewritten by combining $\epsilon_0 K_{ij}$ into a single factor ϵ_{ij} called the "permittivity" of the dielectric at point $\vec{r}$, i.e.,

$$D_i = \epsilon_{ij}(\vec{r}, t) E_j(\vec{r}, t)$$

Remember this equation is not the general one relating $\vec{D}$ and $\vec{E}$, which is $\vec{D} = \epsilon_0 \vec{E} + \vec{P}$. This equation is only true if changes in $\vec{P}$ (and, therefore, also in $\vec{D}$) are caused by and are proportional to changes in $\vec{E}$, with the permittivity, ϵ_{ij} , being the constant of proportionality.

K. Piezoelectric, Pyroelectric and Ferroelectric Materials¹

Piezoelectric, pyroelectric, and ferroelectric materials are special kinds of dielectrics which can be polarized by various causes other than an externally applied $\vec{E}$ field. (Of course, they can also be polarized by an externally applied $\vec{E}$ field as all matter can.) Specifically, piezoelectric materials are those that can be polarized by homogeneous stress.² (Later on, we will extend this usual definition to include inhomogeneous stress, since there are materials that do not polarize under homogeneous stress but do polarize under inhomogeneous stress.) Pyroelectric materials are those that can be polarized by uniform or homogeneous heating.³ Ferroelectric materials are a special class of pyroelectric materials whose direction of polarization under uniform heating can be changed by exposing the material temporarily to a sufficiently strong d.c., electric field prior to uniform heating.⁴

There is another way to see the relationship between these three types of materials, as shown in figure (2K:1). All three kinds of materials are piezoelectric, but pyroelectric materials are a proper subclass of piezoelectric materials that polarize under uniform heating as well as uniform or homogeneous stress, as we will prove later on. Ferroelectrics, as noted above,

¹Nye, pp. 78-81, pp. 110-130.

²"Piezoelectric" is composed of Greek roots which in this context mean: piezo = pressure; electric = electrified or polarized by.

³"Pyroelectric" is composed of Greek roots which in this context mean: pyro = temperature, heat (fire, literally); electric = electrified or polarized by.

⁴"Ferroelectric" materials are so-called because of an analogy with ferromagnetic materials. In ferromagnetic materials, if all the changes in $\vec{B}$ are caused solely by changes in $\vec{H}$, then $\vec{B}$ and $\vec{H}$ are related by a hysteresis loop. Similarly, in ferroelectric materials, if all changes in $\vec{D}$ are caused solely by changes in $\vec{E}$, then $\vec{D}$ and $\vec{E}$ are also related by a hysteresis loop.

Figure (2K:1)

Relation of Piezoelectric, Pyroelectric,
and Ferroelectric Materials

are a proper subclass of pyroelectric materials.

In piezoelectric, pyroelectric, and ferroelectric materials, stress or changes in temperature, ΔT , acting at a point $\vec{r}$ not only polarize the material; but via this polarization they also change or determine the electric field which exists at the point $\vec{r}$. This is their primary effect. Secondly, stress and temperature changes also affect the difference of potential, ΔV , between different points in the dielectric, since by definition¹

$$\Delta V(\vec{r}_1, \vec{r}_2) = - \int_{\vec{r}_1}^{\vec{r}_2} \vec{E} \cdot d\vec{r}.$$

Therefore, the general procedure for calculating the difference of potential between two points in a piezo- or pyroelectric body is first to calculate the primary effect of the pressure or temperature changes, i.e., the electric field, and second to integrate this field between the two points in question to find the difference of potential.

Theoretically, conductors, as well as dielectrics, can polarize under homogeneous heating and stress. However, they are not usually considered to be piezoelectric or pyroelectric because the manifestations of polarization, i.e., the external electric field produced by the bound charge accumulating during polarization, would be extinguished quickly by a redistribution of free charge inside the conductors.

Piezoelectric Materials: The first materials discovered to be piezoelectric were dielectric crystals, such as quartz. However, textures, too, can be piezoelectric, as Shubnikov proved theoretically in the 1940's.²

¹The "V" in " ΔV " does not stand for voltage; it stands for potential. "Voltage" is a difference of potential, and its symbol is ΔV .

²I. S. Zheludev, Physics of Crystalline Dielectrics, p. 537.

Isotropic amorphous materials cannot be piezoelectric for homogeneous stresses, because they have point inversion symmetry. This conclusion can be proved as follows.

In tensor form the relation between polarization and homogeneous stress is expressed by

$$P_i^\sigma = d_{ijk} \sigma_{jk}$$

(If P_i^{total} is not zero when $(\sigma_{jk}) = 0$, as in pyroelectric materials, we regard P_i^σ as a change in polarization rather than the total amount of polarization existing after applying the stress.) Stress, of course, only affects the component P^σ of the total polarization; simultaneously, the electric field, temperature, etc., can also contribute to the total polarization, P^{total} . Since P^σ is known to be a first-rank tensor and (σ_{ij}) is known to be a second-rank tensor, then it follows from the theorem proved in Appendix A that (d_{ijk}) is a third-rank tensor. Hence, as noted above, in isotropic amorphous materials, which have point inversion symmetry, all third-rank tensors, including (d_{ijk}) , must equal zero, as was proved in section E of this chapter. Thus, these materials are not piezoelectric to homogeneous stress.

The elements of the tensor (d_{ijk}) are the piezoelectric moduli of the material. The MKS units of d_{ijk} are coulombs/newton. Often the values of d_{ijk} are cited in cgs units of esu/dyne, which can be converted to MKS units using this relationship:

$$1 \frac{\text{coul}}{\text{newton}} = 3 \times 10^4 \frac{(\text{esu or stat coulomb})}{\text{dyne}}$$

The tensor equation $P_i^\sigma = d_{ijk} \sigma_{jk}$ can be recast into another form, the matrix form. Doing this has the advantages of reducing from nine to six the number of components we must multiply and also allows us to use matrix algebra on the resulting expression. The first step in the reformulation is to

change (σ_{ij}) to a column matrix of six elements by using the fact that $\sigma_{ij} = \sigma_{ji}$, which implies there are only six independent elements in (σ_{ij}) .

These six elements can be renamed according to this scheme:

	Axis along which σ_{lm} tends to produce stretching			Axis about which σ_{lm} tends to produce rotation		
	1	2	3	1	2	3
tensor name	σ_{11}	σ_{22}	σ_{33}	$\sigma_{23}=\sigma_{32}$	$\sigma_{13}=\sigma_{31}$	$\sigma_{12}=\sigma_{21}$
matrix name	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6

The results of this table are easy to remember. Every tensor component of the form σ_{ll} becomes the matrix component of the form σ_l . Every tensor component of the form σ_{lm} where $l \neq m$ becomes the matrix component of the form σ_{n+3} where n is the number of the axis not originally in the tensor subscript; or one can think of n as the axis about which σ_{lm} tends to produce rotation.

The next step in the reformulation is to expand the tensor form

$$P_i^\sigma = d_{ijk} \sigma_{jk}$$

$$= d_{i11} \sigma_{11} + d_{i22} \sigma_{22} + d_{i33} \sigma_{33} + d_{i23} \sigma_{23} + d_{i32} \sigma_{32} + d_{i13} \sigma_{13} + d_{i31} \sigma_{31} + d_{i12} \sigma_{12} + d_{i21} \sigma_{21}$$

Now we relabel the stress components using matrix notation,

$$P_i^\sigma = d_{i11} \sigma_1 + d_{i22} \sigma_2 + d_{i33} \sigma_3 + d_{i23} \sigma_4 + d_{i32} \sigma_4 + d_{i13} \sigma_5 + d_{i31} \sigma_5 + d_{i12} \sigma_6 + d_{i21} \sigma_6$$

Combining terms with the same σ_l factor, we obtain

$$P_i^\sigma = d_{i11} \sigma_1 + d_{i22} \sigma_2 + d_{i33} \sigma_3 + (d_{i23} + d_{i32}) \sigma_4 + (d_{i13} + d_{i31}) \sigma_5 + (d_{i12} + d_{i21}) \sigma_6$$

We almost have the form we want; it can be achieved by making these definitions:

$$\begin{aligned} d_{i11} &= d_{i1} & (d_{i23} + d_{i32}) &= d_{i4} \\ d_{i22} &= d_{i2} & (d_{i13} + d_{i31}) &= d_{i5} \\ d_{i33} &= d_{i3} & (d_{i12} + d_{i21}) &= d_{i6} \end{aligned}$$

(We assume $d_{132} = d_{123}$, $d_{113} = d_{131}$, and $d_{112} = d_{121}$.)

Using the new definitions, we can rewrite the previous equation for P_i^σ as:

$$P_i^\sigma = d_{i1}^\sigma \sigma_1 + d_{i2}^\sigma \sigma_2 + d_{i3}^\sigma \sigma_3 + d_{i4}^\sigma \sigma_4 + d_{i5}^\sigma \sigma_5 + d_{i6}^\sigma \sigma_6$$

or

$$P_i^\sigma = d_{il}^\sigma \sigma_l \quad (i = 1, 2, 3; l = 1, 2, 3, 4, 5, 6)$$

which is the desired form. Q.E.D.

In spite of the fact that piezoelectric moduli written in matrix form, d_{il} , look similar to those in tensor form, d_{ijk} , they are very different. They are, in general, not equal numerically, e.g., $d_{24} = 2d_{223}$, although $d_{21} = d_{211}$. Also (d_{il}) does not change in a simple way under orthogonal transformations of the material; to find the values of (d_{il}) in the transformed material it is easiest to convert (d_{il}) to tensor form (d_{ijk}) , use the tensor rules to calculate $(d'_{i'j'k'})$ and finally convert $(d'_{i'j'k'})$ to matrix form (d'_{il}) . We conclude that although the core letter "d" is the same in matrix, (d_{il}) , and tensor, (d_{ijk}) , notations, a different number of subscripts on "d" signifies an entirely different mathematical entity.

Every material that can be polarized by homogeneous stress (the direct piezoelectric effect) will become strained when it is exposed to a homogeneous electric field, and this strain is linearly related to the electric field components (the converse piezoelectric effect).

Materials that do not show the direct piezoelectric effect do not show the converse piezoelectric effect either; but they, like all materials, do become strained in a homogeneous electric field by another mechanism called electrostriction. The strain of electrostriction depends not linearly on the components of $\vec{E}$, but rather on $\vec{E}^2$, and is generally much

smaller than the strain of converse piezoelectricity. Thus, when the direction or sign of $\vec{E}$ is reversed, the strain due to converse piezoelectricity changes sign, but that due to electrostriction does not. Electrostriction differs from converse piezoelectricity in yet another way: there is nothing comparable to the direct piezoelectric effect for electrostriction. That is, if when a material is placed in a uniform $\vec{E}$ field it becomes strained proportional to E^2 , showing it does not have converse piezoelectricity, it will not become polarized when homogeneously stressed either.¹

Pyroelectric Materials: Next we focus our attention on those piezoelectric materials whose polarization changes when they are heated or cooled so that the temperature remains uniform throughout the material at all times. (We note in passing that there are other materials that do not polarize under uniform temperature changes but that do become polarized when there is a gradient of temperature in the material. These materials, which are all piezoelectric, are not included in what we shall call "pyroelectric" materials in this thesis, although in the literature they are said to manifest tertiary pyroelectricity.)

Uniformly heating a pyroelectric material causes both homogeneous thermal straining and a uniform increase in temperature. In pyroelectric materials each of these two effects contributes to the resulting polarization: the contribution of the temperature rise alone is called primary

¹Zheludev, p. 610.

pyroelectricity, and the contribution of thermal straining alone is called secondary pyroelectricity. (Non-pyroelectric materials also become strained and have their temperatures raised during uniform heating, but symmetry demands that the resulting polarization be zero.) The following equation summarizes all these relations:

$$P_i^{\text{thermal}} = \rho_i^{\text{I}} \Delta T + \rho_i^{\text{II}} \Delta T + P_i^{\text{non-uniform heating}}$$

The coefficients ρ_i^{I} and ρ_i^{II} are the primary and secondary pyroelectric coefficients respectively; and they relate a uniform change in temperature to a change in P_i^{thermal} , the thermally caused component of the total polarization. They must be first-rank tensor quantities, since they each relate a known first-rank tensor (P_i^{thermal}) to a known scalar or zero-rank tensor ΔT .

If a pyroelectric material is at a uniform temperature, T , the material will be polarized homogeneously according to the previous equation without any stress being applied to the material. This implies that on the surfaces of the body there should be net bound charges of density $\vec{P} \cdot \hat{n}$, which should produce an external electric field. (There is no internal volume bound charge density since $\rho_B = -\vec{\nabla} \cdot \vec{P} = 0$.) Bars of pyroelectric materials should, therefore, attract and repel each other like bar magnets. Do they? Not in general, because ambient, free charges are attracted to the areas of excess bound charge of opposite sign and neutralize them, thus extinguishing the external electric field. Only for a brief time after the temperature of the pyroelectric material is uniformly changed, but before the free ambient charges have moved in or out, does the polarization charge produce an external electric field.

