First and Second Order Equations for Piezoelectric Crystals Expressed in Tensor Form

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INTRODUCTION

AEOLOTROPIC substances have been used for a wide variety of elastic piezoelectric, dielectric, pyroelectric, temperature expansive, piezo-optic and electro-optic effects. While most of these effects may be found treated in various publications[1] there does not appear to be any integrated treatment of them by the tensor method which greatly simplifies the method of writing and manipulating the relations between fundamental quantities. Other short hand methods such as the matrix method[2] can also be used for all the linear effects, but for second order effects involving tensors higher than rank four, tensor methods are essential. Accordingly, it is the purpose of this paper to present such a derivation. The notation used is that agreed upon by a committee of piezoelectric experts under the auspices of the Institute of Radio Engineers.

In the first part the definition of stress and strain are given and their interrelation, the generalized Hookes law is discussed. The modifications caused by adiabatic conditions are considered. When electric fields, stresses, and temperature changes are applied, there are nine first order effects each of which requires a tensor to express the resulting constants. The effects are the elastic effect, the direct and inverse piezoelectric effects, the temperature expansion effect, the dielectric effect, the pyroelectric effect, the heat of deformation, the electrocaloric effect, and the specific heat. There are three relations between these nine effects. Making use of the tensor transformation of axes, the results of the symmetries existing for the 32 types of crystals are investigated and the possible constants are derived for these nine effects.

Methods are discussed for measuring these properties for all 32 crystal classes. By measuring the constants of a specified number of oriented cuts for each crystal class, vibrating in longitudinal and shear modes, all of the elastic, dielectric and piezoelectric constants can be obtained. Methods for calculating the properties of the oriented cuts are given and for deriving the fundamental constants from these measurements.

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[1] For example Voigt, "Lehrbuch der Kristall Physik," B. Teubner, 1910; Wooster, "Crystal Physics," Cambridge Press, 1938; Cady "Piezo-electricity" McGraw Hill, 1946.

[2] The matrix method is well described by W. L. Bond "The Mathematics of the Physical Properties of Crystals," B. S. T. J., Vol. 22, pp. 1–72, 1943.

Second order effects are also considered. These effects (neglecting second order temperature effects) are elastic constants whose values depend on the applied stress and the electric displacement, the electrostrictive effect, piezoelectric constants that depend on the applied stress, the piezo-optical effect and the electro-optical effect. These second order equations can also be used to discuss the changes that occur in ferroelectric type crystals such as Rochelle Salt, for which between the temperature of −18°C. and +24°C., a spontaneous polarization occurs along one direction in the crystal. This spontaneous polarization gives rise to a first order piezoelectric deformation and to second order electrostrictive effects. It produces changes in the elastic constants, the piezoelectric constants and the dielectric constants. Some measurements have been made for Rochelle Salt evaluating these second order constants.

Mueller in his theory of Rochelle Salt considers that the crystal changes from an orthorhombic crystal to a monoclinic crystal when it becomes spontaneously polarized. An alternate view developed here is that all of the new constants created by the spontaneous polarization are the result of second order effects in the orthorhombic crystal. As shown in section 7 these produce new constants proportional to the square of the spontaneous polarization which are the ones existing in a monoclinic crystal. On this view "morphic" effects are second order effects produced by the spontaneous polarization.

1. STRESS AND STRAIN RELATIONS IN AEOLOTROPIC CRYSTALS

I.I. *Specification of Stress*

The stresses exerted on any elementary cube of material with its edges along the three rectangular axes X, Y and Z can be specified by considering the stresses on each face of the cube illustrated by Fig. 1. The total stress acting on the face ABCD normal to the X axis can be represented by a resultant force R, with its center of application at the center of the face, plus a couple which takes account of the variation of the stress across the face. The force R is directed outward, since a stress is considered positive if it exerts a tension. As the face is shrunk in size, the force R will be proportional to the area of the face, while the couple will vary as the cube of the dimension. Hence in the limit the couple can be neglected with respect to the force R. The stress (force per unit area) due to R can be resolved into three components along the three axes to which we give the designation

$$T_{xx_2}\,, \qquad T_{yx_2}\,, \qquad T_{zx_2}\,. \tag{1}$$

Here the first letter designates the direction of the stress component and the second letter x_2 denotes the second face of the cube normal to the X axis. Similarly for the first X face OEFG, the stress resultant can be resolved into the components T_{xx_1}, T_{yx_1}, T_{zx_1}, which are oppositely directed to those of the second face. The remaining stress components on the other four faces have the designation

$$\begin{array}{llll} \text{Face OABE} & T_{xy_1}, & T_{yy_1}, & T_{zy_1} \\ \text{CFGD} & T_{xy_2}, & T_{yy_2}, & T_{zy_2} \\ \text{OADG} & T_{xz_1}, & T_{yz_1}, & T_{zz_1} \\ \text{BCFE} & T_{xz_2}, & T_{yz_2}, & T_{zz_2}. \end{array} \qquad (2)$$

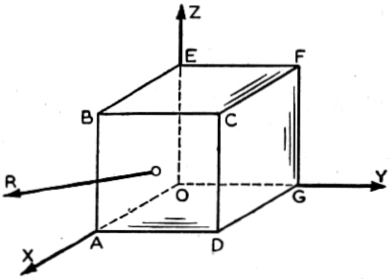

Fig. 1.—Cube showing method for specifying stresses.

The resultant force in the X direction is obtained by summing all the forces with components in the X direction or

$$F_x = (T_{xx_1} - T_{xx_2})\, dydz + (T_{xy_1} - T_{xy_2})\, dxdz + (T_{xz_1} - T_{xz_2})\, dxdy. \qquad (3)$$

But

$$T_{xx_2} = -T_{xx_1} + \frac{\partial T_{xx}}{\partial x}\, dx; \qquad T_{xy_2} = -T_{xy_1} + \frac{\partial T_{xy}}{\partial y}\, dy; \qquad T_{xz_2} = -T_{xz_1} + \frac{\partial T_{xz}}{\partial z}\, dz \qquad (4)$$

and equation (3) can be written in the form

$$F_x = -\left(\frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z}\right) dx\, dy\, dz. \qquad (5)$$

Similarly the resultant forces in the other directions are

$$\begin{aligned} F_y &= -\left(\frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z}\right) dx\, dy\, dz \\ F_z &= -\left(\frac{\partial T_{zx}}{\partial x} + \frac{\partial T_{zy}}{\partial y} + \frac{\partial T_{zz}}{\partial z}\right) dx\, dy\, dz. \end{aligned} \qquad (6)$$

We call the components

$$\begin{vmatrix} T_{xx}, & T_{xy}, & T_{xz} \\ T_{yx}, & T_{yy}, & T_{yz} \\ T_{zx}, & T_{zy}, & T_{zz} \end{vmatrix} = \begin{vmatrix} T_{11}, & T_{12}, & T_{13} \\ T_{21}, & T_{22}, & T_{23} \\ T_{31}, & T_{32}, & T_{33} \end{vmatrix} \tag{7}$$

the stress components exerted on the elementary cube which tend to deform it. The rate of change of these stresses determines the resultant force on the cube. The second form of (7) is commonly used when the stresses are considered as a second rank tensor.

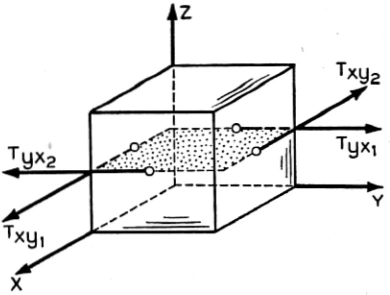

Fig. 2.—Shearing stresses exerted on a cube.

It can be shown that there is a relation between 3 pairs of these components, namely

$$T_{xy} = T_{yx}\,; \qquad T_{xz} = T_{zx}\,; \qquad T_{yz} = T_{zy}\,. \tag{8}$$

To show this consider Fig. 2 which shows the stresses tending to rotate the elementary cube about the Z axis. The stresses T_{yx_2} and T_{yx_1} tend to rotate the cube about the Z axis by producing the couple

$$\frac{T_{yx}\,dx\,dy\,dz}{2}\,. \tag{9}$$

The stresses T_{xy_1} and T_{xy_2} produce a couple tending to cause a rotation in the opposite direction so that

$$\tfrac{1}{2}\,(T_{yx} - T_{xy})\,dx\,dy\,dz = \text{couple} = I\ddot{\omega}_z \tag{10}$$

is the total couple tending to produce a rotation around the Z axis. But from dynamics, it is known that this couple is equal to the product of the moment of inertia of the section times the angular acceleration. This moment of inertia of the section is proportional to the fourth power of the cube edge and the angular acceleration is finite. Hence as the cube edge approaches zero, the right hand side of (10) is one order smaller than the left hand side and hence

$$T_{yx} = T_{xy}. \tag{11}$$

The same argument applies to the other terms. Hence the stress components of (7) can be written in the symmetrical form

$$\begin{vmatrix} T_{xx}, & T_{xy}, & T_{xz} \\ T_{xy}, & T_{yy}, & T_{yz} \\ T_{xz}, & T_{yz}, & T_{zz} \end{vmatrix} = \begin{vmatrix} T_{11}, & T_{12}, & T_{13} \\ T_{12}, & T_{22}, & T_{23} \\ T_{13}; & T_{23}, & T_{33} \end{vmatrix} = \begin{vmatrix} T_1, & T_6, & T_5 \\ T_6, & T_2, & T_4 \\ T_5, & T_4, & T_3 \end{vmatrix}. \tag{12}$$

The last form is a short hand method for reducing the number of indices in the stress tensor. The reduced indices 1 to 6, correspond to the tensor indices if we replace

11 by 1; 22 by 2; 33 by 3; 23 by 4; 13 by 5; 12 by 6.

This last method is the most common way for writing the stresses.