There is an often-used test for pyroelectric behavior that at first sight looks puzzling because it seems to have nothing to do with heat. In this test instead of heating the material, one subjects it to a hydrostatic pressure. If it polarizes under hydrostatic pressure, the material is pyroelectric; and if it does not, the material is not pyroelectric. The hydrostatically-caused polarization is related to the hydrostatic pressure by the equation:

$$P_i^{\text{hydro}} = d_i^{\text{hydro}} (p_{\text{hydro}})$$

Since polarization under hydrostatic pressure, which is just another kind of stress, is a manifestation of piezoelectricity, there must be a relation between d_i^{hydro} , and the piezoelectric moduli, (d_{ij}) , of the material. This relation is

$$d_i^{\text{hydro}} = \sum_{j=1}^3 d_{ij}$$

The basic reason this hydrostatic test works is because both hydrostatic pressure and temperature are scalars or rank-zero tensors, and the point symmetry of the material forces them to be related to rank-one tensors, like polarization, in the same way. Appendix B proves the hydrostatic pressure test and elaborates its results.

One result of the hydrostatic test is important enough to mention here. Before we stated, but did not prove, that pyroelectric materials were a subclass of piezoelectric ones. This result follows easily from the hydrostatic test. If a material polarizes under a uniform temperature, i.e., if it is pyroelectric, $(P_i^I + P_i^{\Pi})$ is not zero for all directions, i.

Therefore, according to the hydrostatic pressure test of Appendix B, d_i^{hydro} , which is equal to $\sum_{j=1}^3 d_{ij}$, is not zero for all directions, i. This implies that some elements of (d_{ij}) are not zero, which means that there are some uniform stresses that will polarize the material. But that statement is just what being piezoelectric means. Therefore, all pyroelectric materials are piezoelectric, too. Q.E.D.

Some kinds of crystals (like tourmaline) and textures (like bone and tendon) can be pyroelectric; but isotropic, amorphous materials cannot be, since they are not even piezoelectric for homogeneous stresses.

Ferroelectric Materials: Now we focus our attention even more sharply, down to a subclass of the pyroelectric materials, the ferroelectric ones, like crystals of BaTiO_3 , barium titanate.

The remarkable feature of these materials is the ease with which we are able to change the arrangement, or order, of their atoms. A strong electric field can shift the atoms from one stable position to another so that the crystallographic, or natural, axes of the material are rotated, although the basic pattern of organization, the crystal class, remains the same. This accounts for the fact that the direction of thermal polarization under moderate uniform heating can be changed by prior exposure to a strong electric field.

Also, it is possible to heat a ferroelectric material to such a high temperature that the atoms inside move so much that an entirely different internal organization results, not like the mere rotation caused by the electric field of the crystallographic axes of one basic pattern of organization. Ultimately if the temperature is raised high enough the atoms

will rearrange in a pattern that is not pyroelectric. This temperature is the Curie point of the material.

This concludes our general discussion of piezoelectric materials and its subdivisions. In the remaining few sections we will consider specific, piezoelectric materials that are especially important in this work.

L. Tendon and Bone¹

The first of the specific piezoelectric materials which we discuss in detail are the biological ones, viz., tendon and bone. Both materials are connective tissues, tissues that mechanically hold the body of the animal together. Bones give the body form and structural strength. Tendons are the strong, inextensible cords that connect contractible muscles to bones.

Both tendons and bones are composed of almost the same basic constituents. Both consist of living cells embedded in a

¹Arthur Ham, Histology, Chapters X, XVII, XVIII.

nonviable matrix. This matrix determines the mechanical properties of the material. The matrix of both bone and tendon contains long fibers of the abundant protein collagen and a little glycoprotein glue to hold the fibers together. Collagen is secreted by the cells as a monomer; once it has polymerized outside the cells to form fibers, it requires no further nourishment from the body. The great tensile strength of both bone and tendon comes from these strong, inextensible collagen fibers. The matrix of bone has an additional component, small crystals that approximate hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, precipitated on the collagen fibers. These crystallites give bone great strength in compression. Because tendon lacks these salts, it also lacks compressive strength.

The basic components are arranged differently in tendon and bone. In tendon the long collagen fibers run parallel to the length of the tendon and are over 90% crystallized.²

² Fukada, "Piezoelectric Effects in Collagen," p. 117.

The organization of these components in bone is much more complex and maybe different in different animal species; both man and cow have the same basic organization of the long bones in their extremities. Since our bone samples come from the long bones of cows, let us examine their structure in detail.

These long bones have two distinct macroscopic patterns of bone organization. At the center of the ends of the long bones, the bone material is organized like a sponge or a grating. It is, therefore, called cancellous bone.¹ The outside layers of the bone have a completely different structure. There the bone is solid and dense, or compact; bone with this organization is, therefore, called compact bone. Compact bone is especially thick in the walls of the shaft, or middle section, of the long bone; and the samples of bone used in this work are compact bone taken from this region.

Let us now take a microscopic view of compact bovine bone. (See figure(2L:1).) It consists of a bundle of parallel rods, like sticks of chalk in a box. These rods are roughly parallel to the length of the bone. Each rod, called an osteon or Haversian system,² has a small central duct (an osteonal or Haversian canal) where blood flows to bring

¹"Cancellous" comes from the Latin word "cancelli," which means a grating. You probably recognize this same Latin word in the English expression "to cancel a check," so called because in cancelling checks, we draw a grating of lines through them.

²"Osteon" comes from the Greek word "os," meaning bone. "Haversian systems" are so called because "Havers," the English anatomist (1650-1702), discovered them.

Figure (2L:1)
Diagrammatic, Microscopic View of Compact, Bovine Bone

nutrients to the bone cells, or osteocytes,¹ that live in the osteon totally encased by bony matrix except for very fine canals, called canaliculi, that conduct nutrients from the central duct to the osteocytes. The bony matrix of each osteon is divided into concentric rings, or lamellae,² about the central canal. In each lamella, the collagen fibers spiral along its length reversing their direction of rotation from one lamella to the adjacent one. Thus, the "average" direction of collagen in bone also points along the length of the osteon; and the osteon runs almost parallel to the longitudinal axis of the macroscopic bone in the region where we took our samples.

Both bone and tendon are textures, probably of the texture class $(\infty)T$, meaning its point symmetry operations are an ∞ -fold axis of rotation with an infinite number of mirror planes containing the ∞ -fold axis.³ This ∞ -fold symmetry axis is parallel to the "average" direction of collagen fibers in both tendon and bone.

Textures of the class $(\infty)T$ have the same forms for second-, third-, and fourth-rank tensors as do the crystals of class 6 when both are measured in their physical frames.⁴ If bone and tendon are textures of type

¹"Osteocyte" comes from the two Greek words "osteon" meaning "bone" and "kytos" meaning "cell" in this context.

²"Lamella" is the diminutive of the Latin word "Lamina", meaning "a thin piece of metal or wood." (Guralnik, p. 790)

³Lang, "Ultrasonic Methods," pp. 101-102.

⁴Ibid.; Lekhnitskii, p. 24.

(∞)T, point symmetry would force the matrix of piezoelectric moduli and all third-rank tensors to take the following form when written in a physical frame whose Z-axis is parallel to the ∞ -fold axis of the texture and whose perpendicular X- and Y-axes may lie anywhere in the isotropic plane perpendicular to the ∞ -fold axis:

$$(d_{ij}) = \begin{pmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}.$$

A d-matrix of this form leads to several predictions. First, since the elements d_{14} , d_{15} , d_{31} , and d_{33} are almost surely not zero, therefore, the material should polarize under homogeneous stress, i.e., be piezoelectric. Fukada's work confirms this prediction. He found that bone and tendon were piezoelectric and measured the following values of the independent, non-zero elements of the d-matrix.¹

Material	Values of piezoelectric moduli (in units of 10^{-8} cgs esu)			
	d_{14}	d_{15}	d_{33}	d_{31}
Horse femur bone	-0.65	0.13	.01	.01
Horse Achilles tendon	-5.7	1.6	0.2	.04

He also noted that the **absolute values of the** moduli decrease as the sample becomes more moist.

A second prediction of this d-matrix is that the material should be pyroelectric. This follows because the sum of the first three elements

¹Fukada, Piezoelectricity in Polymers, p. 230.

in the third row of (d_{ij}) is almost surely not zero; and therefore, the material will polarize under hydrostatic pressure, which, in turn, means it will polarize under uniform heating, as discussed above.

Athenstaedt's work confirms this prediction. He subjected both bone and tendon to hydrostatic pressure and found they did polarize.¹ Lang directly tested bone and tendon for pyroelectricity by uniformly heating them and observing polarization, thus proving conclusively that tendon and bone are pyroelectric, as expected.²

Are bone and tendon also ferroelectric? To date no one has reported any experiments about this.

What is the cause of piezoelectricity and pyroelectricity in bone and tendon? Probably, and surprisingly, these effects are produced by the organic component, collagen, rather than by the inorganic hydroxyapatite salts, for these three reasons:

1. Tendon, which lacks these salts, is piezoelectric.
2. Tendon has a higher density of collagen than bone and also has piezoelectric moduli 10 times as large as those in bone; a greater density of collagen is associated with greater piezoelectricity.
3. Macroscopic-sized crystals of hydroxyapatite salts are not piezoelectric, since they have point inversion symmetry. Hence,

¹Athenstaedt, pp. 830-833.

²Lang, Pyroelectric Effects in Bone and Tendon, pp. 704-5.

as we have shown previously, all elements of their (d_{ij}) must be equal to zero, implying these crystals will not polarize under uniform stress.

The mechanical properties of dry bone are simple: it obeys Hooke's law. When bone is wet, it does not obey Hooke's law and exhibits both stress-relaxation and hysteresis.¹ However, in our experiments, only dry bone was used; thus, we do not have to worry about any viscoelastic effects.

Having discussed the structure, piezoelectric properties, and mechanical properties of the biological materials in these experiments, we next turn our attention to the inorganic, piezoelectric materials used.

¹ Elias Sedlin, "A Rheologic Model for Cortical Bone," Acta Orthopædica Scandinavica, Supplementum 83, p. 69.

M. Quartz and Tourmaline¹

All the tests run on bone and tendon were also run on inorganic, crystals of quartz and tourmaline, which are non-conductors. Our motivation was this: by comparing the piezoelectric behavior of bone and tendon to well-known inorganic materials with similar d-matrices, such as quartz and tourmaline, we hoped to learn what is new and different about the piezoelectric behavior of the biological materials. Also, the well-known, inorganic materials served as standards to check our theoretical expectations and experimental procedures. Selecting these particular piezoelectric crystals, quartz and tourmaline, had one other advantage: it allowed us to determine whether the observed effects depended on pyroelectricity, since quartz is not pyroelectric, but tourmaline is.

Quartz: Below 573°C quartz crystallizes in the alpha form with a d-matrix written in the physical frame of the material as follows:

$$(\tilde{d}_{ij}) = \begin{pmatrix} \tilde{d}_{11} & \tilde{d}_{12} & 0 & \tilde{d}_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & \tilde{d}_{25} & \tilde{d}_{26} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

where²

$\tilde{d}_{11}$	=	-2.3×10^{-12}	$\frac{\text{coulombs}}{\text{newton}}$
$\tilde{d}_{12}$	= $-\tilde{d}_{11}$	= $+2.3 \times 10^{-12}$	"
$\tilde{d}_{14}$	=	$-.67 \times 10^{-12}$	"
$\tilde{d}_{25}$	= $-\tilde{d}_{14}$	= $+.67 \times 10^{-12}$	"
$\tilde{d}_{26}$	= $-2\tilde{d}_{11}$	= $+4.6 \times 10^{-12}$	"

¹Zhedulev, pp. 563-572.

²Nye, p. 126.

The "tildes" emphasize that this matrix is written in the physical frame, not the laboratory frame, where the calculations are done.

We want to cut and position our quartz sample so that its d-matrix in the laboratory frame, where the calculations are done, will be very similar to the d-matrix of bone and tendon as seen in the laboratory frame. By the way Bassett cut his samples, he selected the laboratory frame of bone to be the same as the physical frame, a convention we wish to maintain. Therefore, the previously listed d-matrix for bone and tendon applies equally well in either the laboratory frame or physical frame. Clearly, the d-matrix of quartz in the physical frame does not appear similar to that of bone in the laboratory frame, implying we should not select the physical frame of quartz as the laboratory frame. In particular, the previously listed d-matrices of bone and quartz, both of which are written in their physical frames, differ in these significant features:

1. If quartz is subjected to hydrostatic pressure, then P_1 will be the only non-zero component of $\vec{P}$ in the physical frame, since only in the first row of the d-matrix is the sum of the first three elements not zero. On the other hand, in bone and tendon, it is P_3 that will be non-zero in the physical frame.
2. d_{24} is zero in the physical frame of quartz, but it is not zero in the physical frame of bone.

In Chapter III we will see that d_{24} in the laboratory frame must be non-zero, according to the standard theory of piezoelectricity, in order that the difference of potential across a cantilever-bent, piezoelectric bar be non-zero.

If we cut and position the quartz sample in the following way relative to the laboratory frame, then the d-matrix of quartz as measured in the laboratory frame will take on a form very similar to the d-matrix of bone or tendon in the laboratory frame, which is what we want. The way to position the quartz in laboratory frame is first to align the physical axes with laboratory axes and then rotate the material to a new position where the physical axes, (OX_1, OX_2, OX_3) , are related to the laboratory axes, (X, Y, Z) , by this relation:

$$OX_1 = Z$$

$$OX_2 = -Y$$

$$OX_3 = X$$

The transformation matrix $(A_{i,i})$ of this orthogonal transformation of the material is:

$$(A_{i,i}) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

(See figure (2M:1)).)

Now we want to calculate what the d-matrix of quartz will look like in the laboratory frame after transformation, knowing that before transformation, when the physical frame and laboratory frames coincided exactly, the d-matrix in the laboratory frame had the form previously listed for quartz. The easiest way to do this is first to convert each element of the d-matrix after transformation into tensor form, e.g., $d'_{35} = 2d'_{313}$. Next, in order to find out what the expression for this unknown element is in terms of the known elements before transformation, we use the usual, simple tensor equation:

Figure (2M:1)

Finding the Transformation Matrix to Make the d-Matrix of
Quartz and Bond Similar in the Laboratory Frame

$$\begin{aligned}
 d'_{313} &= A_{3i} A_{1j} A_{3k} \tilde{d}_{ijk} \\
 &= (+1)(+1)(+1) \tilde{d}_{131}
 \end{aligned}$$

Finally, we convert both sides of this expression back to matrix form

$$\frac{1}{2} d'_{35} = \frac{1}{2} d_{15}$$

or

$$d'_{35} = \tilde{d}_{15}$$

Performing the same process on all the other elements of (d'_{ij}) results in the following expression for the d-matrix of quartz as seen in the laboratory frame after transformation, viz.,

$$(d'_{ij}) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & d_{24} & d_{25} & 0 \\ 0 & d_{32} & d_{33} & 0 & 0 & d_{36} \end{pmatrix}$$

where

$$\begin{aligned}
 d_{24} &= +2\tilde{d}_{11} \\
 d_{25} &= -\tilde{d}_{14} \\
 d_{32} &= \tilde{d}_{12} \\
 d_{33} &= \tilde{d}_{11} \\
 d_{36} &= -\tilde{d}_{14}
 \end{aligned}$$

Notice how similar this d-matrix for quartz in the laboratory frame is now in all essential respects to the d-matrix for bone in the laboratory frame.

There are many other possible ways to cut and, thus, position the quartz sample; some might have produced a d-matrix for quartz in the laboratory frame even more similar to that of bone and tendon than the method we used. However, these other cuts were also much more expensive.

Tourmaline: Because this dielectric crystal has an extremely variable composition, its physical properties, like color and piezoelectric moduli, vary significantly from sample to sample. In the physical frame, its d-matrix has this form:

$$(\tilde{d}_{ij}) = \begin{pmatrix} 0 & 0 & 0 & 0 & \tilde{d}_{15} & -\tilde{d}_{22} \\ -\tilde{d}_{22} & \tilde{d}_{22} & 0 & \tilde{d}_{15} & 0 & 0 \\ \tilde{d}_{31} & \tilde{d}_{31} & \tilde{d}_{33} & 0 & 0 & 0 \end{pmatrix}.$$

And approximate values for its elements are the following, though they vary from sample to sample:¹

	Value in cgs esu
$\tilde{d}_{15}$	10.9×10^{-8}
$\tilde{d}_{22}$	1.0×10^{-8}
$\tilde{d}_{31}$	1.03×10^{-8}
$\tilde{d}_{33}$	5.5×10^{-8}

The samples of tourmaline used were "X-cut," meaning that the physical OX_1 -axis is normal to the broad face of the bar, and the same as the laboratory Y-axis. The physical OX_3 -axis is the same as the laboratory Z-axis, and the physical OX_2 -axis is the same as the laboratory (-Y)-axis. Just as for quartz, the d-matrix takes on a new form in the laboratory frame; and it is this:

$$(d_{ij}) = \begin{pmatrix} d_{11} & d_{12} & 0 & 0 & d_{15} & 0 \\ 0 & 0 & d_{23} & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix}$$

¹Zheludev, p. 572.

where:

$$d_{11} = -\tilde{d}_{22}$$

$$d_{24} = +\tilde{d}_{15}$$

$$d_{12} = -\tilde{d}_{21}$$

$$d_{31} = +\tilde{d}_{32}$$

$$d_{15} = +\tilde{d}_{24}$$

$$d_{32} = +\tilde{d}_{31}$$

$$d_{33} = +\tilde{d}_{16}$$

$$d_{33} = +\tilde{d}_{33}$$

This d-matrix in the laboratory frame is similar to that of bone in all essential respects.

N. Summary

In this chapter we have seen how to describe the structure of a material by symmetry operations and its physical properties by tensors. Two second-rank tensors, stress and strain, plus a first-rank tensor, polarization, are the main properties involved in the phenomena of piezoelectricity, pyroelectricity, and ferroelectricity. We examined in some detail organic piezoelectric materials, such as bone and tendon, and inorganic ones, like tourmaline and quartz, because these are the materials we will use in our experiments.

III. FAILURE OF STANDARD PIEZOELECTRIC THEORY FOR BENT BONE

A. Introduction

We began our investigation of piezoelectricity in bone and tendon by examining the case of cantilever bending, following Bassett's example. Initially we investigated the qualitative aspects of the phenomenon.

We asked these questions:

1. What is the shape of the voltage response curve from a cantilever-bent, bone sample when its end is suddenly depressed, held down briefly, and then released, i.e., square-wave loaded. Is it a bi-phasic voltage pulse, as described in the literature; or is that bi-phasic pulse an artifact?
2. How does the sign of the voltage measured from the center of the convex surface to the center of the concave surface of a cantilever-bent bone change if the specimen is placed in a different orientation in the clamp, e.g., flipped end for end? Do the piezoelectric minerals, quartz and tourmaline, behave the same as bone in this respect?

Next we examined the classical theory of piezoelectricity to determine its predictions of the sign changes of the voltage. In the above experiments quartz and tourmaline obeyed the classical prediction, but bone and tendon did not. This finding means that the standard, or classical, formulation of the piezoelectric theory is inadequate to treat bent bone.

This chapter discusses in detail the aforementioned topics.

B. True Shape of the Bone Signal

As a point of reference, we first examined how a bar of a well-known, piezoelectric material, i.e., quartz, behaved under a square-wave load.

Figure (3B:1) shows that we connected the sample directly to a Cary 401, vibrating-reed electrometer. We used this instrument because of its high input impedance ($Z_{in} > 10^{16}$), which prevents free charges from flowing through the voltmeter and annihilating the piezoelectric voltage signal. (At this stage in the experiment, no precautions were taken to counteract the effects of shunt capacitance.) The sample was loaded in three-point loading by placing a 136 gm, copper weight asymmetrically on the (.19 cm X 1.02 cm X 9.40 cm) quartz bar. Although this is not pure cantilever bending, the qualitative voltage results one obtains are the same as when the sample is loaded more carefully in pure cantilever bending. The voltage was measured between copper-foil electrodes (2.0 cm X .8 cm) placed at the center of the bar. Details of these electrodes, the quartz sample, etc., are discussed in Chapter IV.

The quartz sample produced a square-wave response to a square-wave loading of 136 grams as shown in figure (3B:2). If a resistor is connected across the leads of the quartz bar before the square-wave loading, the voltage signal, instead of being a square-wave, is a biphasic pulse of the type described in the literature for bone. The smaller the shunting resistance, the faster the pulse decays. As shown in figure (3B:3), by the time the shunting resistance has decreased to $10^{10} \Omega$, the decay is so fast the signal looks like a series of spikes.

Figure (3B:1)
 Apparatus Used to Determine Shape of and Piezoelectric
 Voltage Response to Square-Wave Loading

Figure (3B:2)
Raw Data of Voltage Response of a Quartz Bar to
Square-Wave Loading

Figure (3B:3)
Voltage Response of Quartz Bar to Square-Wave Loading
When Electrodes on Bar Are Shunted by Various Sized Resistors

The flow of free charge through the shunting resistor causes both pulses in quartz. Initially, after the load is applied, there is a piezoelectric voltage between the electrodes on the sample, but no excess free charge on either electrode. However, the electric field produced by the piezoelectric effect attracts free negative charges, i.e., electrons, from the electrode at lower potential through the shunting resistor to the electrode at higher potential, which creates a new, opposing electric field to cancel the one caused by piezoelectricity. Thus, the initial pulse decays. When the stress is suddenly released, the piezoelectric electric field disappears almost immediately, leaving the opposing field caused by excess free charge on the electrodes. This field, of course, causes a voltage between the electrodes of polarity opposite to that caused by piezoelectricity initially. The opposing field set up by the excess free electrons themselves repels enough electrons back through the shunting resistor to the positive electrode to neutralize both electrodes and return the voltage difference to zero. Thus the opposite pulse is formed and decays.¹

We believe that the same process occurs in the cantilever bending of bone and tendon as in quartz; that is, the bi-phasic pulse is caused by the motion of free charge in the electric field produced piezoelectrically. However, in the case of bone and tendon, the free charges, probably ions, instead of flowing around the sample through an external shunting resistor, flow through the sample internally. The reasons we hold this belief are the following:

¹This explanation entirely ignores any effects produced by shunting capacitance. These will be discussed in detail in Chapter V.

1. The shapes of the voltage-decay curves in bone and in quartz shunted by a resistor are the same, i.e., bi-phasic pulses that decay exponentially.
2. If we decrease the internal resistance of bone by making it more moist, we increase the rate of decay of the voltage. (See Chapter V for details.) This situation is analogous to the effect in quartz, where decreasing the shunt resistance increases the rate of decay.

Therefore, we believe that the same general mechanism produces the electrical signal in both quartz and bone. That is, if all internal conduction could be eliminated from bone--although we have not yet succeeded in doing this--then the voltage signal from bone would be a square-wave voltage in response to a square-wave loading. This result confirms the position taken by Shamos and Lavine.¹

Because of this view, we will be concerned with the sign and, later on, with the magnitude of the initial pulse on loading rather than the second pulse, which occurs when the load is removed. Thus, for example, when we report later on in Chapter V that the voltage signal from bone is +50 mV on loading, we mean the sign of the initial pulse was positive and its peak amplitude was 50 mV.

¹Morris Shamos and Leroy Lavine, "Physical Bases for Bioelectric Effects in Mineralized Tissues," Clinical Orthopedics, V. 35, July/August 1964, pp. 182-184.

C. Changes in Voltage Polarity Upon Rotation of Specimen

Another interesting question about the basic qualitative behavior of piezoelectric specimens in cantilever bending is this: how does the sign of the voltage measured from the center of the convex surface to the center of the concave surface change if the specimen is placed in a different orientation in the sample holder, e.g., flipped end for end?

Figure (3C:1) shows a diagram of the apparatus used to answer this question. A clamp holds one end of the specimen, and a force, F , pushes down on the other. A Cary 401, vibrating-reed electrometer measures the voltage between electrodes, which are attached to opposite points at the center of the convex and concave surfaces of the sample. (The electrode's construction is discussed in detail in Chapter V.) The standard laboratory frame is defined with its origin at the center of the bar in the cross section, or plane, where the force is applied. The Z-axis is horizontal and parallel to the bar's length increasing in value toward the clamped end. X- and Y-axes are horizontal and vertical, respectively, forming, together with the Z-axis, a right-handed, Cartesian frame. The details about the size, source, preparation, etc., of the samples is given in Chapter V. (No attempt was made, at this time, to prevent shunt capacitance from reducing the magnitude of the measured voltages.)

The following table summarizes the results of these qualitative experiments.

Figure (3C:1)

Diagram of Apparatus Used to Measure How the Sign of the Piezoelectric Voltage Depends on Orientation of Sample

Table (3C:1)

Axis about which sample was rotated 180°	Sign of resulting voltage, ΔV_m			
	Quartz (Y-cut)	Tourmaline (X- or Y-cut)	Bone	Tendon
X	-	-	+	+
Y	-	-	+	+
Z	+	+	+	+

where: - = sign of ΔV reversed.

+ = sign of ΔV unchanged.

For example, the table reports that if one first measures ΔV from the convex to the concave surface of a cantilever-bent quartz bar, then rotates the bar by 180° about the X-axis, bends it again, and remeasures the voltage from the convex to the concave surface, the sign of the voltage will have reversed.¹

At first we regarded the facts in table(3C:1) as interesting because they show there is a clear-cut difference between the behavior of the organic, piezoelectric materials and the inorganic ones. Only after calculating in detail the prediction of classical piezoelectric theory, did we realize the fundamental problem this table poses. This calculation will be done in the next section.

¹Another way to reverse the sign of ΔV without moving the bar is to leave the sample in the clamp and reverse the direction of pulling, e.g., pulling up rather than pushing down. This also will reverse the sign of ΔV in every case because the convex and concave surfaces have been reversed by changing the direction of the force.