1.2 *Strain Components*

The types of strain present in a body can be specified by considering two points P and Q of a medium, and calculating their separation in the strained condition. Let us consider the point P at the origin of coordinates and the point Q having the coordinates x, y and z as shown by Fig. 3. Upon straining the body, the points change to the positions P', Q'. In order to specify the strains, we have to calculate the difference in length after straining, or have to evaluate the distance $P'Q'-PQ$. After the material has stretched the point P' will have the coordinates ξ_1, η_1, ζ_1, while Q' will have the coordinates $x + \xi_2$; $y + \eta_2$; $z + \zeta_2$. But the displacement is a continuous function of the coordinates x, y and z so that we have

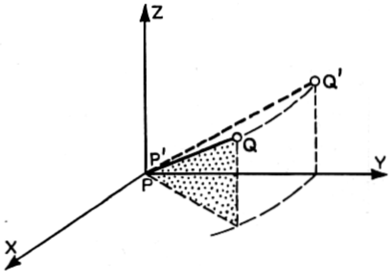

Fig. 3.—Change in length and position of a line due to strain in a solid body.

$$\xi_2 = \xi_1 + \frac{\partial \xi}{\partial x} x + \frac{\partial \xi}{\partial y} y + \frac{\partial \xi}{\partial z} z.$$

Similarly

$$\begin{aligned} \eta_2 &= \eta_1 + \frac{\partial \eta}{\partial x} x + \frac{\partial \eta}{\partial y} y + \frac{\partial \eta}{\partial z} z \\ \zeta_2 &= \zeta_1 + \frac{\partial \zeta}{\partial x} x + \frac{\partial \zeta}{\partial y} y + \frac{\partial \zeta}{\partial z} z. \end{aligned} \tag{13}$$

Hence subtracting the two lengths, we find that the increases in separation in the three directions are

$$\begin{aligned} \delta_x &= x \frac{\partial \xi}{\partial x} + y \frac{\partial \xi}{\partial y} + z \frac{\partial \xi}{\partial z} \\ \delta_y &= x \frac{\partial \eta}{\partial x} + y \frac{\partial \eta}{\partial y} + z \frac{\partial \eta}{\partial z} \\ \delta_z &= x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} + z \frac{\partial \zeta}{\partial z}. \end{aligned} \tag{14}$$

The net elongation of the line in the x direction is $x \frac{\partial \xi}{\partial x}$ and the elongation per unit length is $\frac{\partial \xi}{\partial x}$ which is defined as the linear strain in the x direction. We have therefore that the linear strains in the x, y and z directions are

$$S_1 = \frac{\partial \xi}{\partial x}; \qquad S_2 = \frac{\partial \eta}{\partial y}; \qquad S_3 = \frac{\partial \zeta}{\partial z}. \tag{15}$$

The remaining strain coefficients are usually defined as

$$S_4 = \frac{\partial \zeta}{\partial y} + \frac{\partial \eta}{\partial z}; \qquad S_5 = \frac{\partial \xi}{\partial z} + \frac{\partial \zeta}{\partial x}; \qquad S_6 = \frac{\partial \eta}{\partial x} + \frac{\partial \xi}{\partial y} \tag{16}$$

and the rotation coefficients by the equations

$$\omega_x = \frac{\partial \zeta}{\partial y} - \frac{\partial \eta}{\partial z}; \qquad \omega_y = \frac{\partial \xi}{\partial z} - \frac{\partial \zeta}{\partial x}; \qquad \omega_z = \frac{\partial \eta}{\partial x} - \frac{\partial \xi}{\partial y}. \tag{17}$$

Hence the relative displacement of any two points can be expressed as

$$\begin{aligned} \delta_x &= xS_1 + y\left(\frac{S_6 - \omega_z}{2}\right) + z\left(\frac{S_5 + \omega_y}{2}\right) \\ \delta_y &= x\left(\frac{S_6 + \omega_z}{2}\right) + yS_2 + z\left(\frac{S_4 - \omega_x}{2}\right) \\ \delta_z &= x\left(\frac{S_5 - \omega_y}{2}\right) + y\left(\frac{S_4 + \omega_x}{2}\right) + zS_3 \end{aligned} \tag{18}$$

which represents the most general type of displacement that the line $P\,Q$ can undergo.

As discussed in section 4 the definition of the shearing strains given by equation (16) does not allow them to be represented as part of a tensor. If however we defined the shearing strains as

$$2S_{23} = S_4 = \left(\frac{\partial\zeta}{\partial y} + \frac{\partial\eta}{\partial z}\right); \qquad 2S_{13} = S_5 = \frac{\partial\xi}{\partial z} + \frac{\partial\zeta}{\partial x}; \qquad 2S_{12} = S_6 = \frac{\partial\eta}{\partial x} + \frac{\partial\xi}{\partial y} \tag{19}$$

they can be expressed in the form of a symmetrical tensor

$$\begin{vmatrix} S_{11} & S_{12} & S_{13} \\ S_{12} & S_{22} & S_{23} \\ S_{13} & S_{23} & S_{33} \end{vmatrix} = \begin{vmatrix} S_1 & \frac{S_6}{2} & \frac{S_5}{2} \\ \frac{S_6}{2} & S_2 & \frac{S_4}{2} \\ \frac{S_5}{2} & \frac{S_4}{2} & S_3 \end{vmatrix}. \tag{20}$$

For an element suffering a shearing strain $S_6 = 2S_{12}$ only, the displacement along x is proportional to y, while the displacement along y is proportional to the x dimension. A cubic element of volume will be strained into a rhombic form, as shown by Fig. 4, and the cosine of the resulting angle θ measures the shearing deformation. For an element suffering a rotation ω_z only, the displacement along x is proportional to y and in the negative y direction, while the displacement along y is in the positive x direction. Hence a rectangle has the displacement shown by Fig. 5, which is a pure rotation of the body without change of form, about the z axis. For any

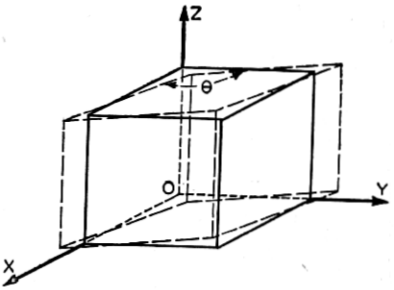

Fig. 4.—Distortion due to a shearing strain.

body in equilibrium or in nonrotational vibration, the ω's can be set equal to zero.

The total potential energy stored in a general distortion can be calculated as the sum of the energies due to the distortion of the various modes. For example in expanding the cube in the x direction by an amount $\frac{\partial \xi}{\partial x}\, dx = S_1\, dx$, the work done is the force times the displacement. The force wil be the force T_1 and will be $T_1\, dy\, dz$. Hence the potential energy stored in this distortion is

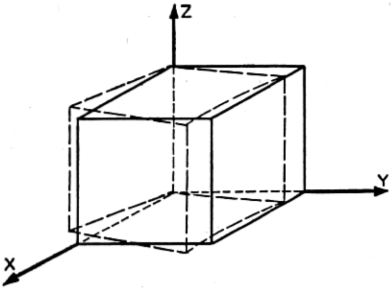

Fig. 5.—A rotation of a solid body.

$$T_1\, dS_1\;\, dx\, dy\, dz$$

For a shearing stress T_6 of the type shown by Fig. 4 the displacement $\frac{dS_6\, dx}{2}$ times the force $T_6\, dy\, dz$ and the displacement $\frac{dS_6\, dy}{2}$ times the force $T_6\, dx\, dz$ equals the stored energy or

$$\Delta PE_6 = \tfrac{1}{2}\,(dS_6T_6 + dS_6T_6)\, dx\, dy\, dz = dS_6T_6\, dx\, dy\, dz.$$

Hence for all modes of motion the stored potential ener gy is equal to

$$\Delta PE = [T_1\, dS_1 + T_2\, dS_2 + T_3\, dS_3 + T_4\, dS_4 + T_5\, dS_5 + T_6\, dS_6]\, dx\, dy\, dz. \tag{21}$$

1.3 *Generalized Hooke's Law*

Having specified stresses and strains, we next consider the relationship between them. For small displacements, it is a consequence of Hooke's Law that the stresses are proportional to the strains. For the most unsymmetrical medium, this proportionality can be written in the form

$$\begin{aligned}
T_1 &= c_{11}S_1 + c_{12}S_2 + c_{13}S_3 + c_{14}S_4 + c_{15}S_5 + c_{16}S_6 \\
T_2 &= c_{21}S_1 + c_{22}S_2 + c_{23}S_3 + c_{24}S_4 + c_{25}S_5 + c_{26}S_6 \\
T_3 &= c_{31}S_1 + c_{32}S_2 + c_{33}S_3 + c_{34}S_4 + c_{35}S_5 + c_{36}S_6 \\
T_4 &= c_{41}S_1 + c_{42}S_2 + c_{43}S_3 + c_{44}S_4 + c_{45}S_5 + c_{46}S_6 \\
T_5 &= c_{51}S_1 + c_{52}S_2 + c_{53}S_3 + c_{54}S_4 + c_{55}S_5 + c_{56}S_6 \\
T_6 &= c_{61}S_1 + c_{62}S_2 + c_{63}S_3 + c_{64}S_4 + c_{65}S_5 + c_{66}S_6
\end{aligned} \tag{22}$$

where c_{11} for example is an elastic constant expressing the proportionality between the S_1 strain and the T_1 stress in the absence of any other strains.

It can be shown that the law of conservation of energy, it is a necessary consequence that

$$c_{12} = c_{21} \text{ and in general } c_{ij} = c_{ji}\,. \tag{23}$$

This reduces the number of independent elastic constants for the most unsymmetrical medium to 21. As shown in a later section, any symmetry existing in the crystal will reduce the possible number of elastic constants and simplify the stress strain relationship of equation (22).

Introducing the values of the stresses from (22) in the expression for the potential energy (21), this can be written in the form

$$\begin{aligned}
2PE = c_{11}S_1^2 &+ 2c_{12}S_1S_2 + 2c_{13}S_1S_3 + 2c_{14}S_1S_4 + 2c_{15}S_1S_5 + 2c_{16}S_1S_6 \\
&+ c_{22}S_2^2 + 2c_{23}S_2S_3 + 2c_{24}S_2S_4 + 2c_{25}S_2S_5 + 2c_{26}S_2S_6 \\
&+ c_{33}S_3^2 + 2c_{34}S_3S_4 + 2c_{35}S_3S_5 + 2c_{36}S_3S_6 \\
&+ c_{44}S_4^2 + 2c_{45}S_4S_5 + 2c_{46}S_4S_6 \\
&+ c_{55}S_5^2 + 2c_{56}S_5S_6 \\
&+ c_{66}S_6^2\,.
\end{aligned} \tag{24}$$

The relations (22) thus can be obtained by differentiating the potential energy according to the relation

$$T_1 = \frac{\partial PE}{\partial S_1}; \qquad \cdots; \qquad T_6 = \frac{\partial PE}{\partial S_6}\,. \tag{25}$$

It is sometimes advantageous to express the strains in terms of the stresses. This can be done by solving the equations (22) simultaneously for the strains resulting in the equations

$$\begin{aligned}
S_1 &= s_{11}T_1 + s_{12}T_2 + s_{13}T_3 + s_{14}T_4 + s_{15}T_5 + s_{16}T_6 \\
S_2 &= s_{21}T_1 + s_{22}T_2 + s_{23}T_3 + s_{24}T_4 + s_{25}T_5 + s_{26}T_6 \\
S_3 &= s_{31}T_1 + s_{32}T_2 + s_{33}T_3 + s_{34}T_4 + s_{35}T_5 + s_{36}T_6 \\
S_4 &= s_{41}T_1 + s_{42}T_2 + s_{43}T_3 + s_{44}T_4 + s_{45}T_5 + s_{46}T_6 \\
S_5 &= s_{51}T_1 + s_{52}T_2 + s_{53}T_3 + s_{54}T_4 + s_{55}T_5 + s_{56}T_6 \\
S_6 &= s_{61}T_1 + s_{62}T_2 + s_{63}T_3 + s_{64}T_4 + s_{65}T_5 + s_{66}T_6
\end{aligned} \tag{26}$$

where

$$s_{ij} = \frac{(-1)^{i+j}\,\Delta^c_{ij}}{\Delta^c} \tag{27}$$

for which Δ^c is the determinant of the c_{ij} terms of (28) and Δ^c_{ij} the minor obtained by suppressing the ith and jth column

$$\Delta^c = \begin{vmatrix}
c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\
c_{12} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\
c_{13} & c_{23} & c_{33} & c_{34} & c_{35} & c_{36} \\
c_{14} & c_{24} & c_{34} & c_{44} & c_{45} & c_{46} \\
c_{15} & c_{25} & c_{35} & c_{45} & c_{55} & c_{56} \\
c_{16} & c_{26} & c_{36} & c_{46} & c_{56} & c_{66}
\end{vmatrix}. \tag{28}$$

Since $c_{ij} = c_{ji}$ it follows that $s_{ij} = s_{ji}$. The potential energy can be expressed in the form.

$$\begin{aligned}
2PE = s_{11}T_1^2 &+ 2s_{12}T_1T_2 + 2s_{13}T_1T_3 + 2s_{14}T_1T_4 + 2s_{15}T_1T_5 + 2s_{16}T_1T_6 \\
&+ s_{22}T_2^2 + 2s_{23}T_2T_3 + 2s_{24}T_2T_4 + 2s_{25}T_2T_5 + 2s_{26}T_2T_6 \\
&+ s_{33}T_3^2 + 2s_{34}T_3T_4 + 2s_{35}T_3T_5 + 2s_{36}T_3T_6 \\
&+ s_{44}T_4^2 + 2s_{45}T_4T_5 + 2s_{46}T_4T_6 \\
&+ s_{55}T_5^2 + 2s_{56}T_5T_6 \\
&+ s_{66}T_6^2.
\end{aligned} \tag{29}$$

The relations (26) can then be derived from expressions of the type

$$S_1 = \frac{\partial PE}{\partial T_1}; \qquad \cdots; \qquad S_6 = \frac{\partial PE}{\partial T_6}. \tag{30}$$

1.4 *Isothermal and Adiabatic Elastic Constants*

We have so far considered only the elastic relations that can be measured statically at a constant temperature. The elastic constants are then the isothermal constants. For a rapidly vibrating body, however, there is no chance for heat to equalize and consequently the elastic constants operative are the adiabatic constants determined by the fact that no heat is added or subtracted from any elemental volume. For gases there is a marked difference between the adiabatic and the isothermal constants, but for piezoelectric crystals the difference is small and can usually be neglected.

To investigate the relation existing we can write from the first and second laws of thermodynamics, the relations

$$\begin{aligned} dU = [&T_1\, dS_1 + T_2\, dS_2 + T_3\, dS_3 \\ &+ T_4\, dS_4 + T_5\, dS_5 + T_6\, dS_6] + \Theta\, d\sigma \end{aligned} \tag{31}$$

which expresses the fact that the change in the total energy U is equal to the change in the potential energy plus the added heat energy $dQ = \Theta\, d\sigma$ where Θ is the temperature and σ the entropy. Developing the strains and entropy in terms of the partial differentials of the stresses and temperature, we have

$$\begin{aligned} dS_1 &= \frac{\partial S_1}{\partial T_1} dT_1 + \frac{\partial S_1}{\partial T_2} dT_2 + \frac{\partial S_1}{\partial T_3} dT_3 \\ &\qquad + \frac{\partial S_1}{\partial T_4} dT_4 + \frac{\partial S_1}{\partial T_5} dT_5 + \frac{\partial S_1}{\partial T_6} dT_6 + \frac{\partial S_1}{\partial \Theta} d\Theta \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ dS_6 &= \frac{\partial S_6}{\partial T_1} dT_1 + \frac{\partial S_6}{\partial T_2} dT_2 + \frac{\partial S_6}{\partial T_3} dT_3 \\ &\qquad + \frac{\partial S_6}{\partial T_4} dT_4 + \frac{\partial S_6}{\partial T_5} dT_5 + \frac{\partial S_6}{\partial T_6} dT_6 + \frac{\partial S_6}{\partial \Theta} d\Theta \\ d\sigma &= \frac{\partial \sigma}{\partial T_1} dT_1 + \frac{\partial \sigma}{\partial T_2} dT_2 + \frac{\partial \sigma}{\partial T_3} dT_3 \\ &\qquad + \frac{\partial \sigma}{\partial T_4} dT_4 + \frac{\partial \sigma}{\partial T_5} dT_5 + \frac{\partial \sigma}{\partial T_6} dT_6 + \frac{\partial \sigma}{\partial \Theta} d\Theta. \end{aligned} \tag{32}$$

The partial derivatives of the strains with regard to the stresses are readily seen to be the isothermal elastic compliances. The partial derivatives of the strains by the temperatures are the six temperature coefficients of expansion, or

$$\frac{\partial S_1}{\partial \Theta} = \alpha_1 ; \qquad \cdots ; \qquad \frac{\partial S_6}{\partial \Theta} = \alpha_6 . \tag{33}$$

To evaluate the partial derivatives of the entropy with respect to the stresses we make use of the fact that U is a perfect differential so that

$$\frac{\partial S_1}{\partial \Theta} = \frac{\partial \sigma}{\partial T_1} = \alpha_1 ; \qquad \cdots ; \qquad \frac{\partial S_6}{\partial \Theta} = \frac{\partial \sigma}{\partial T_6} = \alpha_6 . \tag{34}$$

Finally multiplying through the last of equation (32) by Θ we can write them as

$$\begin{aligned} S_1 &= s_{11}^{\Theta}T_1 + s_{12}^{\Theta}T_2 + s_{13}^{\Theta}T_3 + s_{14}^{\Theta}T_4 + s_{15}^{\Theta}T_5 + s_{16}^{\Theta}T_6 + \alpha_1\, d\Theta \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ S_6 &= s_{16}^{\Theta}T_1 + s_{26}^{\Theta}T_2 + s_{36}^{\Theta}T_3 + s_{46}^{\Theta}T_4 + s_{56}^{\Theta}T_5 + s_{66}^{\Theta}T_6 + \alpha_6\, d\Theta \\ dQ &= \Theta\, d\sigma = \Theta[\alpha_1T_1 + \alpha_2T_2 + \alpha_3T_3 + \alpha_4T_4 + \alpha_5T_5 + \alpha_6T_6] + \rho C_p\, d\Theta \end{aligned} \tag{35}$$

since $\Theta \dfrac{\partial\sigma}{\partial\Theta}$ is the total heat capacity of the unit volume at constant stress, which is equal to ρC_p, where ρ is the density and C_p the heat capacity at constant stress per gram of the material.