D. Sign of ΔV_0 Across a Cantilever-Bent Bar According to the Classical Piezoelectric Theory

Derivation of the Basic Equation: We wish to calculate the difference of potential, ΔV_0 , between the two electrodes placed opposite each other at the centers of the concave and convex surfaces of a cantilever-bent, piezoelectric bar. The electrodes are at positions $(+h)$ and $(-h)$ on the Y-axis, as seen in figure (3D:1).

The following conditions are assumed to prevail during the experiment which the calculations describe:

1. Our system, the piezoelectric bar, is assumed to be in an equilibrium state at all times; and all changes are reversible. Therefore, we do not have to worry about such complications as polarization not "keeping up" with its causes and dielectric constants being complex numbers.
2. The piezoelectric bar neither gains nor loses mass, but it does acquire energy from its surroundings.
3. If the sample happens to be pyroelectric as well as piezoelectric, we assume that the macroscopic electric field due only to room-temperature, thermal polarization has been entirely annihilated by ambient free charges before the start of the experiment. Therefore, the net, macroscopic electric field is only caused by changes of stress we apply during the experiment.
4. The electrodes bear no excess free charge.

Figure (3D:1)

Calculating Voltage Between Electrodes According to Classical Theory

cross-sectional view of bar

However, during the actual measurements described previously in section B, excess free charge did flow onto the electrodes. Standard piezoelectric theory predicts that the excess free charge on the electrodes will reduce the magnitude of the voltage below that occurring when there is no free charge present, which we assume here, but will not change the sign of the voltage. (Chapter V proves this.) Thus, the equation we will derive in this section will correctly give the predictions of the standard theory for the sign, but not the magnitude, of the voltage under the actual conditions of measurement in section B.

The basic strategy we will use to predict ΔV_0 between the electrodes on opposite surfaces of the bent bar is to calculate E_2 , the component of the total electric field along the Y-axis, and then to integrate E_2 along the Y-axis from one electrode to the other, i.e.,

$$\Delta V_0 = - \int_{-h}^{+h} E_2 dY \quad (3D:1)$$

We will show that stress, (σ_{ij}) , and electric displacement, (D_i) , are convenient variables in terms of which to express E_2 , since in our experiment one of these variables, (D_i) , actually drops out of the formulation leaving E_2 as a function only of (σ_{ij}) , a particularly simple and convenient result. The implementation of this strategy now follows.

To find E_2 , we first consider what forms of energy leave or enter our system, the piezoelectric bar, during the experiment. The correct way to select the independent variables to describe E_2 is to choose one of each of the conjugate pairs of macroscopic variables corresponding to

each form of transferred energy.¹ Forms of energy likely exchanged between the system and its surroundings during the experiment are these:

Form of energy	Conjugate pair of variables associated with this form of energy transfer
heat	temperature, entropy/unit volume
mechanical energy	stress, strain
electric energy	$\vec{D}$, $\vec{E}$

We will select stress, entropy per unit volume, and electric displacement as a convenient set of independent variables to describe E_2 . Thus, E_2 can be written as a function of stress, (σ_j) , displacement, (D_k) , and entropy/unit volume, S :

$$E_2 = E_2(\sigma_j, D_k, S). \quad (3D:2)$$

In differential form this becomes

$$dE_2 = \frac{\partial E_2}{\partial \sigma_j} \sigma_{j \neq j, D_k, S} + \frac{\partial E_2}{\partial D_k} D_{k \neq 1, \sigma_j, S} + \frac{\partial E_2}{\partial S} \sigma_j, D_k \quad (3D:3)$$

where we assume each partial derivative is taken with all independent variables, except the one in the "denominator", held constant. By relabeling the partial derivatives, this equation becomes:

$$dE_2 = -g_{2j} d\sigma_j + \beta_{2k} dD_k + \phi dS \quad (3D:4)$$

where $j = 1, 2, \dots, 6$

$k = 1, 2, 3.$

¹Nye, pp. 178-179.

We can assume that the experiment takes place adiabatically, implying $dS = \frac{dQ}{T} = 0$.¹ Assuming adiabatic conditions, our previous equation becomes

$$dE_2 = -g_{2j}d\sigma_j + \beta_{2k}dD_k \quad (3D:5)$$

Next we integrate both sides of the equation in state space from an initial state before the bar is stressed in which (σ_j) and (D_k) are both zero (or at least defined to be zero for reference purposes) to the final state which occurs after the stress is fully applied:

$$\int_{\text{initial state}}^{\text{final state}} dE_2 = \int_{\text{initial state}}^{\text{final state}} -g_{2j}d\sigma_j + \int_{\text{initial state}}^{\text{final state}} \beta_{2k}dD_k$$

Assuming the coefficients g_{2j} and β_{2k} remain constant during this reversible process, they can be brought out of the integral signs and the equation becomes

$$E_2 (\text{final}) - E_2 (\text{initial}) = -g_{2j} [\sigma_j (\text{final}) - \sigma_j (\text{initial})] + \beta_{2k} [D_k (\text{final}) - D_k (\text{initial})] \quad (3D:7)$$

Since the initial values of all the variables are zero and the final values are just the values E_2 , σ_j , and D_k existing after the stress is fully applied, this equation becomes

$$E_2 = -g_{2j}\sigma_j + \beta_{2k}D_k \quad (3D:8)$$

As before, summation over repeated indices is implied.

¹D. A. Berlincourt, D. R. Curran, and H. Jaffe, "Piezoelectric and Piezomagnetic Materials and Their Function in Transducers," Physical Acoustics, Vol. 1A (Editor, W. P. Mason), p. 188.

The previous equation is not yet in suitable form for finding ΔV_0 , since E_2 is expressed in terms of coefficients g_{2j} and β_{2k} , that have not been evaluated. We would like to express g_{2j} and β_{2k} in terms of known coefficients, such as (d_{ij}) and the permittivity, (ϵ_{ij}) , of the material. To accomplish this, we express D_k as a function of $\vec{E}$, and σ_j , now considered as independent variables, i.e.,

$$D_k = D_k(E_i, \sigma_j). \quad (3D:9)$$

In differential form, this expression becomes

$$dD_k = \left. \frac{\partial D_k}{\partial E_i} \right|_{E_l \neq i, \sigma_j} dE_i + \left. \frac{\partial D_k}{\partial \sigma_j} \right|_{\sigma_l \neq j, E_i} d\sigma_j, \quad (3D:10)$$

The coefficient, $\partial D_k / \partial E_i$, evaluated with all other variables constant, we recognize as the permittivity, ϵ_{ki} , of the material, since it is a coefficient relating changes in D_k caused only by changes in E_i .

The second coefficient, $(\partial D_k / \partial \sigma_j)$, evaluated with all other independent variables including E_i constant, is the piezoelectric coefficient, d_{kj} .

To prove this, we write the basic definition of D_k , viz.,

$$D_k = \epsilon_0 E_k + P_k$$

and express it in differential form as

$$dD_k = \epsilon_0 dE_k + dP_k. \quad (3D:11)$$

This differential expression is then evaluated under the same conditions assumed to prevail when the partial derivative is evaluated, viz., σ_j can change but no other independent variable, e.g., E_k , can change. Thus dE_k is zero under these conditions, but dP_k equals $d_{kj}(d\sigma_j)$, since σ_j is the only cause of P_k in a piezoelectric material than can change. Substituting these findings into equation (3D:11), it becomes:

$$dD_k = 0 + d_{kj} d\sigma_j \quad (3D:12)$$

or equivalently,

$$\frac{dD_k}{d\sigma_j} = d_{kj} \quad (3D:13)$$

Since this derivative is written assuming only σ_j and D_k can vary, it is really a partial derivative, which proves that

$$\left. \frac{\partial D_k}{\partial \sigma_j} \right|_{\substack{\text{other variables} \\ \text{constant}}} = d_{jk} \quad (3D:14)$$

Q.E.D.

The values of d_{kj} evaluated under isothermal or adiabatic conditions are almost the same; they differ by less than 1%.¹ Therefore, when checking a d -value in the literature, one need not worry about the exact thermal conditions under which it was measured.

Using the results of the last two paragraphs, equation (3D:10) can be rewritten as:

$$dD_k = \epsilon_{ki} dE_i + d_{kj} d\sigma_j \quad (3D:15)$$

Upon integration from an initial state where all variables are zero to a final one where all variables reach their final values, this equation becomes

$$D_k = \epsilon_{ki} E_i + d_{kj} \sigma_j \quad (3D:16)$$

The final step in finding g_{2j} and β_{2k} is to regard both equations (3D:8) and (3D:16) as matrix equations, since the multiplication or summation indicated in these equations is exactly the same as is done in multiplying the associated matrices. Equation (3D:16) can be written as a matrix equation merely by placing parentheses around the variables to indicate

¹Nye, p. 188.

they are now arrays of numbers. We obtain

$$(D_k) = (\epsilon_{ki})(E_i) + (d_{kj})(\sigma_j) \quad (3D:17)$$

where two parentheses placed side by side indicates matrix multiplication. Equation (3D:8) can be written in matrix form, if we replace E_2 by the general component E_i and write:

$$(E_i) = -(g_{ij})(\sigma_j) + (\beta_{ik})(D_k) \quad (3D:18)$$

The strategy now is to rewrite equation (3D:17) in the form of equation (3D:18) and equate coefficients. First in equation (3D:17) we transfer the (E_i) -term to the left side and (D_k) to the right side to obtain

$$(\epsilon_{ki})(E_i) = -(d_{kj})(\sigma_j) + (D_k) \quad (3D:19)$$

Since this is a matrix equation, we must be careful not to change the order of matrix factors in a matrix product or to divide by a matrix. However, we can solve equation (3D:19) for (E_i) by multiplying through by $(\epsilon_{ki})^{-1}$. (The matrix (ϵ_{ki}) actually does have an inverse because it is square, 3 X 3, and non-singular, i.e., its determinant is non-zero.)

Doing the matrix multiplication, we obtain

$$(E_i) = -(\epsilon_{ki})^{-1}(d_{kj})(\sigma_j) + (\epsilon_{ki})^{-1}(D_k) \quad (3D:20)$$

By equating coefficients in the equations (3D:20) and (3D:18), we see that

$$(\beta_{ik}) = (\epsilon_{ki})^{-1} \quad (3D:21)$$

$$(g_{ij}) = (\epsilon_{ki})^{-1}(d_{kj}) \quad (3D:22)$$

In quartz and tourmaline (ϵ_{ki}) has non-zero entries only down the principal diagonal in the laboratory frame.¹ If bone and tendon are really of texture (oo)T., they also have non-zero elements only down the principal diagonal.² Therefore, the form of $(\epsilon_{ki})^{-1}$ can easily be evaluated using standard rules of matrix algebra:

$$\beta_{ik} \equiv \epsilon_{ki}^{-1} = \frac{(-1)^{i+k} \Delta_{ki}}{\Delta} \quad (3D:23)$$

where

$$\Delta_{ki} = (ki)\text{-th cofactor of } (\epsilon_{ki})$$

$$\Delta = \text{determinant of } (\epsilon_{ki})$$

Using this formula, we discover that $(\epsilon_{ki})^{-1}$ has the form

¹In Nye (pp. 296-301), (ϵ_{ij}) in the physical frame is listed with non-zero elements only down the principal diagonal. However, the physical frame of quartz and tourmaline samples is not the same as the laboratory frame, but the values of the permittivity, (ϵ'_{ij}) , in the laboratory frame can be calculated from those (ϵ_{ij}) in the physical frame by the equation

$$\epsilon'_{i'j'} = A_{i'i} A_{j'j} \epsilon_{ij}$$

where:

$$(A_{i'i}) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad \text{for Y-cut quartz}$$

$$(A_{i'i}) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{for X-cut tourmaline}$$

By calculating each element of (ϵ'_{ij}) with this rule, one discovers that only the elements on the principal diagonal of (ϵ'_{ij}) are non-zero.

²A. Gjelsvik, "Bone Remodeling and Piezoelectricity—I," Journal of Biomechanics, Vol. 6, 1973, p. 70.

$$(\epsilon_{ki})^{-1} = \begin{pmatrix} \frac{1}{\epsilon_{11}} & 0 & 0 \\ 0 & \frac{1}{\epsilon_{22}} & 0 \\ 0 & 0 & \frac{1}{\epsilon_{33}} \end{pmatrix}$$

or, in terms of individual elements,

$$\beta_{ik} = \epsilon_{ki}^{-1} = \frac{\delta_{ki}}{\epsilon_{ii}} \quad (3D:24)$$

Having evaluated (β_{ik}) , finding (g_{ij}) is easy

$$\begin{aligned} g_{ij} &= \epsilon_{ki}^{-1} d_{kj} \\ g_{ij} &= \frac{\delta_{ki}}{\epsilon_{ii}} d_{kj} \\ g_{ij} &= \frac{d_{ij}}{\epsilon_{ii}} \end{aligned} \quad (3D:25)$$

Finally, using equation (3D:24) and (3D:25), we can express the unknowns g_{2j} and β_{2k} in equation (3D:8) in terms of known variables

$$\begin{aligned} g_{2j} &= \frac{d_{2j}}{\epsilon_{22}} \\ \beta_{2k} &= \frac{\delta_{k2}}{\epsilon_{22}} = \frac{1}{\epsilon_{22}} \end{aligned}$$

Upon substituting, equation (3D:8) becomes:

$$\boxed{E_2 = \frac{-d_{2j}}{\epsilon_{22}} \sigma_j + \frac{1}{\epsilon_{22}} D_2} \quad (3D:26)$$

Let us pause briefly in this long derivation to notice something important; the utility of the matrix formulation of the equations of

piezoelectricity. Because we transformed our equations (3D:8) and (3D:16) into matrix equations, we were able to use the standard theorems of matrix algebra to solve for (β_{ik}) and (g_{ij}) by finding $(\epsilon_{ki})^{-1}$.