To get the adiabatic elastic constants which correspond to no heat loss from the element, or $dQ = 0$, $d\Theta$ can be eliminated from (35) giving

$$\begin{aligned} S_1 &= s_{11}^{\sigma}T_1 + s_{12}^{\sigma}T_2 + s_{13}^{\sigma}T_3 + s_{14}^{\sigma}T_4 + s_{15}^{\sigma}T_5 + s_{16}^{\sigma}T_6 + (\alpha_1/\rho C_p)\, dQ \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ S_6 &= s_{16}^{\sigma}T_1 + s_{26}^{\sigma}T_2 + s_{36}^{\sigma}T_3 + s_{46}^{\sigma}T_4 + s_{56}^{\sigma}T_5 + s_{66}^{\sigma}T_6 + (\alpha_6/\rho C_p)\, dQ \end{aligned} \tag{36}$$

where

$$s_{ij}^{\sigma} = s_{ij}^{\Theta} - \frac{\alpha_i\,\alpha_j\,\Theta}{\rho C_p}. \tag{37}$$

For example for quartz, the expansion coefficients are

$$\alpha_1 = 14.3 \times 10^{-6}/°\mathrm{C}; \quad \alpha_2 = 14.3 \times 10^{-6}/°\mathrm{C}; \quad \alpha_3 = 7.8 \times 10^{-6}/°\mathrm{C};$$

$$\alpha_4 = \alpha_5 = \alpha_6 = 0$$

The density and specific heat at constant pressure are

$$\rho = 2.65 \text{ grams/cm}^3; \quad C_p = 7.37 \times 10^6 \text{ ergs/cm}^3.$$

Hence the only constants that differ for adiabatic and isothermal values are

$$s_{11} = s_{22};\ s_{12};\ s_{13};\ s_{33}.$$

Taking these values as[3]

$$s_{11}^{\sigma} = 127.9 \times 10^{-14} \text{ cm}^2/\text{dyne}; \quad s_{12}^{\sigma} = -15.35 \times 10^{-14};$$

$$s_{13}^{\sigma} = 11.0 \times 10^{-14}; \quad s_{33}^{\sigma} = 95.6 \times 10^{-14}.$$

We find that the corresponding isothermal values are

$$s_{11}^{\Theta} = 128.2 \times 10^{-14}; \quad s_{12}^{\Theta} = -15.04 \times 10^{-14};$$

$$s_{13}^{\Theta} = 10.83 \times 10^{-14}; \quad s_{33}^{\Theta} = 95.7 \times 10^{-14} \text{ cm}^2/\text{dyne}$$

---

[3] See "Quartz Crystal Applications" Bell System Technical Journal, Vol. XXII, No. 2, July 1943, W. P. Mason.

at 25°C. or 298° absolute. These differences are probably smaller than the accuracy of the measured constants.

If we express the stresses in terms of the strains by solving equation (35) simultaneously, we find for the stresses

$$\begin{aligned} T_1 &= c_{11}^{\Theta} S_1 + c_{12}^{\Theta} S_2 + c_{13}^{\Theta} S_3 + c_{14}^{\Theta} S_4 + c_{15}^{\Theta} S_5 + c_{16}^{\Theta} S_6 - \lambda_1 \, d\Theta \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ T_6 &= c_{16}^{\Theta} S_1 + c_{26}^{\Theta} S_2 + c_{36}^{\Theta} S_3 + c_{46}^{\Theta} S_4 + c_{56}^{\Theta} S_5 + c_{66}^{\Theta} S_6 - \lambda_6 \, d\Theta \end{aligned} \tag{38}$$

where

$$\begin{aligned} \lambda_1 &= \alpha_1 c_{11}^{\Theta} + \alpha_2 c_{12}^{\Theta} + \alpha_3 c_{13}^{\Theta} + \alpha_4 c_{14}^{\Theta} + \alpha_5 c_{15}^{\Theta} + \alpha_6 c_{16}^{\Theta} \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \lambda_6 &= \alpha_1 c_{16}^{\Theta} + \alpha_2 c_{26}^{\Theta} + \alpha_3 c_{36}^{\Theta} + \alpha_4 c_{46}^{\Theta} + \alpha_5 c_{56}^{\Theta} + \alpha_6 c_{66}^{\Theta} . \end{aligned}$$

The λ's represent the temperature coefficients of stress when all the strains are zero. The negative sign indicates that a negative stress (a compression) has to be applied to keep the strains zero. If we substitute equations (38) in the last of equations (35), the relation between increments of heat and temperature, we have

$$\begin{aligned} dQ = \Theta d\sigma &= \Theta[\lambda_1 S_1 + \lambda_2 S_2 + \lambda_3 S_3 + \lambda_4 S_4 + \lambda_5 S_5 + \lambda_6 S_6] \\ &\quad + [\rho C_p - \Theta(\alpha_1\lambda_1 + \alpha_2\lambda_2 + \alpha_3\lambda_3 + \alpha_4\lambda_4 + \alpha_5\lambda_5 + \alpha_6\lambda_6)] d\Theta . \end{aligned} \tag{39}$$

If we set the strains equal to zero, the size of the element does not change, and hence the ratio between dQ and $d\Theta$ should equal ρ times the specific heat at constant volume C_v. We have therefore the relation

$$\rho[C_p - C_v] = \Theta[\alpha_1\lambda_1 + \alpha_2\lambda_2 + \alpha_3\lambda_3 + \alpha_4\lambda_4 + \alpha_5\lambda_5 + \alpha_6\lambda_6]. \tag{40}$$

The relation between the adiabatic and isothermal elastic constants c_{ij} thus becomes

$$c_{ij}^{\sigma} = c_{ij}^{\Theta} + \frac{\lambda_i \lambda_j \Theta}{\rho C_v} . \tag{41}$$

Since the difference between the adiabatic and isothermal constants is so small, no differentiation will be made between them in the following sections.

2. EXPRESSION FOR THE ELASTIC, PIEZOELECTRIC, PYROELECTRIC AND DIELECTRIC RELATIONS OF A PIEZOELECTRIC CRYSTAL

When a crystal is piezoelectric, a potential energy is stored in the crystal when a voltage is applied to the crystal. Hence the energy expressions of (31) requires additional terms to represent the increment of energy dU. If we employ CGS units which have so far been most widely used, as applied to piezoelectric crystals, the energy stored in any unit volume of the crystal is

$$
\begin{aligned}
dU = {} & T_1\,dS_1 + T_2\,dS_2 + T_3\,dS_3 + T_4\,dS_4 + T_5\,dS_5 + T_6\,dS_6 \\
& + E_1\frac{dD_1}{4\pi} + E_2\frac{dD_2}{4\pi} + E_3\frac{dD_3}{4\pi} + \Theta\,d\sigma
\end{aligned}
\tag{42}
$$

where E_1, E_2 and E_3 are the components of the field existing in the crystal and D_1, D_2 and D_3 the components of the electric displacement. In order to avoid using the factor $1/4\pi$ we make the substitution

$$\frac{D}{4\pi} = \delta. \tag{43}$$

The normal component of δ at any bounding surface is δ_0 the surface charge. On the other hand if we employ the MKS systems of units the energy of any component is given by $E_n dD_n$ directly and in the following formulation δ can be replaced by D.

There are two logical methods of writing the elastic, piezoelectric, pyroelectric and dielectric relations. One considers the independent variables as the stresses, fields, and temperature, and the dependent variables as the strains, displacements and entropy. The other system considers the strains, displacements and entropy as the fundamental independent variables and the stresses, fields, and temperature as the independent variables. The first system appears to be more fundamental for ferroelectric types of crystals.

If we develop the stresses, fields, and temperature in terms of their partial derivatives, we can write

$$
\begin{aligned}
T_1 = {} & \left.\frac{\partial T_1}{\partial S_1}\right)_{D,\sigma} dS_1 + \left.\frac{\partial T_1}{\partial S_2}\right)_{D,\sigma} dS_2 + \left.\frac{\partial T_1}{\partial S_3}\right)_{D,\sigma} dS_3 + \left.\frac{\partial T_1}{\partial S_4}\right)_{D,\sigma} dS_4 \\
& + \left.\frac{\partial T_1}{\partial S_5}\right)_{D,\sigma} dS_5 + \left.\frac{\partial T_1}{\partial S_6}\right)_{D,\sigma} dS_6 + \left.\frac{\partial T_1}{\partial \delta_1}\right)_{S,\sigma} d\delta_1 + \left.\frac{\partial T_1}{\partial \delta_2}\right)_{S,\sigma} d\delta_2 \\
& + \left.\frac{\partial T_1}{\partial \delta_3}\right)_{S,\sigma} d\delta_3 + \left.\frac{\partial T_1}{\partial \sigma}\right)_{S,D} d\delta \\
& \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
T_6 = {} & \left.\frac{\partial T_6}{\partial S_1}\right)_{D,\sigma} dS_1 + \left.\frac{\partial T_6}{\partial S_2}\right)_{D,\sigma} dS_2 + \left.\frac{\partial T_6}{\partial S_3}\right)_{D,\sigma} dS_3 + \left.\frac{\partial T_6}{\partial S_4}\right)_{D,\sigma} dS_4 \\
& + \left.\frac{\partial T_6}{\partial S_5}\right)_{D,\sigma} dS_5 + \left.\frac{\partial T_6}{\partial S_6}\right)_{D,\sigma} dS_6 + \left.\frac{\partial T_6}{\partial \delta_1}\right)_{S,\sigma} d\delta_1 + \left.\frac{\partial T_6}{\partial \delta_2}\right)_{S,\sigma} d\delta_2 \\
& + \left.\frac{\partial T_6}{\partial \delta_3}\right)_{S,\sigma} d\delta_3 + \left.\frac{\partial T_6}{\partial \sigma}\right)_{S,D} d\sigma
\end{aligned}
\tag{44 A}
$$

$$\begin{aligned} E_x = E_1 = {} & \left.\frac{\partial E_1}{\partial S_1}\right)_{D,\sigma} dS_1 + \left.\frac{\partial E_1}{\partial S_2}\right)_{D,\sigma} dS_2 + \left.\frac{\partial E_1}{\partial S_3}\right)_{D,\sigma} dS_3 + \left.\frac{\partial E_1}{\partial S_4}\right)_{D,\sigma} dS_4 \\ & + \left.\frac{\partial E_1}{\partial S_5}\right)_{D,\sigma} dS_5 + \left.\frac{\partial E_1}{\partial S_6}\right)_{D,\sigma} dS_6 + \left.\frac{\partial E_1}{\partial \delta_1}\right)_{S,\sigma} d\delta_1 + \left.\frac{\partial E_1}{\partial \delta_2}\right)_{S,\sigma} d\delta_2 \\ & + \left.\frac{\partial E_1}{\partial \delta_3}\right)_{S,\sigma} d\delta_3 + \left.\frac{\partial E_1}{\partial \sigma}\right)_{S,D} d\sigma \end{aligned}$$

……

$$\begin{aligned} E_z = E_3 = {} & \left.\frac{\partial E_3}{\partial S_1}\right)_{D,\sigma} dS_1 + \left.\frac{\partial E_3}{\partial S_2}\right)_{D,\sigma} dS_2 + \left.\frac{\partial E_3}{\partial S_3}\right)_{D,\sigma} dS_3 + \left.\frac{\partial E_3}{\partial S_4}\right)_{D,\sigma} dS_4 \\ & + \left.\frac{\partial E_3}{\partial S_5}\right)_{D,\sigma} dS_5 + \left.\frac{\partial E_3}{\partial S_6}\right)_{D,\sigma} dS_6 + \left.\frac{\partial E_3}{\partial \delta_1}\right)_{S,\sigma} d\delta_1 + \left.\frac{\partial E_3}{\partial \delta_2}\right)_{S,\sigma} d\delta_2 \\ & + \left.\frac{\partial E_3}{\partial \delta_3}\right)_{S,\sigma} d\delta_3 + \left.\frac{\partial E_3}{\partial \sigma}\right)_{S,D} d\sigma \qquad (44\text{ B}) \end{aligned}$$

$$\begin{aligned} d\Theta = {} & \left.\frac{\partial \Theta}{\partial S_1}\right)_{D,\sigma} dS_1 + \left.\frac{\partial \Theta}{\partial S_2}\right)_{D,\sigma} dS_2 + \left.\frac{\partial \Theta}{\partial S_3}\right)_{D,\sigma} dS_3 + \left.\frac{\partial \Theta}{\partial S_4}\right)_{D,\sigma} dS_4 \\ & + \left.\frac{\partial \Theta}{\partial S_5}\right)_{D,\sigma} dS_5 + \left.\frac{\partial \Theta}{\partial S_6}\right)_{D,\sigma} dS_6 + \left.\frac{\partial \Theta}{\partial \delta_1}\right)_{S,\sigma} d\delta_1 + \left.\frac{\partial \Theta}{\partial \delta_2}\right)_{S,\sigma} d\delta_2 \\ & + \left.\frac{\partial \Theta}{\partial \delta_3}\right)_{S,\sigma} d\delta_3 + \left.\frac{\partial \Theta}{\partial \sigma}\right)_{S,D} d\sigma. \end{aligned}$$

The subscripts under the partial derivatives indicate the quantities kept constant. A subscript D indicates that the electric induction is held constant, a subscript σ indicates that the entropy is held constant, while a subscript S indicates that the strains are held constant.

Examining the first equation, we see that the partial derivatives of the stress T_1 by the strains are the elastic constants c_{ij} which determine the ratios between the stress T_1 and the appropriate strain with all other strains equal to zero. To indicate the conditions for the partial derivatives, the superscripts D and σ are given to the elastic constants and they are written $c_{ij}^{D,\sigma}$. The partial derivatives of the stresses by $\delta = D/4\pi$ are the piezoelectric constants h_{ij} which measure the increases in stress necessary to hold the crystal free from strain in the presence of a displacement. Since if the crystal tends to expand on the application of a displacement, the stress to keep it from expanding has to be a compression or negative stress, the negative sign is given to the h_{ij}^{σ} constants. As the only meaning of the h constants is obtained by measuring the ratio of the stress to $\delta = D/4\pi$ at constant strains, no superscript S is added. However there is a difference between isothermal and adiabatic piezoelectric constants in general, so that these piezoelectric constants are written h^{σ}_{ij}. Finally the last partial derivatives of the stresses by the entropy σ can be written

$$\left.\frac{\partial T_n}{\partial \sigma}\right)_{S,D} d\sigma = \frac{1}{\Theta}\left.\frac{\partial T_n}{\partial \sigma}\right)_{S,D} \Theta\, d\sigma = \frac{1}{\Theta}\left.\frac{\partial T_n}{\partial \sigma}\right)_{S,D} dQ = -\gamma_n^{S,D}\, dQ \qquad (45)$$

where dQ is the added heat. We designate $1/\Theta$ times the partial derivative as $-\gamma_n^{S,D}$ and note that it determines the negative stress (compression) necessary to put on the crystal to keep it from expanding when an increment of heat dQ is added to the crystal. The electric displacement is held constant and hence the superscripts S, and D are used. The first six equations then can be written in the form

$$\begin{aligned} T_n = c_{n1}^{D,\sigma} S_1 + c_{n2}^{D,\sigma} S_2 + c_{n3}^{D,\sigma} S_3 + c_{n4}^{D,\sigma} S_4 + c_{n5}^{D,\sigma} S_5 + c_{n6}^{D,\sigma} S_6 \\ - h^{\sigma}_{n1}\delta_1 - h^{\sigma}_{n2}\delta_2 - h^{\sigma}_{n3}\delta_3 - \gamma_n^{S,D}\, dQ. \end{aligned} \qquad (46)$$

To evaluate the next three equations involving the fields, we make use of the fact that the expression for dU in equation (42) is a perfect differential. As a consequence there are relations between the partial derivatives, namely

$$\frac{\partial T_m}{\partial \delta_n} = \frac{\partial E_n}{\partial S_m}; \qquad \frac{\partial T_m}{\partial \sigma} = \frac{\partial \Theta}{\partial S_m}; \qquad \frac{\partial E_n}{\partial \sigma} = \frac{\partial \Theta}{\partial \delta_n}. \qquad (47)$$

We note also that

$$\left.\frac{\partial E_m}{\partial \delta_n}\right)_{S,\sigma} = 4\pi\beta_{mn}^{S,\sigma} \qquad (48)$$

where β is the so called "impermeability" matrix obtained from the dielectric matrix ϵ_{nm} by means of the equation

$$\beta_{mn} = \frac{(-1)^{m+n}\Delta^{m,n}}{\Delta} \qquad (49)$$

where Δ is the determinant

$$\Delta = \begin{vmatrix} \epsilon_{11}, & \epsilon_{12}, & \epsilon_{13} \\ \epsilon_{12}, & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13}, & \epsilon_{23}, & \epsilon_{33} \end{vmatrix} \qquad (50)$$

and $\Delta^{m,n}$ the minor obtained by suppressing the mth row and nth column.

The partial derivatives of the fields by the entropy can be written

$$\left.\frac{\partial E_m}{\partial \sigma}\right)_{S,D} d\sigma = \frac{1}{\Theta}\left.\frac{\partial E_m}{\partial \sigma}\right)_{S,D} \Theta\, \delta\sigma = \frac{1}{\Theta}\left.\frac{\partial E_m}{\partial \sigma}\right)_{S,D} dQ = -q_m^{S,D}\, dQ \qquad (51)$$

where $q_n^{S,D}$ is a pyroelectric constant measuring the increase in field required to produce a zero charge on the surface when a heat dQ is added to the crystal. Since the voltage will be of opposite sign to the charge generated on the surface of the crystal in the absence of this counter voltage a negative sign is given to $q_n^{S,D}$.

Finally the last partial derivative

$$\left.\frac{\partial \Theta}{\partial \sigma}\right)_{S,D} d\sigma = \frac{1}{\Theta}\left.\frac{\partial \Theta}{\partial \sigma}\right)_{S,D} \Theta\, d\sigma = \frac{1}{\Theta}\left.\frac{\partial \Theta}{\partial \sigma}\right)_{S,D} dQ = \frac{dQ}{\rho C_v^D} \tag{52}$$

represents the ratio of the increase in temperature due to the added amount of heat dQ when the strains and electric displacements are held constant. It is therefore the inverse of the specific heat at constant volume and constant electric displacement per gram of material times the density ρ. Hence the ten equations of equation (44) can be written in the generalized forms

$$\begin{aligned}
T_n &= c_{n1}^{D,\sigma} S_1 + c_{n2}^{D,\sigma} S_2 + c_{n3}^{D,\sigma} S_3 + c_{n4}^{D,\sigma} S_4 + c_{n5}^{D,\sigma} S_5 + c_{n6}^{D,\sigma} S_6 \\
&\qquad -h_{n1}^{\sigma}\delta_1 - h_{n2}^{\sigma}\delta_2 - h_{n3}^{\sigma}\delta_3 - \gamma_n^{S,D}\, dQ \\
E_m &= -h_{1m}^{\sigma} S_1 - h_{2m}^{\sigma} S_2 - h_{3m}^{\sigma} S_3 - h_{4m}^{\sigma} S_4 - h_{5m}^{\sigma} S_5 - h_{6m}^{\sigma} S_6 + 4\pi\beta_{m1}^{S,\sigma}\delta_1 \\
&\qquad + 4\pi\beta_{m2}^{S,\sigma}\delta_2 + 4\pi\beta_{m3}^{S,\sigma}\delta_3 - q_m^{S,D}\, dQ \\
d\Theta &= -\Theta[\gamma_1^{S,D} S_1 + \gamma_2^{S,D} S_2 + \gamma_3^{S,D} S_3 + \gamma_4^{S,D} S_4 + \gamma_5^{S,D} S_5 + \gamma_6^{S,D} S_6] \\
&\qquad -\Theta[q_1^{S,D}\delta_1 + q_2^{S,D}\delta_2 + q_3^{S,D}\delta_3] + \frac{dQ}{\rho C_v^D}. \\
&\qquad n = 1 \text{ to } 6;\ m = 1 \text{ to } 3
\end{aligned} \tag{53}$$

If, as is usually the case with vibrating crystals the vibration occurs with no interchange of heat between adjacent elements $dQ = 0$ and the ten equations reduce to the usual nine given by the general forms

$$\begin{aligned}
T_n &= c_{n1}^{D} S_1 + c_{n2}^{D} S_2 + c_{n3}^{D} S_3 + c_{n4}^{D} S_4 + c_{n5}^{D} S_5 + c_{n6}^{D} S_6 \\
&\qquad - h_{n1}\delta_1 - h_{n2}\delta_2 - h_{n3}\delta_3 \\
E_m &= -h_{1m} S_1 - h_{2m} S_2 - h_{3m} S_3 - h_{4m} S_4 - h_{5m} S_5 - h_{6m} S_6 \\
&\qquad + 4\pi\beta_{m1}^{S}\delta_1 + 4\pi\beta_{m2}^{S}\delta_2 + 4\pi\beta_{m3}^{S}\delta_3.
\end{aligned} \tag{54}$$

In these equations the superscript σ has been dropped since the ordinary constants are adiabatic. The tenth equation of (53) determines the increase in temperature caused by the strains and displacements in the absence of any flow of heat.