Before integrating equation (3D:26) to find ΔV_0 , we can simplify the equation by showing D_2 in our experiment is always zero. We assume our sample is very thin in the Y-direction and the electrodes are centrally placed on the upper and lower surfaces, as shown in figure (3D:2). To prove D_2 is zero in this case, we use fact that

$$\vec{\nabla} \cdot \vec{D} = \rho_{\text{free}}$$

and integrate both sides of the equation over the volume of a Gaussian pillbox located in the region of the electrodes, where we wish to know D_2 . The top and bottom surfaces of this pillbox are parallel to the upper and lower surfaces of the bar and are located infinitesimally outside of the bar itself. After integration the previous equation becomes

$$\int \vec{\nabla} \cdot \vec{D} dV = \int \rho_{\text{free}} dV.$$

Since, by hypothesis, neither the dielectric nor the electrodes contain excess free charge, the right side of the equation is zero. The left side can be converted to a surface integral over the surface, S , of the Gaussian pillbox by using Gauss' Theorem. Thus, the previous equation becomes:

$$\int \vec{D} \cdot d\vec{S} = 0.$$

The integration can be divided into two regions, over the sides and over the top and bottom of the pillbox,

$$\int_{\text{sides}} \vec{D} \cdot d\vec{S} + \int_{\text{top and bottom}} \vec{D} \cdot d\vec{S} = 0$$

Figure (3D:2)

Showing D_2 is Zero for a Thin Bar

cross-sectional view of bar

We assume the pillbox is so thin and, therefore, the area of the curved sides of the pillbox is so small that the integral over the sides is negligible compared to the one over the top and bottom--no matter what value $\vec{D}$ happens to have on the sides of the pillbox. Therefore, the previous equation becomes

$$0 + \int_{\text{top and bottom}} \vec{D} \cdot d\vec{S} = 0$$

Next resolve $\vec{D}$ on the top and bottom of the pillbox into two components, $\vec{D}_{\parallel}$ and $\vec{D}_{\perp}$. $\vec{D}_{\parallel}$ is parallel to the Gaussian surface; and $\vec{D}_{\perp}$ is perpendicular to it with its positive sense along the outward normal. Thus, the previous equation becomes

$$\int_{\text{top and bottom}} (\vec{D}_{\perp} + \vec{D}_{\parallel}) \cdot d\vec{S} = 0$$

$$\int_{\text{top and bottom}} \vec{D}_{\perp} \cdot d\vec{S} + \int_{\text{top and bottom}} \vec{D}_{\parallel} \cdot d\vec{S} = 0$$

The second term on the left is zero because the angle between the normally directed $d\vec{S}$ and $\vec{D}_{\parallel}$ is 90° . However, the first term is not zero, since the angle between $\vec{D}_{\perp}$ and $d\vec{S}$ is 0° . Thus, we can rewrite the previous equation as

$$\int_{\text{top}} D_{\perp} \cos(0^\circ) dS + \int_{\text{bottom}} D_{\perp} \cos(0^\circ) dS + 0 = 0$$

Assuming the area, ΔS , of the top and bottom surfaces of the pillbox are small enough so $D_{\perp}$ is constant over each of them, we obtain

$$(D_{\perp})_{\text{top}} \Delta S + (D_{\perp})_{\text{bottom}} \Delta S = 0$$

The only way the two terms on the left can always add to zero for all possible $\vec{D}$ fields is if each is individually zero, implying $D_{\perp}$, which is just another name for D_2 , is zero on the top and bottom surfaces, infinitesimally outside the material. Since there is no free charge on

the surface or on the electrodes, D_2 is conserved and is zero just inside the material, too. Because the sample is thin, D_2 must never differ much at any interior point from its value at the surface. Therefore, D_2 must be zero everywhere between the electrodes on opposite sides of a thin dielectric. This result applies even if the dielectric, which may be piezoelectric, is bent, since the argument would proceed in that case in exactly the same way.

The essential point is that D_2 is only zero for a thin specimen; if the bar is not thin, the previous argument fails. Practically speaking, this means we must use thin specimens if the resulting mathematical equations are to be simple, or tractable.

The fact that D_2 is zero also confirms the wisdom of using $\vec{D}$ rather than $\vec{P}$ as an independent variable in our problem. We want to use a variable that will make the equation for E_2 as simple as possible; and $\vec{D}$, in effect, drops out of the problem if the sample is thin, leaving only one independent variable, σ_{ij} . This result occurs because the general equation, (3D:26), for E_2 in either a thin or thick bar involves only the D_2 -component of $\vec{D}$, i.e.,

$$E_2 = \frac{-d_{2j}}{\epsilon_{22}} \sigma_j + \frac{1}{\epsilon_{22}} D_2$$

and in a thin sample even D_2 is zero. Therefore,

$$E_2 = \frac{-d_{2j}\sigma_j}{\epsilon_{22}} + 0 \quad (3D:27)$$

Q.E.D.

However, had we selected $\vec{P}$ as the independent variable, again E_2 would only have depended on P_2 by an analogous argument; but P_2 would not have been zero in the stressed piezoelectric bars even if the bars were thin. Thus, $\vec{P}$ would have been a poor choice for an independent variable, since it would not have led to a simple equation for E_2 .¹

To complete our derivation, we integrate E_2 in real space over the Y-axis between the electrodes

$$\Delta V_o = - \int_{-h}^{+h} E_2 dY,$$

Substituting for E_2 in terms of σ_j from equation (3D:27), we obtain

$$\Delta V_o = + \frac{d_{2j}}{\epsilon_{22}} \int_{-h}^{+h} \sigma_j dY \quad (3D:28)$$

To evaluate this integral, we assume that (σ_j) is determined almost entirely by the applied forces and is, to a first approximation, the same as the stress produced in an isotropic bar in cantilever bending, viz.,²

$$(\sigma_j) = (0, 0, \frac{-3F}{2bh^3} YZ, \frac{-3F}{4bh^3} (h^2 - Y^2), 0, 0)$$

where

X, Y, Z = distances measured in the standard laboratory frame
described in figure (3C:1) and section C

F = force depressing end of bar--assumed uniformly
distributed across the end of the bar

b = width of the bar in X-direction

2h = thickness of the bar in Y-direction.

¹Although $\vec{P}$ is not used as an independent variable, $\vec{P}$ is physically important, since it is what really produces the electric field.

²S. Timoshenko & J. N. Goodier, Theory of Elasticity, p. 35.

When these values are substituted in equation (3D:28), and the integrations in Y done between $(-h)$ and $(+h)$, the result is:

$$\Delta V_o = \frac{-d_{24} F}{b \epsilon_{22}}$$

As we proved in sections L and M of Chapter II, d_{24} is not zero for any of the materials used in our experiments as viewed in the laboratory frame. Thus, ΔV_o is not zero for these materials either. The value of d_{24} in the laboratory frame depends on a combination of two factors, the point symmetry of the material and the position of the material in the laboratory frame. However, as we shall see in the next subsection, the numerical value of d_{24} does not determine whether ΔV_o will change sign following a repositioning of the bar. This depends solely on the fact that d_{24} , or $2d_{223}$, is a third-rank tensor, irrespective of its numerical value.

The previous assumption about the value of (σ_j) requires some justification. An order of magnitude calculation in Appendix C shows that almost all the stress and strain in the piezoelectric bars comes from the applied mechanical forces, not from the electric fields which develop during bending. Thus, we can evaluate (σ_j) in our piezoelectric samples by the same techniques used for non-piezoelectric materials. Our approximation for (σ_j) given in equation (3D:29) is the exact solution of (σ_j) for an isotropic, elastic bar in plane cantilever bending ignoring any piezoelectric effect, which is permissible according to Appendix C. That this plane stress distribution is appropriate for materials like tendon and bone is proved in Chapter V. That this stress distribution is also appropriate for quartz and tourmaline follows because the equation (3D:30), which results from using the approximation for (σ_j) , accurately predicts

the behavior of quartz and tourmaline, as we shall see in the next section of this chapter. and also in Chapter V.

Prediction of Sign Changes of ΔV_0 : According to the Standard Theory: We now investigate the sign change predicted by the equation from standard theory,

$$\Delta V_0 = - \frac{d_{24}}{\epsilon_{22}} \frac{F}{b}$$

for a cantilever-bent bar if the specimen is repositioned in its holder, e.g., by being rotated end-for-end.

First let us note that rotating the bar does not rotate the laboratory co-ordinates, X, Y, and Z, or the force, which we will assume for simplicity in this discussion is always applied downward.¹ The only factors in the equation for ΔV_0 that can change value when the sample is rotated are intrinsic properties of the sample, viz., ϵ_{22} and d_{24} . Therefore, changes in ϵ_{22} and d_{24} will determine how the sign of ΔV_0 changes following rotation of the bar.

The factors d_{24} and ϵ_{22} represent the piezoelectric modulus and permittivity not at just one point in the material, but at all points along a path from one electrode to the other through the material because the equation for ΔV_0 came by integrating E_2 along this path. We must be sure that d_{24} and ϵ_{22} transform the same way following rotation at all points, or atoms, along this path, because if d_{24} and ϵ_{22} changed differently

¹If the direction of the force were reversed, i.e., if the bar were pulled up, the equation predicts ΔV_0 would change sign. This behavior is seen in all the materials tested.

at different atoms there would be no simple way to predict from the equation for ΔV_0 how ΔV_0 would change following rotation of the bar. In fact, we can be sure that d_{24} and ϵ_{22} , which are intrinsic properties, change the same at all points following a rigid-body rotation of the homogeneous bar. This follows because the value of an intrinsic, tensor property at an atom following a transformation depends only on the value of the tensor before transformation and the transformation matrix, $(A_{i,i})$, at that atom. These two factors are the same at all atoms in our case: the intrinsic properties are the same at every atom before transformation because the material is homogeneous, and $(A_{i,i})$ is the same at all atoms because the transformation, a rigid-body rotation, is orthogonal. Therefore, since d_{24} and ϵ_{22} are the same everywhere before rotation and $(A_{i,i})$ is the same everywhere, too, d_{24} and ϵ_{22} must be the same everywhere after rotation as well. Q.E.D. Thus, by checking how d_{24} and ϵ_{22} change following rotation at any one point in the material, we can predict how ΔV_0 between the electrodes will change following the same rotation.

First let us examine what happens to the value of ϵ_{22} at an arbitrary atom in the material when the sample is rotated by 180° about the X-, Y-, or Z-axes. Because permittivity is a second-rank tensor, it is easy to predict its value, ϵ'_{22} , in the laboratory frame at the same atom after the material is rigidly rotated. The correct equation is

$$\epsilon'_{22} = A_{2i} A_{2j} \epsilon_{ij}$$

where (ϵ_{ij}) is the value of the permittivity tensor before rotation.

The permittivity tensor (ϵ_{ij}) in unstressed quartz, tourmaline, bone, and tendon has non-zero elements only down the principal diagonal, i.e.,¹

$$\epsilon_{ij} = \delta_{ij} \epsilon_{ii}$$

However, our equation for ΔV_0 applies for the material when it is stressed. We assume that the deformation caused by the stress is such a small perturbation that it does not appreciably change the point symmetry properties of the material nor, therefore, the form of its tensors either. Hence, it is appropriate to use (ϵ_{ij}) for the unstressed material in previous equation for calculating ϵ_{22} .

Substituting the expression

$$\epsilon_{ij} = \delta_{ij} \epsilon_{ii}$$

into the equation for ϵ_{22} yields

$$\epsilon'_{22} = A_{2i} A_{2j} \delta_{ij} \epsilon_{ii}$$

or

$$\epsilon'_{22} = A_{2j} A_{2j} \epsilon_{jj}$$

The transformation matrices, (A_{ij}), for rotation by 180° about the X-, Y-, and Z-axes, respectively, are:

$$\begin{pmatrix} +1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +1 \end{pmatrix}$$

In all three of these matrices, the only non-zero element in the second row is the (+1) in the second column. Therefore, no matter if the bar

¹This argument assumes that tendon and bone are (oo)T textures.

is rotated about the X-, Y-, or Z-axis, the previous equation for ϵ_{22} becomes

$$\epsilon'_{22} = (+1)(+1)\epsilon_{22}$$

$$\epsilon'_{22} = +\epsilon_{22}$$

That is, rotation by 180° about the X-, Y-, or Z-axis does not change the sign or magnitude of ϵ_{22} .