If we introduce the expression of equations (53) into equation (42) the total energy of the crystal is per unit volume.

$$\begin{aligned}
2U = {} & c_{11}^{D,\sigma}S_1^2 + 2c_{12}^{D,\sigma}S_1S_2 + 2c_{13}^{D,\sigma}S_1S_3 + 2c_{14}^{D,\sigma}S_1S_4 + 2c_{15}^{D,\sigma}S_1S_5 + 2c_{16}^{D,\sigma}S_1S_6 \\
& + c_{22}^{D,\sigma}S_2^2 + 2c_{23}^{D,\sigma}S_2S_3 + 2c_{24}^{D,\sigma}S_2S_4 + 2c_{25}^{D,\sigma}S_2S_5 + 2c_{26}^{D,\sigma}S_2S_6 \\
& + c_{33}^{D,\sigma}S_3^2 + 2c_{34}^{D,\sigma}S_3S_4 + 2c_{35}^{D,\sigma}S_3S_5 + 2c_{36}^{D,\sigma}S_3S_6 \\
& + c_{44}^{D,\sigma}S_4^2 + 2c_{45}^{D,\sigma}S_4S_5 + 2c_{46}^{D,\sigma}S_4S_6 \\
& + c_{55}^{D,\sigma}S_5^2 + 2c_{56}^{D,\sigma}S_5S_6 \\
& + c_{66}^{D,\sigma}S_6^2 \qquad (55) \\
& - (2h_{11}^{\sigma}\delta_1S_1 + 2h_{12}^{\sigma}\delta_1S_2 + 2h_{13}^{\sigma}\delta_1S_3 + 2h_{14}^{\sigma}\delta_1S_4 + 2h_{15}^{\sigma}\delta_1S_5 + 2h_{16}^{\sigma}\delta_1S_6) \\
& - (2h_{21}^{\sigma}\delta_2S_1 + 2h_{22}^{\sigma}\delta_2S_2 + 2h_{23}^{\sigma}\delta_2S_3 + 2h_{24}^{\sigma}\delta_2S_4 + 2h_{25}^{\sigma}\delta_2S_5 + 2h_{26}^{\sigma}\delta_2S_6) \\
& - (2h_{31}^{\sigma}\delta_3S_1 + 2h_{32}^{\sigma}\delta_3S_2 + 2h_{33}^{\sigma}\delta_3S_3 + 2h_{34}^{\sigma}\delta_3S_4 + 2h_{35}^{\sigma}\delta_3S_5 + 2h_{36}^{\sigma}\delta_3S_6) \\
& - (2\gamma_1^{S,D}S_1dQ + 2\gamma_2^{S,D}S_2dQ + 2\gamma_3^{S,D}S_3\,dQ \\
& \qquad + 2\gamma_4^{S,D}S_4dQ + 2\gamma_5^{S,D}S_5dQ + 2\gamma_6^{S,D}S_6dQ) \\
& + 4\pi[\beta_{11}^{S,\sigma}\delta_1^2 + 2\beta_{12}^{S,\sigma}\delta_1\delta_2 + 2\beta_{13}^{S,\sigma}\delta_1\delta_3 + \beta_{22}^{S,\sigma}\delta_2^2 + 2\beta_{23}^{S,\sigma}\delta_2\delta_3 + \beta_{33}^{S,\sigma}\delta_3^2] \\
& - (2q_1^{S,D}\delta_1dQ + 2q_2^{S,D}\delta_2dQ + 2q_3^{S,D}\delta_3dQ) + \frac{(dQ)^2}{{}_\rho C_v^D}\,.
\end{aligned}$$

Equations (53) can be derived from this expression by employing the partial derivatives

$$T_n = \frac{\partial U}{\partial S_n}\,; \quad E_m = \frac{\partial U}{\partial \delta_m}\,; \quad d\Theta = \frac{\partial U}{\partial(dQ)} \qquad (56)$$

The other form for writing the elastic, piezoelectric, pyroelectric and dielectric relations is to take the strains, displacements, and entropy as the fundamental variables and the stresses, fields and temperature increments as the dependent variables. If we develop them in terms of their partial derivatives as was done in (44), use the relations between the partial derivatives shown in equation (57).

$$\frac{\partial \delta_m}{\partial T_n} = \frac{\partial S_n}{\partial E_m}\,; \quad \frac{\partial S_n}{\partial \Theta} = \frac{\partial \sigma}{\partial T_n}\,; \quad \frac{\partial \delta_m}{\partial \Theta} = \frac{\partial \sigma}{\partial E_m} \qquad (57)$$

and substitute for the partial derivatives their equivalent elastic, piezoelectric, pyroelectric, temperature expansions, dielectric and specific heat constants, there are 10 equations of the form

$$
\begin{aligned}
S_n &= s_{n1}^{E,\Theta}T_1 + s_{n2}^{E,\Theta}T_2 + s_{n3}^{E,\Theta}T_3 + s_{n4}^{E,\Theta}T_4 + s_{n5}^{E,\Theta}T_5 + s_{n6}^{E,\Theta}T_6 + d_{n1}^{\Theta}E_1 \\
&\qquad + d_{n2}^{\Theta}E_2 + d_{n3}^{\Theta}E_3 + \alpha_n^E d\Theta \\
\delta_m &= d_{1m}^{\Theta}T_1 + d_{2m}^{\Theta}T_2 + d_{3m}^{\Theta}T_3 + d_{4m}^{\Theta}T_4 + d_{5m}^{\Theta}T_5 + d_{6m}^{\Theta}T_6 \\
&\qquad + \frac{\epsilon_{m1}^{T,\Theta}}{4\pi}E_1 + \frac{\epsilon_{m2}^{T,\Theta}}{4\pi}E_2 + \frac{\epsilon_{m3}^{T,\Theta}}{4\pi}E_3 + p_m^T d\Theta \qquad (58) \\
dQ &= \Theta\, d\sigma = \Theta[\alpha_1^E T_1 + \alpha_2^E T_2 + \alpha_3^E T_3 + \alpha_4^E T_4 + \alpha_5^E T_5 + \alpha_6^E T_6] \\
&\qquad + \Theta[p_1^T E_1 + p_2^T E_2 + p_3^T E_3] + pC_p^E d\Theta. \\
&\qquad n = 1 \text{ to } 6, \qquad m = 1 \text{ to } 3
\end{aligned}
$$

The superscripts E, Θ, and T indicate respectively constant field, constant temperature and constant stress for the measurements of the respective constants. It will be noted that the elastic compliance and the piezoelectric constants d_{mn} are for isothermal conditions. The α^E constants are the temperature expansion constants measured at constant field, while the p^T constants are the pyroelectric constants relating the ratio of $\delta = D/4\pi$ to increase in temperature $d\Theta$, measured at constant stress. Since there is constant stress, these constants take into account not only the "true" pyroelectric effect which is the ratio of $\delta = D/4\pi$ to the temperature at constant volume, but also the so called "false" pyroelectric effect of the first kind which is the polarization caused by the temperature expansion of the crystal. This appears to be a misnomer. A better designation for the two effects is the pyroelectric effect at constant strain and the pyroelectric effect at constant stress. C_p^E is the specific heat at constant pressure and constant field.

If we substitute these equations into equation (42), the total free energy becomes

$$
\begin{aligned}
2U = \sum_{m=1}^{6}\sum_{n=1}^{6} s_{mn}^{E,\Theta}T_mT_n + 2\sum_{n=1}^{6}\sum_{0=1}^{3} d_{n0}^{\Theta}T_nE_0 + 2\sum_{n=1}^{6}\alpha_n^E T_n d\Theta \\
+ \sum_{0=1}^{3}\sum_{p=1}^{3}\frac{\epsilon_{0p}^{T,\Theta}}{4\pi}E_0E_p + 2\sum_{0=1}^{3} p_0^T E_p d\Theta + \frac{\rho C_p^E}{\Theta}d\Theta.
\end{aligned}
\qquad (59)
$$

Equation (58) can then be obtained by partial derivatives of the sort

$$
S_n = \frac{\partial U}{\partial T_n}; \qquad \delta_0 = \frac{\partial U}{\partial E_p}; \qquad d\sigma = \frac{dQ}{\Theta} = \frac{\partial U}{\partial(d\Theta)}.
$$

By tensor transformations the expression for U in (59) can be shown to be equal to the expression for U in (55).