Therefore, we must look to the d_{24} factor for any possible sign changes of ΔV_o , since it is the only other factor that could change sign under rotation of the bar.¹ To permit easy calculation of the piezoelectric modulus after rotation, d'_{24} should be written in tensor form as $2d'_{223}$ or just d'_{223} . The transformation equation is

$$d'_{223} = A_{2i} A_{2j} A_{3k} d_{ijk}$$

First let us consider rotation of the sample by 180° about the X-axis, for which:

$$A_{2i} = -1\delta_{2i}$$

$$A_{2j} = -1\delta_{2j}$$

$$A_{3k} = -1\delta_{3k}$$

Substituting these values into the transformation equation yields:

$$d'_{223} = (-1)\delta_{2i}(-1)\delta_{2j}(-1)\delta_{3k}d_{ijk}$$

$$d'_{223} = (-1)d_{223}$$

¹By using the simplified form of (σ_{ij}) we also assumed that (σ_{ij}) would not change when the bar was rotated, since the simple form of (σ_{ij}) does not depend on the elastic constants, intrinsic properties of the material. However, as we shall see in Appendix E, (σ_{ij}) in general does depend on the elastic constants and would in general change in magnitude by a small amount when the bar is rotated, even though the same external forces act on it. Thus, in general there might be other factors to influence the sign of ΔV_o , aside from d_{24} ; but these would be of small influence.

Therefore, rotation of the sample by 180° about the X-axis would change the sign of d_{24} and also ΔV_o . Similar analyses for rotation of the sample by 180° about the Y- and Z-axes lead to these predictions for how ΔV_o should change sign according to the standard theory.

Table (3D:1)

Rotation by 180° about this axis	Sign change in d_{24} and ΔV_o
X	-
Y	-
Z	+

where:

- = ΔV_o reverses sign

+ = ΔV_o retains same sign.

The experimental results from section C show that quartz and tourmaline obey these predictions, while bone and tendon do not.

Answering Possible Objections: We have just shown that the classical theory predicts sign changes in ΔV_o upon various rotations of the bar that are inconsistent with the observed behavior in bone and tendon. This result came about because in equation (3D:28), viz.,

$$\Delta V_o = \frac{d_{2j}}{\epsilon_{22}} \int_{-h}^h \sigma_j dY.$$

We assumed that the only non-zero elements of (σ_j) were σ_3 and σ_4 . The former, σ_3 , integrated to zero; and the latter contributed a factor d_{24} to the final result, viz.,

$$\Delta V_o = \frac{-d_{24}^F}{\epsilon_{22}^b}.$$

This factor, d_{24} , determines that the sign of ΔV_0 should change following certain rotations in a manner which is inconsistent with the actual behavior of bone and tendon bars.

However, there are other elements of (d_{ij}) which do have the same sign invariance under 180° rotation about X-, Y-, or Z-axes as does the observed ΔV_0 for bone and tendon. These elements are d_{14} , d_{25} , and d_{36} .¹ Why do they not appear in the equation for ΔV_0 and thus give the calculated ΔV_0 the same invariance of sign under rotation as the observed ΔV_0 in bone and tendon has? The elements d_{14} and d_{36} do not appear because they would contribute to the electric field in the X- and Z-directions, respectively, not in the Y-direction, which is the one along which ΔV_0 is calculated. The element d_{25} does not appear because σ_5 , whose integral would multiply d_{25} in the final expression, is negligibly small in bone and tendon, as the analysis in Chapter V shows.

Another possible objection to our conclusion that the standard theory is incompatible with the observed sign invariance of ΔV_0 in bone and tendon is this: what effect might inhomogeneities in bone and tendon have on the results? Let us suppose that the bone sample is so inhomogeneous that d_{2j} cannot be regarded as a constant. Then our equation for ΔV_0 becomes the one preceding equation (3D:28), the first place

¹Careful analysis shows that only those piezoelectric moduli which in tensor form, d_{ijk} , have subscripts that are a permutation of (1,2,3) can possibly be invariant under rotation by 180° about the X-, Y-, or Z-axes. Appendix D proves this statement in detail. Of course, d_{14} , d_{25} , and d_{36} , when written in tensor form, are the only elements of (d_{ij}) that satisfy this condition.

we assumed d_{2j} was homogeneous. That is, the equation becomes

$$\Delta V_o = \int_{-h}^h \frac{d_{2j}}{\epsilon_{22}} \sigma_j dy.$$

We can divide the path of integration up into segments small enough so d_{2j} and ϵ_{22} are constant in each segment and, thus, replace the integration by a summation,

$$\Delta V_o = \sum_k \frac{d_{2j}}{\epsilon_{22}} \sigma_j \Delta y_k.$$

Assuming σ_3 and σ_4 are the only significant non-zero elements of (σ_j) , the equation becomes

$$\Delta V_o = \sum_k \left[\frac{d_{23}}{\epsilon_{22}} \sigma_3 + \frac{d_{24}}{\epsilon_{22}} \sigma_4 \right] \Delta y_k.$$

Since ϵ_{22} never changes sign following 180° rotation about the X-, Y-, or Z-axes, the sign of ΔV_o will vary under rotation the same way d_{23} and d_{24} change sign. The following table lists how these various factors change sign following 180° -rotations.

Table (3D:2)

Rotation by 180° about the following axis	How d_{ij} changes sign under this rotation		
	d_{23}	d_{24}	$\left(\frac{d_{23}\sigma_3}{\epsilon_{22}} + \frac{d_{24}\sigma_4}{\epsilon_{22}} \right)$
X	-	-	-
Y	+	-	+ or -
Z	-	+	+ or -

where: - = sign reverses upon rotation.

+ = sign does not reverse upon rotation.

The main point of this table is that according to it the standard theory of piezoelectricity predicts that ΔV_o would change sign following a 180° rotation about the X-axis because d_{23} and d_{24} change sign and σ_3 and σ_4 do not change sign in the previous equation. That is, the standard theory predicts a sign change of ΔV_o in very inhomogeneous materials that in fact is not seen in the behavior of bone and tendon. Therefore, even if bone and tendon were very inhomogeneous, the standard theory of piezoelectricity would be inadequate to describe piezoelectric effects either material.

E. Summary

The qualitative experiments described in this chapter established two important features of piezoelectric voltage signals from bone and tendon in cantilever bending; viz.:

1. Apart from the slight decay produced by leakage of free charge through the specimen, the voltage signal in response to a square wave in loading is also a square wave.
2. The voltage, ΔV_o , measured from the middle of convex to the middle of concave surfaces of a cantilever-bent bone or tendon is always of the same sign no matter what its orientation in the clamp.

This latter finding was shown to be inconsistent with the standard theory of piezoelectricity, which, however, did accurately describe the sign changes of ΔV_0 in quartz and tourmaline. Some extension of the standard theory is needed to predict the piezoelectric behavior of bone and tendon. This extension is the subject of the next chapter.

IV. THE EXTENDED THEORY OF PIEZOELECTRICITY AND ITS APPLICATION TO CANTILEVER BENDING

A. Introduction

Chapter III demonstrated that the classical theory of piezoelectricity could not correctly predict even the most basic, qualitative features of the piezoelectric behavior of bone and tendon during cantilever bending. A new approach is clearly needed.

One conceivable way to amend the classical theory is to consider possible non-linear effects. The classical theory assumes that the electric field produced by piezoelectricity is a linear function of stress and that the piezoelectric moduli are true constants, independent of stress. Perhaps assuming that the piezoelectric moduli change with stress, which would result in a non-linear relation of stress and electric field, would produce an adequate equation for the voltage across a thin bar. Appendix D shows this is not likely.

Fukada also recognized that the classical theory of piezoelectricity could not explain the piezoelectric behavior of tendon and bone in cantilever bending.¹ We arrived at the same conclusion independently of Fukada, and for different reasons, which have been fully elaborated in Chapter III. Fukada suggested the correct way to amend the classical theory would be to introduce a new variable, the stress- gradient, $\partial\sigma_{ij}/\partial x_k$, rather than to consider non-linearities in the relation of stress and electric field. The stress gradient at point $\vec{r}$ is the rate at which the various components of stress change in distance along the three

¹Fukada, "Piezoelectricity in Polymers," p. 230.

co-ordinate axes at point $\vec{r}$ in the material; and Fukada assumed that this spatial rate of change of σ_{ij} was even more significant in determining the electric field at $\vec{r}$ than the magnitude of the stress itself at point $\vec{r}$. He did not suggest discarding σ_{ij} as a variable, but only supplementing it with $\partial\sigma_{ij}/\partial x_k$.

Fukada's suggestion was motivated by some new experimental findings, viz., that shock waves in NaCl cause piezoelectric polarization. This result cannot be explained by the classical piezoelectric theory because NaCl has point inversion symmetry at each point in the material, and should, therefore, have all its piezoelectric moduli zero and, hence, not polarize under stress. Kogan suggested a few years earlier that such behavior could be explained by assuming that the stress-gradient was an important variable in this kind of problem.¹ Fukada thought the same explanation might also work for bone and tendon in cantilever bending.

Fukada never developed the gradient extension any further. The rest of this thesis is essentially an elaboration of this idea and a report of experimental confirmation of its predictions. This chapter, V, develops a general extended theory of piezoelectricity, which includes the stress gradient as a variable, and applies this extended theory specifically to the case of cantilever bending. Chapter VI describes the

¹Sh. M. Kogan, "Piezoelectric Effect During Inhomogeneous Deformation and Acoustic Scattering of Carriers in Crystals," Soviet Physics-Solid State, Vol. 5, No. 10, April 1964, pp. 2069-2070.

experiments that confirm the predictions of the extended theory of piezoelectricity. The succeeding chapter applies the extended theory to the case of pure bending of piezoelectric bars.

B. Derivation of the General Equation for the Electric Field

According to the Extended Theory of Piezoelectricity

As before, our ultimate aim is to calculate the difference of potential, ΔV_0 , between two electrodes without excess free charge on them and positioned along the Y-axis. To do this, we first must know E_2 at each point $\vec{r}$, and then integrate E_2 in real space to find ΔV_0 . Our immediate purpose in this section is, therefore, to find E_2 .

Fukada suggested that to calculate E_2 a new variable, $\partial\sigma_{ij}/\partial X_k$, should be added to the usual ones; viz., (D_k) , (σ_{ij}) , and S ; i.e., entropy per unit volume. Symbolically, this may be expressed¹

¹Including $(\partial\sigma_{ij}/\partial X_k)$ as an independent variable also implies that there is a corresponding conjugate variable, whose product with $(\partial\sigma_{ij}/\partial X_k)$ has units of energy per unit volume. Thus, there must be another way to add mechanical energy to a body in addition to stress and its conjugate variable, strain.

$$E_{\ell} = E_{\ell} (\sigma_{jk}, D_i, \partial \sigma_{mn} / \partial x_o, S) .$$

This "extended" theory does not discard (σ_{ij}) as a variable, since all our piezoelectric materials are known to polarize and develop an electric field in response to a homogeneous stress alone. However, the extended theory allows for the possibility that an inhomogeneity in the stress could produce new effects which might dominate the effects of (σ_{ij}) alone. The standard theory does not allow for this possibility; it assumes that whatever happens in the case of inhomogeneous stress can be calculated simply by summing up only the effects of a varying (σ_{ij}) acting at each point in the material without considering the effects due to a spatial derivative of (σ_{ij}) .

The above equation for E_l , can be expressed in differential form as follows:

$$dE_l = \frac{\partial E_l}{\partial \sigma_{jk}} d\sigma_{jk} + \frac{\partial E_l}{\partial D_i} dD_i + \frac{\partial E_l}{\partial (\partial \sigma_{mn} / \partial X_o)} d\left(\frac{\partial \sigma_{mn}}{\partial X_o}\right) + \frac{\partial E_l}{\partial S} dS$$

where we assume each partial derivative is evaluated allowing only the specific component of the tensor in its denominator to vary: all other components of that tensor and all other tensor variables are held constant. Relabeling the partial derivatives simplifies the equation and emphasizes the tensor nature of these coefficients; thus, the equation becomes:

$$dE_l = -g_{ljk} d\sigma_{jk} + \beta_{li} dD_i - k_{lmno} d\left(\frac{\partial \sigma_{mn}}{\partial X_o}\right) + \phi_l dS.$$

The minus signs are chosen for later simplification of this equation.

As in Chapter III, we assume the process is almost adiabatic and neglect the last term. Thus, the equation reduces to:

$$dE_l = -g_{ljk} d\sigma_{jk} + \beta_{li} dD_i - k_{lmno} d\left(\frac{\partial \sigma_{mn}}{\partial X_o}\right).$$

To find E_l itself, we integrate the above equation in state space from an initial state where all independent variables are zero to a final one where they have achieved their final values. We assume in performing the integration that the coefficients g_{ljk} , β_{li} , and k_{lmno} are independent, respectively, of σ_{jk} , D_i , and $(\partial \sigma_{mn} / \partial X_o)$ so that they may each be brought out of the integration sign. The result is:

$$E_l = -g_{ljk} \sigma_{jk} + \beta_{li} D_i - k_{lmno} \left(\frac{\partial \sigma_{mn}}{\partial X_o}\right) \quad (4B:1)$$

where the variables mentioned are the final value of these variables when the force is fully applied to the sample.

To express these unknown coefficients, g_{ljk} , etc., in terms of known ones, we will write D_i as a function of σ_{jk} , E_l , $\frac{\partial \sigma_{mn}}{\partial X_o}$, again neglecting S .

$$D_i = D_i(\sigma_{jk}, E_l, \frac{\partial \sigma_{mn}}{\partial X_o}).$$

In differential form this equation is:

$$dD_i = \frac{\partial D_i}{\partial \sigma_{jk}} d\sigma_{jk} + \frac{\partial D_i}{\partial E_l} dE_l + \frac{\partial D_i}{\partial (\partial \sigma_{mn} / \partial X_o)} d\left(\frac{\partial \sigma_{mn}}{\partial X_o}\right).$$

For the same reasons as in Chapter III, we identify $(\partial D_i / \partial \sigma_{jk})$ as the piezoelectric modulus d_{ijk} , and $(\partial D_i / \partial E_l)$ as the permittivity component ϵ_{il} . In addition, there is a new coefficient $\partial D_i / \partial (\partial \sigma_{mn} / \partial X_o)$ which we label as f_{imno} . Just as d_{ijk} is a coefficient relating σ_{jk} to P_i (or to D_i when $\vec{E} = 0$), so f_{imno} is a coefficient relating $(\partial \sigma_{mn} / \partial X_o)$ to P_i (or to D_i when $\vec{E} = 0$, which is assumed in the previous equation).¹ Thus, the previous equation can be rewritten as:

$$dD_i = d_{ijk} d\sigma_{jk} + \epsilon_{il} dE_l + f_{imno} d(\partial \sigma_{mn} / \partial X_o).$$

To find D_i , instead of dD_i , we integrate both sides of the equation in state space from an initial state where all independent variables are zero to a final one in which the independent variables have reached their full values after the sample is fully loaded. We assume the coefficients d_{ijk} , ϵ_{il} , and f_{imno} do not depend on their corresponding independent variables and, thus, come out of the integral signs. The result of the integration is:

$$D_i = d_{ijk} \sigma_{jk} + \epsilon_{il} E_l + f_{imno} \frac{\partial \sigma_{mn}}{\partial X_o}.$$

In order to solve this equation for E_l , we will rewrite it in matrix form,

$$D_i = d_{ij} \sigma_j + \epsilon_{il} E_l + f_{ip} \left(\frac{\partial \sigma}{\partial X} \right)_p$$

¹Both d_{ijk} and f_{imno} give the effect of purely mechanical deformation to polarization, not including any effect of polarization by an electric field. Why is this so, since in general, a mechanical polarization also produces an electric field? Because d_{ijk} and f_{imno} are measured under short-circuit conditions, where $\vec{E}$ is forced to remain zero, implying no effects of electrical polarization are included in d_{ijk} and f_{imno} .

where we now think of the 27-element tensor $(\partial \sigma_{mn} / \partial X_o)$, as a (1 X 27) column matrix. To show that we now regard each factor as a matrix, we put parentheses about each factor

$$(D_i) = (d_{ij})(\sigma_j) + (\epsilon_{il})(E_l) + (f_{ip}) \left(\frac{\partial \sigma}{\partial X} \right)_p$$

Since our aim is to find (E_l) , we isolate the term $(\epsilon_{il})(E_l)$ on the left side of the equation and multiply by the inverse, $(\epsilon_{il})^{-1}$, of the square, non-singular permittivity matrix to obtain:

$$(E_l) = -(\epsilon_{il})^{-1} (d_{ij})(\sigma_j) + (\epsilon_{il})^{-1} (D_i) - (\epsilon_{il})^{-1} (f_{ip}) \left(\frac{\partial \sigma}{\partial X} \right)_p$$

For all materials in our experiment

$$(\epsilon_{il})^{-1} = \frac{\delta_{il}}{\epsilon_{ii}}$$

as was shown in Chapter III.

Now reverting to component form, our equation becomes

$$E_l = - \frac{\delta_{il}}{\epsilon_{ii}} d_{ij} \sigma_j + \frac{\delta_{il}}{\epsilon_{ii}} D_i - \frac{\delta_{il}}{\epsilon_{ii}} f_{ip} \left(\frac{\partial \sigma}{\partial X} \right)_p$$

or

$$E_l = - \frac{d_{lj}}{\epsilon_{ll}} \sigma_j + \frac{D_l}{\epsilon_{ll}} - \frac{f_{lp}}{\epsilon_{ll}} \left(\frac{\partial \sigma}{\partial X} \right)_p$$

Expanding the equation to full tensor form, so we can compare it to equation (4B:1), it becomes:

$$E_l = - \frac{d_{ljk}}{\epsilon_{ll}} \sigma_{jk} + \frac{D_l}{\epsilon_{ll}} - \frac{f_{lmno}}{\epsilon_{ll}} \frac{\partial \sigma_{mn}}{\partial X_o} \quad (4B:3)$$

This is the general equation for calculating E_l in bone, quartz, etc., under adiabatic conditions according to the extended piezoelectric theory. In order for equations (4B:3) and (4B:1) to be equal for all values of the independent variables, the coefficients of the independent variables must be equal. Therefore,

$$g_{ljk} = \frac{d_{ljk}}{\epsilon_{ll}}, \quad \beta_{li} = \frac{\delta_{li}}{\epsilon_{ll}}, \quad k_{lmno} = \frac{f_{lmno}}{\epsilon_{ll}}$$

Also notice this important feature of the general equation of the extended theory. If f_{lmno} is zero, then the general equation of the extended theory reduces to the equation of the standard theory. Thus, the standard theory is a special case of this extended theory of piezoelectricity.

C. Applying General Equation for E_θ to Piezoelectric Bars in Cantilever Bending

Next we will apply the extended theory, developed in section B, to the special problem of finding the voltage between two electrodes on opposite faces of a thin bar bent as a cantilever and subject to the same conditions we assumed in Chapter III; viz.:

1. All processes are reversible in our system, the piezoelectric bar.
2. Our system neither gains nor loses mass, but it may exchange energy with its surroundings.
3. The only uncompensated electric field in the bar is caused by the applied stress, not by the pyroelectricity, whose effect has been neutralized
4. The electrodes have no excess free charge on them; i.e., they are open circuited. If excess free charge

is present on the electrodes, the effect will be merely to reduce the value of the difference of potential calculated in this section by a factor. The sign of the voltage will not be affected, as Chapter V proves.

The basic strategy is the same here as in Chapter III: find E_2 at each point $\vec{r}$ and integrate E_2 parallel to the Y-axis to find ΔV_o . First we find E_2 by letting $\ell = 2$ in equation (4B:3); i.e.,

$$E_2 = -\frac{d_{2jk}}{\epsilon_{22}} \sigma_{jk} + \frac{D_2}{\epsilon_{22}} - \frac{f_{2mno}}{\epsilon_{22}} \frac{\partial \sigma_{mn}}{\partial X_o}.$$

For thin bars, D_2 is zero, as we proved in Chapter III. Therefore,

$$E_2 = -\frac{d_{2jk}}{\epsilon_{22}} \sigma_{jk} - \frac{f_{2mno}}{\epsilon_{22}} \frac{\partial \sigma_{mn}}{\partial X_o}. \quad (4C:1)$$

To complete our calculation of E_2 , we need to know (σ_{jk}) in the materials tested in these experiments, and especially for bone and tendon, the materials which motivated the development of the extended theory. Just as in Chapter III, (σ_{jk}) is probably determined

almost entirely by the applied forces rather than the converse piezoelectric effect.¹ Therefore, $(\partial\sigma_{mn}/\partial X_o)$ must also be determined almost exclusively by the applied forces. Appendix E proves that the same plane stress distribution we used in Chapter III is a reasonable approximation for (σ_{ij}) in the center region of our bars of bone and tendon, where our electrodes are located. That is, we assume

$$(\sigma_{ij}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \sigma_{23} \\ 0 & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

where

$$\sigma_{23} = \sigma_{32} = \frac{-3F}{4bh^3} (h^2 - Y^2)$$

$$\sigma_{33} = \frac{-3F}{2bh^3} YZ$$

b = width of bar along X-axis

2h = height of bar along Y-axis

F = force depressing the bar near its free end.

Substituting this approximate form of (σ_{ij}) into equation (4C:1) for E_2 , we obtain

$$E_2 = \frac{-1}{\epsilon_{22}} \left[d_{223}\sigma_{23} + d_{232}\sigma_{32} + d_{233}\sigma_{33} + f_{223p} \frac{\partial\sigma_{23}(Y)}{\partial X_p} + f_{232p} \frac{\partial\sigma_{32}(Y)}{\partial X_p} + f_{233p} \frac{\partial\sigma_{33}(Y,Z)}{\partial X_p} \right]$$

¹If there is any new converse effect corresponding to $(\partial\sigma_{mn}/\partial X_o)$, it probably is no more effective in determining the strain in the material than the ordinary, homogeneous converse piezoelectric effect, since experiments show that the direct piezoelectric effects of (σ_{mn}) and $(\partial\sigma_{mn}/\partial X_o)$ are of roughly the same order of magnitude.

Remembering that σ_{23} equals σ_{32} and that consequently their corresponding partials are also equal, this equation can be rewritten as:

$$E_2 = \frac{-1}{\epsilon_{22}} \left[(d_{232} + d_{223})\sigma_{23} + d_{233}\sigma_{33} + (f_{232p} + f_{223p}) \frac{\partial \sigma_{23}(Y)}{\partial x_p} + f_{233p} \frac{\partial \sigma_{33}(Y,Z)}{\partial x_p} \right].$$

Since σ_{33} depends only on Y and Z, only its (Y- and Z- partial derivatives are non-zero. Similarly, since σ_{23} depends only on Y, only its Y-partial is non-zero. Incorporating these facts into the previous equation, it becomes:

$$E_2 = \frac{-1}{\epsilon_{22}} \left[(d_{232} + d_{223})\sigma_{23} + d_{233}\sigma_{33} + (f_{2322} + f_{2232}) \frac{\partial \sigma_{23}}{\partial x_2} + f_{2332} \frac{\partial \sigma_{33}}{\partial x_2} + f_{2333} \frac{\partial \sigma_{33}}{\partial x_3} \right]. \quad (4C:2)$$

To find ΔV_o , we integrate E_2 in between the electrodes, i.e.,

$$\Delta V_o = - \int_{-h}^h E_2 dY,$$

When we substitute equation (4C:2) for E_2 , many terms on the right hand side of the previous equation integrate to zero, viz., all those terms which are odd in Y, since the integration is between symmetric limits in Y. Specifically the terms going to zero upon integration are those involving σ_{33} , $\frac{\partial \sigma_{23}}{\partial Y}$, $\frac{\partial \sigma_{33}}{\partial Z}$. This leaves only the following terms after integration:

$$\Delta V_o = \frac{-1}{\epsilon_{22}} \frac{F}{b} \left[d_{24} + \frac{3f_{2332}Z}{h^2} \right] \quad (4C:3)$$

where we have relabeled $(d_{223} + d_{232})$ as d_{24} in matrix form. This equation is the prediction of the extended theory of piezoelectricity

of how the equilibrium difference of potential across a thin bar of piezoelectric material should depend on deflecting force, F ; distance, Z , from the electrodes to where the force is applied; and several geometrical properties, b and h , of the bar.

Notice that if f_{2332} is zero, then the equation becomes

$$\Delta V_o = \frac{-F}{\epsilon_{22}} \frac{d_{24}}{b}$$

which is the same as the prediction made by the standard theory of piezoelectricity.

If f_{2332} is important, as we suppose it is, why was it never detected before and measured? Because the standard way to observe the piezoelectric effect is to subject the material in question to a homogeneous stress and observe the voltages that exist or free charge that flows between electrodes on its surface. However, f_{2332} would only manifest itself during inhomogeneous stress, which is not produced during the usual tests.

D. Sign Changes of ΔV_0 According to Extended Theory Following

Rotation of the Sample

We hypothesize in the present section that the term containing f_{2332} dominates the term containing d_{24} in determining ΔV_0 . When the bar is rotated, only those quantities, like ϵ_{22} , f_{2332} , etc., that are intrinsic properties of the material of the bar change in value. The only such intrinsic properties in the term which we assume dominates are f_{2332} and ϵ_{22} . Chapter III proved that ϵ_{22} never changes sign following 180° -rotation of the bar about the X-, Y-, or Z-axes. Therefore, according to the extended theory, f_{2332} in the dominating term entirely determines how ΔV_0 will change following a rotation of the bar. If f_{2332} were a component of a tensor, it would be easy to predict how its value would change due to these 180° -rotations and, thus, to know how the value of ΔV_0 would be expected to change. The remainder of this section will show that, indeed, f_{2332} is a component of a fourth-rank tensor; that f_{2332} and, hence, ΔV_0 do not change value following 180° -rotations about the X-, Y-, or Z-axes; and that f_{2332} is not zero, implying that the term containing f_{2332} could, in fact, dominate in determining ΔV_0 .