The adiabatic equations holding for a rapidly vibrating crystal can be obtained by setting dQ equal to zero in the last of equations (58) and eliminating $d\Theta$ from the other nine equations. The resulting equations are

$$\begin{aligned} S_n &= s^E_{n1}T_1 + s^E_{n2}T_2 + s^E_{n3}T_3 + s^E_{n4}T_4 \\ &\qquad + s^E_{n5}T_5 + s^E_{n6}T_6 + d_{n1}E_1 + d_{n2}E_2 + d_{n3}E_3 \\ \delta_m &= d_{1m}T_1 + d_{2m}T_2 + d_{3m}T_3 + d_{4m}T_4 \\ &\qquad + d_{5m}T_5 + d_{6m}T_6 + \frac{\epsilon^T_{m1}}{4\pi}E_1 + \frac{\epsilon^T_{m2}}{4\pi}E_2 + \frac{\epsilon^T_{m3}}{4\pi}E_3 \end{aligned} \tag{60}$$

where the symbol σ for adiabatic is understood and where the relations between the isothermal and adiabatic constants are given by

$$s^{E,\sigma}_{mn} = s^{E,\Theta}_{mn} - \frac{\alpha^E_m \alpha^E_n \Theta}{\rho C^E_p}; \qquad d^\sigma_\ell = d^\Theta_{\ell m} - \frac{\alpha^E_m p^T_\ell \Theta}{\rho C^E_p}; \qquad \frac{\epsilon^{T,\sigma}_{mn}}{4\pi} = \frac{\epsilon^{T,\Theta}_{mn}}{4\pi} - \frac{p^T_m p^T_n \Theta}{\rho C^E_p}.$$

Hence the piezoelectric and dielectric constants are identical for isothermal and adiabatic conditions provided the crystal is not pyroelectric, but differ if the crystal is pyroelectric. The difference between the adiabatic and isothermal elastic compliances was discussed in section (1.4) and was shown to be small. Hence the equations in the form (60) are generally used in discussing piezoelectric crystals.

Two other mixed forms are also used but a discussion of them will be delayed until a tensor notation for piezoelectric crystals has been discussed. This simplifies the writing of such equations.

3. General Properties of Tensors

The expressions for the piezoelectric relations discussed in section 2 can be considerably abbreviated by expressing them in tensor form. Furthermore, the calculation of elastic constants for rotated crystals is considerably simplified by the geometrical transformation laws established for tensors. Hence it has seemed worthwhile to express the elastic, electric, and piezoelectric relations of a piezoelectric crystal in tensor form. It is the purpose of this section to discuss the general properties of tensors applicable to Cartesian coordinates.

If we have two sets of rectangular axes (Ox, Oy, Oz) and (Ox', Oy', Oz) having the same origin, the coordinates of any point P with respect to the second set are given in terms of the first set by the equations

$$\begin{aligned} x' &= \ell_1 x + m_1 y + n_1 z \\ y' &= \ell_2 x + m_2 y + n_2 z \\ z' &= \ell_3 x + m_3 y + n_3 z. \end{aligned} \tag{61}$$

The quantities ($\ell_1, \cdots, n_3$) are the cosines of the angles between the various axes; thus ℓ_1 is the cosine of the angle between the axes Ox', and Ox; n_3 the cosine of the angle between Oz' and Oz, and so on. By solving the equations (61) simultaneously, the coordinates x, y, z can be expressed in terms of x', y', z' by the equations.

$$\begin{aligned} x &= \ell_1 x' + \ell_2 y' + \ell_3 z' \\ y &= m_1 x' + m_2 y' + m_3 z' \\ z &= n_1 x' + n_2 y' + n_3 z'. \end{aligned} \tag{62}$$

We can shorten the writing of equations (61) and (62) considerably by changing the notation. Instead of x, y, z let us write x_1, x_2, x_3 and in place of x', y', z' we write x_1', x_2', x_3'. We can now say that the coordinates with respect to the first system are x_i, where i may be 1, 2, 3 while those with respect of the second system are x_j', where $j = 1$, 2 or 3. Then in (61) each coordinate x_j' is expressed as the sum of three terms depending on the three x_i. Each x_i is associated with the cosine of the angle between the direction of x_i increasing and that of x_j' increasing. Let us denote this cosine by a_{ij}. Then we have for all values of j,

$$x_j' = a_{1j}x_1 + a_{2j}x_2 + a_{3j}x_3 = \sum_{i=1}^{3} a_{ij}x_i. \tag{63}$$

Conversely equation (62) can be written

$$x_i = \sum_{j=1}^{3} a_{ij}x_j' \tag{64}$$

where the a_{ij} have the same value as in (63), for the same values of i and j, since in both cases the cosine of the angle is between the values of x_i and x_j increasing. Such a set of three quantities involving a relation between two coordinate systems is called a tensor of the first rank or a vector.

We note that each of the equations (63), (64) is really a set of three equations. Where the suffix i or j appears on the left it is to be given in turn all the values 1, 2, 3 and the resulting equation is one of the set. In each such equation the right side is the sum of three terms obtained by giving j or i the values 1, 2, 3 in turn and adding. Whenever such a summation occurs a suffix is repeated in the expression for the general term as $a_{ij}x_j'$. We make it a regular convention that whenever a suffix is repeated it is to be given all possible values and that the terms are to be added for all. Then (63) can be written simply as

$$x_j' = a_{ij}x_i$$

the summation being automatically understood by the convention.

There are single quantities such as mass and distance, that are the same for all systems of coordinates. These are called tensors of the zero rank or scalars.

Consider now two tensors of the first rank u_i and v_k. Suppose that each component of one is to be multiplied by each component of the other, then we obtain a set of nine quantities expressed by $u_i\, v_k$, where i and k are independently given all the values 1, 2, 3. The components of $u_i\, v_k$ with respect to the x'_j set of axes are $u'_j\, v'_\ell$, and

$$u'_j\, v'_\ell = (a_{ij} u_i)\,(a_{k\ell} v_k) = a_{ij}\, a_{k\ell}\, u_i v_k\,. \tag{65}$$

The suffixes i and k are repeated on the right. Hence (65) represents nine equations, each with nine terms. Each term on the right is the product of two factors, one of the form $a_{ij} a_{k\ell}$, depending only on the orientation of the axes, and the other of the form $u_i v_k$, representing the products of the components referred to the original axes. In this way the various $u'_j\, v'_\ell$ can be obtained in terms of the original $u_i v_k$. But products of vectors are not the only quantities satisfying the rule. In general a set of nine quantities w_{ik} referred to a set of axes, and transformed to another set by the rule

$$w'_{j\ell} = a_{ij} a_{k\ell}\, w_{ik} \tag{66}$$

is called a tensor of the second rank.

Higher orders tensors can be formed by taking the products of more vectors. Thus a set of n quantities that transforms like the vector product $x_i\, x_j \cdots x_p$ is called a tensor of rank n, where n is the number of factors.

On the right hand side of (66) the i and k are dummy suffices; that is, they are given the numbers 1 to 3 and summed. It, therefore, makes no difference which we call i and which k so that

$$w'_{j\ell} = a_{ij} a_{k\ell} w_{ik} = a_{kj} a_{i\ell} w_{k\ell}\,. \tag{67}$$

Hence $w_{k\ell}$ transforms by the same rule as w_{ik} and hence is a tensor of the second rank. The importance of this is that if we have a set of quantities

$$\begin{vmatrix} w_{11} & w_{12} & w_{13} \\ w_{21} & w_{22} & w_{23} \\ w_{31} & w_{32} & w_{33} \end{vmatrix} \tag{68}$$

which we know to be a tensor of the second rank, the set of quantities

$$\begin{vmatrix} w_{11} & w_{21} & w_{31} \\ w_{12} & w_{22} & w_{32} \\ w_{13} & w_{23} & w_{33} \end{vmatrix} \tag{69}$$

is another tensor of the second rank. Hence the sum $(w_{ik} + w_{ki})$ and the difference $(w_{ik} - w_{ki})$ are also tensors of the second rank. The first of these has the property that it is unaltered by interchanging i and k and therefore it is called a symmetrical tensor. The second has its components reversed in sign when i and k are interchanged. It is therefore an antisymmetrical tensor. Clearly in an antisymmetric tensor the leading diagonal components will all be zero, i.e., those with $i = k$ will be zero. Now since

$$w_{ik} = \tfrac{1}{2}(w_{ik} + w_{ki}) + \tfrac{1}{2}(w_{ik} - w_{ki}) \tag{70}$$

we can consider any tensor of the second rank as the sum of a symmetrical and an antisymmetrical tensor. Most tensors in the theory of elasticity are symmetrical tensors.

The operation of putting two suffixes in a tensor equal and adding the terms is known as contraction of the tensor. It gives a tensor two ranks lower than the original one. If for instance we contract the tensor $u_i v_k$ we obtain

$$u_i v_i = u_1 v_1 + u_2 v_2 + u_3 v_3 \tag{71}$$

which is the scalar product of u_i and v_k and hence is a tensor of zero rank.

We wish now to derive the formulae for tensor transformation to a new set of axes. For a tensor of the first rank (a vector) this has been given by equation (61). But the direction consines ℓ_1 to n_3 can be expressed in the form

$$\begin{aligned}
\ell_1 &= \frac{\partial x'}{\partial x} = \frac{\partial x_1'}{\partial x_1}; & m_1 &= \frac{\partial x'}{\partial y} = \frac{\partial x_1'}{\partial x_2}; & n_1 &= \frac{\partial x'}{\partial z} = \frac{\partial x_1'}{\partial x_3} \\
\ell_2 &= \frac{\partial y'}{\partial x} = \frac{\partial x_2'}{\partial x_1}; & m_2 &= \frac{\partial y'}{\partial y} = \frac{\partial x_2'}{\partial x_2}; & n_2 &= \frac{\partial y'}{\partial z} = \frac{\partial x_2'}{\partial x_3} \\
\ell_3 &= \frac{\partial z'}{\partial x} = \frac{\partial x_3'}{\partial x_1}; & m_3 &= \frac{\partial z'}{\partial y} = \frac{\partial x_3'}{\partial x_2}; & n_3 &= \frac{\partial z'}{\partial z} = \frac{\partial x_3'}{\partial x_3}.
\end{aligned} \tag{72}$$