That f_{2332} is a Component of a Fourth-Rank Tensor: The factor f_{ijkl} is defined as a coefficient linking the i^{th} component of the polarization vector at a point $\vec{r}$ to the spatial rate of change of stress, $\frac{\partial \sigma_{jk}}{\partial x_i}$, at that point, i.e.,

$$P_i = f_{ijkl} \frac{\partial \sigma_{jk}}{\partial x_l}$$

(P_i) is known to be a first-rank tensor. If $(\partial \sigma_{jk} / \partial x_l)$ were a third-rank tensor, then, by the theorem proved in Appendix A, (f_{ijkl}) would

necessarily be a fourth-rank tensor, as claimed. Thus, the proof hinges on showing $(\partial \sigma_{jk} / \partial X_l)$ is a third-rank tensor, which means showing two things: that $(\partial \sigma_{jk} / \partial X_l)$ has 3^3 components and that it changes value under an orthogonal transformation according to the usual rules for tensors.

Clearly $(\partial \sigma_{jk} / \partial X_l)$ has the correct number of components. The three indices j , k , and l are independent and can each assume any one of the values 1, 2, or 3. Thus, there are 3^3 possible sets of index values; and each of these sets determines one possible component of $(\partial \sigma_{jk} / \partial X_l)$. Therefore, there are 3^3 components in $(\partial \sigma_{jk} / \partial X_l)$.

The difficult part of this proof is to show that $(\partial \sigma_{jk} / \partial X_l)$ changes value following an orthogonal transformation the way a third-rank tensor should. We begin this proof by noting that since (σ_{jk}) is known to be a second-rank tensor, its value, (σ'_{ij}) , after an orthogonal transformation is related to its value before as follows:

$$\sigma'_{ij} = A_{i' i} A_{j' j} \sigma_{ij} \quad (4D:1)$$

We differentiate both sides with respect to $X_{k'}$

$$\frac{\partial \sigma'_{ij}}{\partial X_{k'}} = \frac{\partial}{\partial X_{k'}} (A_{i' i} A_{j' j} \sigma_{ij})$$

to form on the left side one of the desiderata, the stress gradient

after transformation. Since the transformation is orthogonal, the transformation matrix, $(A_{i' i})$, is independent of position $X_{k'}$. Therefore, $A_{i' i}$ and $A_{j' j}$ come out of the differentiation operation; and the previous equation becomes

$$\frac{\partial \sigma'_{ij}}{\partial X_{k'}} = A_{i' i} A_{j' j} \frac{\partial \sigma_{ij}}{\partial X_{k'}} \quad (4D:2)$$

We really want the partial with respect to X_k , not $X_{k'}$, on the right side. To get it, we recall that for a particular orthogonal transformation, the location of an atom i after transformation, i.e., $(X_{k'})$, depends only on where it was before transformation, i.e. (X_k) . Therefore, the previous equation can be rewritten as

$$\frac{\partial \sigma'_{i'j'}}{\partial X_{k'}} = A_{i'i} A_{j'j} \frac{\partial \sigma_{ij}}{\partial X_k} \frac{\partial X_k}{\partial X_{k'}}.$$

The factor $\partial X_k / \partial X_{k'}$ is just the cosine of the angle between the k' -axis after orthogonal transformation and the k -axis before transformation, i.e.,

$$\frac{\partial X_k}{\partial X_{k'}} = \cos \angle(k, k') = \cos \angle(k', k) \equiv A_{k'k}.$$

Substituting this in the previous equation, it becomes

$$\frac{\partial \sigma'_{i'j'}}{\partial X_{k'}} = A_{i'i} A_{j'j} \frac{\partial \sigma_{ij}}{\partial X_k} A_{k'k}.$$

Since the order of factors in a tensor equation makes no difference, the equation can be rewritten as

$$\frac{\partial \sigma'_{i'j'}}{\partial X_{k'}} = A_{i'i} A_{j'j} A_{k'k} \frac{\partial \sigma_{ij}}{\partial X_k}$$

which we recognize as the correct rule for the change of a third-rank tensor following orthogonal transformation. Thus, we have shown $(\partial \sigma_{jk} / \partial X_i)$ has the two necessary and sufficient properties to be a third-rank tensor.

Having established that $(\partial \sigma_{jk} / \partial X_i)$ is a valid third-rank tensor, it follows by the theorem of Appendix A that (f_{ijkl}) is a fourth-rank tensor and f_{2332} is one of its components. Q.E.D.

That f_{2332} Does Not Change Sign Following 180° Rotations of Bar:

Since (f_{ijkl}) is a fourth-rank tensor, its component $f'_{2'3'3'2'}$ after orthogonal transformation must be related as follows to its components

(f_{ijkl}) before transformation in this way,

$$f'_{2332} = A_{2i} A_{3j} A_{3k} A_{2l} f_{ijkl} \quad (4D:4)$$

The transformation matrices for 180° -rotations about the X-, Y-, and Z-axes, which are all orthogonal transformations, are, respectively:

$$\begin{pmatrix} +1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +1 \end{pmatrix}$$

E.g., for 180° rotation about the Y-axis

$$A_{2m} = \delta_{2m}$$

$$A_{3m} = -\delta_{3m}$$

and, thus, for 180° -rotations about the Y-axis,

$$f_{2332} = \delta_{2i} (-1) \delta_{3j} (-1) \delta_{3k} \delta_{2l} f_{ijkl}$$

$$f'_{2332} = (-1)^2 f_{2332}$$

$$f'_{2332} = + f_{2332}$$

Directly substituting the values of $(A_i'{}_i)$ for the other rotations into equation (4D:4) establishes the fact that f'_{2332} equals $+f_{2332}$ in all cases.¹

¹A general relation can be obtained by observing that the transformation matrices for 180° -rotations show that in all cases

$$A_{ij} = \pm \delta_{ij}$$

The (+1) value appertains if the 180° rotation is about the i^{th} axis; otherwise the value is (-1). This chart follows as a result.

Number of times an axis
is mentioned in subscript
of f_{ijkl}

Relation of $f'_{i'j'k'l'}$ and f_{ijkl}

0	$f' = (-1)(-1)(-1)(-1) = +f$
1	$f' = (+1)(-1)(-1)(-1) = -f$
2	$f' = (+1)(+1)(-1)(-1) = +f$
3	$f' = (+1)(+1)(+1)(-1) = -f$
4	$f' = (+1)(+1)(+1)(+1) = +f$

Thus, to be invariant under 180° -rotations about all three axes, a component of (f_{ijkl}) must have each axis mentioned in its subscript 0, 2, or 4 times, i.e., an even number of times.

Since f_{2332} can never change magnitude or sign under 180° -rotation about the X-, Y-, or Z-axes, ΔV_0 would never change sign either if it depended primarily on the term containing f_{2332} .

That f_{2332} is Non-Zero: It is all well and good that f_{2332} has the correct sign invariance under 180° rotations, but if f_{2332} happened to be zero, the f_{2332} -containing term could not dominate and thus determine the sign of ΔV_0 . Hence, we need to show f_{2332} is not required by point symmetry considerations to be zero.

The most direct way to show this would be write down the equation for the change of f_{ijkl} under an orthogonal transformation whose transformation matrix is (A_{ij}) , i.e.,

$$f'_{i'j'k'l'} = A_{i'i} A_{j'j} A_{k'k} A_{l'l} f_{ijkl}$$

Then we would find (A_{ij}) for all point symmetry operations, which are orthogonal transformations for homogeneous materials. For these particular orthogonal, symmetry transformations, we would write

$$f_{ijkl} = f'_{i'j'k'l'} = A_{i'i} A_{j'j} A_{k'k} A_{l'l} f_{ijkl}$$

This would yield up to 3^4 or 81 independent equations which we would have to solve for the elements of (f_{ijkl}) . All this is a lot of work.

A much easier way to solve the problem would be to derive the answer from what we already know about the form of bone's elastic constants, (c_{ijkl}) , which is also a fourth-rank tensor. We will show that if the element c_{2332} is not zero, then f_{2332} is not required by point symmetry to be zero. There are two reasons why any elements of (c_{ijkl}) might be zero:

1. The point symmetry of the material requires it.
2. Other considerations besides point symmetry require it.

These two factors operate independently in this sense: if point symmetry alone requires that c_{ijkl} be zero, no other factor can negate that and make it non-zero. Thus, if c_{2332} equals zero, we cannot be sure whether the point symmetry of the material required it or other factors required it. But if c_{2332} is not zero, then we can be sure neither point symmetry nor any other consideration requires c_{2332} to be zero. Point symmetry of a material requires exactly the same form for all fourth-rank, intrinsic tensor properties. This means that if c_{2332} is not zero, point symmetry alone does not require the 2332-element of this fourth-rank tensor or any other fourth-rank tensor to be zero. In particular, point symmetry does not require f_{2332} to be zero. We assume, of course, that both f_{2332} and c_{2332} are measured relative to the same orthogonal frame at the point in question.

The last step in proving that f_{2332} need not be zero because of point symmetry is now clear: just show c_{2332} measured in the same frame is not zero. We do have Lang's data about (c_{ijkl}) in bone, and fortunately it is measured relative to the natural axes of bone, which in our experiment are the same as the laboratory axes at each point, which is also the frame f_{2332} is measured in.¹ Thus, we can use Lang's values directly to find c_{2332} in the laboratory frame. However, Lang wrote the elastic

¹Lang, "Ultrasonic Methods....," pp. 101-105.

constants of bone in matrix form, (c_{mn}) , where the first two and last two indices are condensed according to the rules for writing stress in matrix form. Which elements of c_{mn} correspond to c_{2332} or, more to the point, to f_{2332} ? There is really nothing immutable about the order of the subscripts in f_{2332} : we could have defined the coefficients so that the order could have been f_{3322} . Thus, there are two possible elements of (c_{mn}) corresponding to f_{2332} , viz., c_{44} and c_{23} , but neither is zero according to Lang.

Therefore, since neither c_{44} nor c_{23} is zero in the laboratory frame, neither is f_{2332} nor f_{2233} zero in the laboratory frame. Thus, the f_{2332} -bearing term could really dominate in the equation for ΔV_0 , allowing f_{2332} to determine the sign changes of ΔV_0 following 180° -rotation. Since f_{2332} does not change sign following 180° -rotation about the X-, Y-, or Z-axes, neither should ΔV_0 change sign following these rotations, provided that the f_{2332} -term does indeed dominate and that the prediction of the extended theory is correct. Chapter V will set limits on exactly how big f_{2332} must be for the term containing it to dominate in the equation for ΔV_0 .

E. Further Tests of the Extended Theory

We have shown that the extended theory does predict the correct changes in the sign of ΔV_o following 180° rotation about the principal axes in the laboratory frame, but we need more proof that the extended theory is really correct. We need to find some other easily-tested prediction of the extended theory that is radically different from the prediction of the standard theory and then to test by experiment which prediction is correct in reality.

The crucial test is easily seen from merely looking at the equations that the standard and extended theories offer for ΔV_o :

$$\Delta V_o = \frac{-F d_{24}}{\epsilon_{22} b} \quad (\text{standard theory})$$

$$\Delta V_o = \frac{-F}{\epsilon_{22} b} \left[d_{24} + \frac{3f_{2332} Z}{h^2} \right] \quad (\text{extended theory})$$

The extended theory predicts that if f_{2332} is to determine the sign changes of ΔV_o , then the term containing f_{2332} must dominate. However, this term also contains Z , a dependence on the distance from the cross section containing the sensing electrodes to the cross section where the depressing force is applied. The standard theory predicts ΔV_o should be independent of Z , i.e., no matter where along the bar the electrodes are placed the same ΔV_o should be measured. This is because in the standard theory the only component of the stress that effectively contributes to ΔV_o is the integrated value of σ_{23} , which is constant through every cross section of the bar. Figure (4E:1) summarizes these predictions.

This graph also shows that when the bar is rotated end-for-end either about the X- or Y-axes that both theories predict the curves are shifted down because d_{24} , being a third-rank tensor quantity, reverses sign.

Figure (4E:1)
 Predictions for ΔV_0 Across a Thin Piezoelectric Bar According
 to the Standard and Extended Theories of Piezoelectricity

F. Summary

This chapter showed that by introducing a new variable, the stress gradient, into piezoelectric theory, a new equation for ΔV_0 is produced containing a component of a fourth-rank tensor, f_{2332} . If the term containing f_{2332} dominates in determining ΔV_0 , ΔV_0 will not change sign following 180° -rotation of the bar about the X-, Y-, or Z-axes because f_{2332} does not. This concurs with previous experimental findings for bone and tendon. However, the new equation makes another astonishing, further prediction: if ΔV_0 does not change sign following rotations of the bar because the f_{2332} -term dominates, then ΔV_0 must increase linearly as the electrodes are moved further back from the depressed end of the bar. The standard theory predicts ΔV_0 should not vary with position along the bar. The next chapter describes in detail the experiments which were done to determine which of these predictions is correct.