Hence equation (61) can be expressed in the tensor form

$$x_j' = \frac{\partial x_j'}{\partial x_i} x_i = a_{ij} x_i. \tag{73}$$

Similarly since a tensor of the second rank can be regarded as the product of two vectors, it can be transformed according to the equation

$$x_j' x_\ell' = \left(\frac{\partial x_j'}{\partial x_i} x_i\right)\left(\frac{\partial x_\ell'}{\partial x_k} x_k\right) = \frac{\partial x_j'}{\partial x_i}\frac{\partial x_\ell'}{\partial x_k} x_i x_k \tag{74}$$

which can also be expressed in the generalized form

$$w_{j\ell}' = \frac{\partial x_j'}{\partial x_i}\frac{\partial x_\ell'}{\partial x_k} w_{ik}. \tag{75}$$

In general the transformation equation of a tensor of the *n*th rank can be written

$$X'_{k_1\cdots k_n} = \frac{\partial x_{k'_2}}{\partial x_{j_1}} \frac{\partial x_{k'_2}}{\partial x_{j_2}} \cdots \frac{\partial x_{k'_n}}{\partial x_{j_n}} X_{j_1 j_2 \cdots j_n}\,. \tag{76}$$

4. APPLICATION OF TENSOR NOTATION TO THE ELASTIC, PIEZOELECTRIC AND DIELECTRIC EQUATIONS OF A CRYSTAL

Let us consider the stress components of equation (7)

$$\begin{vmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yx} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{vmatrix}$$

from which equation (8) is derived

$$T_{xy} = T_{yx}\ ;\ T_{xz} = T_{zx}\ ;\ T_{yz} = T_{zy}$$

and designate them in the manner shown by equation (77) to correspond with tensor notations

$$\begin{vmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{vmatrix} = \begin{vmatrix} T_{11} & T_{12} & T_{13} \\ T_{12} & T_{22} & T_{23} \\ T_{13} & T_{23} & T_{33} \end{vmatrix} \tag{77}$$

by virtue of the relations of (8). We wish to show now that the set of 9 elements of the equation constitutes a tensor, and by virtue of the relations of (8) a symmetrical tensor.

The transformation of the stress components to a new set of axes x', y', z' has been shown by Love[4] to take the form

$$T'_{xx} = \ell_1^2\, T_{xx} + m_1^2 T_{yy} + n_1^2 T_{zz} + 2\ell_1 m_1 T_{xy} + 2\ell_1 n_1 T_{xz} + 2m_1 n_1 T_{yz}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \tag{78}$$

$$\begin{aligned} T'_{xy} = \ell_1\ell_2 T_{xx} + m_1 m_2 T_{yy} + n_1 n_2 T_{zz} + (\ell_1 m_2 + \ell_2 m_1) T_{xy} + (\ell_1 n_2 + \ell_2 n_1) T_{xz} \\ + (m_1 n_2 + n_1 m_2) T_{yz} \end{aligned}$$

where ℓ_1 to n_3 are the direction cosines between the axes as specified by equation (61). Noting that from (72)

$$\ell_1 = \frac{\partial x'_1}{\partial x_1}, \qquad \cdots, \qquad n_3 = \frac{\partial x'_3}{\partial x_3}$$

the first of these equations can be put in the form

---

[4] See "Theory of Elasticity," Love, Page 80.

$$
\begin{aligned}
T'_{11} = \left(\frac{\partial x_1'^2}{\partial x_1}\right) T_{11} + \frac{\partial x_1'}{\partial x_1}\frac{\partial x_1'}{\partial x_2} T_{12} + \frac{\partial x_1'}{\partial x_1}\frac{\partial x_1'}{\partial x_3} T_{13} \\
+ \frac{\partial x_1'}{\partial x_2}\frac{\partial x_1'}{\partial x_1} T_{21} + \left(\frac{\partial x_1'^2}{\partial x_2}\right) T_{22} + \frac{\partial x_1'}{\partial x_2}\frac{\partial x_1'}{\partial x_3} T_{23} = \frac{\partial x_1'}{\partial x_k}\frac{\partial x_1'}{\partial x_\ell} T_{k\ell} \\
+ \frac{\partial x_1'}{\partial x_3}\frac{\partial x_1'}{\partial x_1} T_{31} + \frac{\partial x_1'}{\partial x_3}\frac{\partial x_1'}{\partial x_2} T_{32} + \left(\frac{\partial x_1}{\partial x_3}\right)^2 T_{33}
\end{aligned}
\tag{79}
$$

while the last equation takes the form

$$
\begin{aligned}
T'_{12} = \frac{\partial x_1'}{\partial x_1}\frac{\partial x_2'}{\partial x_1} T_{11} + \frac{\partial x_1'}{\partial x_1}\frac{\partial x_2'}{\partial x_2} T_{12} + \frac{\partial x_1'}{\partial x_1}\frac{\partial x_2'}{\partial x_3} T_{13} \\
+ \frac{\partial x_1'}{\partial x_2}\frac{\partial x_2'}{\partial x_1} T_{21} + \frac{\partial x_1'}{\partial x_2}\frac{\partial x_2'}{\partial x_2} T_{22} + \frac{\partial x_1'}{\partial x_2}\frac{\partial x_2'}{\partial x_3} T_{23} = \frac{\partial x_1'}{\partial x_k}\frac{\partial x_2'}{\partial x_\ell} T_{k\ell} \\
+ \frac{\partial x_1'}{\partial x_3}\frac{\partial x_2'}{\partial x_1} T_{31} + \frac{\partial x_1'}{\partial x_3}\frac{\partial x_2'}{\partial x_2} T_{32} + \frac{\partial x_1'}{\partial x_3}\frac{\partial x_2'}{\partial x_3} T_{33} .
\end{aligned}
\tag{80}
$$

The general expression for any component then is

$$
T'_{ij} = \frac{\partial x_i'}{\partial x_k}\frac{\partial x_j'}{\partial x_\ell} T_{k\ell}
\tag{81}
$$

which is the transformation equation of a tensor of the second rank. Hence the stress components satisfy the conditions for a second rank tensor.

The strain components

$$
\begin{vmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{vmatrix}
$$

do not however satisfy the conditions for a second rank tensor. This is shown by the transformation of strain components to a new set of axes, which have been shown by Love to satisfy the equations

$$
\begin{aligned}
S'_{xx} &= \ell_1^2 S_{xx} + m_1^2 S_{yy} + n_1^2 S_{zz} + \ell_1 m_1 S_{xy} + \ell_1 n_1 S_{zx} + m_1 n_1 S_{yz} \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
S'_{xy} &= 2\ell_1\ell_2 S_{xx} + 2m_1m_2 S_{yy} + 2n_1n_2 S_{zz} + (\ell_1 m_2 + \ell_2 m_1) S_{xy} \\
&\quad + (\ell_1 n_2 + n_1 \ell_2) S_{xz} + (m_1 n_2 + m_2 n_1) S_{xy} .
\end{aligned}
\tag{82}
$$

If, however, we take the strain components as

$$S_{11} = S_{xx} = \frac{\partial \xi}{\partial x}; \qquad S_{22} = S_{yy} = \frac{\partial \eta}{\partial y}; \qquad S_{33} = S_{zz} = \frac{\partial \zeta}{\partial z}$$

$$S_{12} = S_{21} = \frac{S_{xy}}{2} = \frac{1}{2}\left(\frac{\partial \eta}{\partial x} + \frac{\partial \xi}{\partial y}\right); \qquad S_{13} = S_{31} = \frac{S_{xz}}{2} \tag{83}$$

$$= \frac{1}{2}\left(\frac{\partial \xi}{\partial x} + \frac{\partial \zeta}{\partial x}\right); \qquad S_{23} = S_{32} = \frac{S_{yz}}{2} = \frac{1}{2}\left(\frac{\partial \zeta}{\partial y} + \frac{\partial \eta}{\partial z}\right)$$

the nine components

$$\begin{vmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{vmatrix} \tag{83}$$

will form a tensor of the second rank, as can be shown by the transformation equations of (82).

The generalized Hooke's law given by equation (22) becomes

$$T_{ij} = c_{ijk\ell} S_{k\ell} \tag{84}$$

$c_{ijk\ell}$ is a fourth rank tensor. The right hand side of the equation being the product of a fourth rank tensor by a second rank tensor is a sixth rank tensor, but since it has been contracted twice by having k and ℓ in both terms the resultant of the right hand side is a second rank tensor. Since $c_{ijk\ell}$ is a tensor of the fourth rank it will, in general, have 81 terms, but on account of the symmetry of the T_{ij} and $S_{k\ell}$ tensors, there are many equivalences between the resulting elastic constants. These equivalences can be determined by expanding the terms of (84) and comparing with the equivalent expressions of (22). For example

$$\begin{aligned} T_{11} = {} & c_{1111}S_{12} + c_{1112}S_{12} + c_{1113}S_{13} \\ & + c_{1121}S_{21} + c_{1122}S_{22} + c_{1123}S_{23} \\ & + c_{1131}S_{31} + c_{1132}S_{32} + c_{1133}S_{33}. \end{aligned} \tag{85}$$

Comparing this equation with the first of (22) noting that $S_{12} = S_{21} = \frac{S_{xy}}{2}$, etc., we have

$$\begin{aligned} & c_{1111} = c_{11}\,;\ c_{1112} = c_{1121} = c_{16}\,;\ c_{1133} = c_{13}\,;\ c_{1113} = c_{1131} = c_{15}\,; \\ & c_{1122} = c_{12}\,;\ c_{1123} = c_{1132} = c_{14}\,. \end{aligned} \tag{86}$$

In a similar manner it can be shown that the elastic constants of (22) correspond to the tensor elastic constants $c_{ijk\ell}$ according to the relations

$$\begin{gathered}
c_{11} = c_{1111} \,;\, c_{12} = c_{1122} = c_{2211} \,;\, c_{13} = c_{1133} = c_{3311} \,;\, c_{14} = c_{1123} = c_{1132} = \\
c_{2311} = c_{3211} \,;\, c_{15} = c_{1113} = c_{1131} = c_{1311} = c_{3111} \,;\, c_{16} = c_{1112} = c_{1121} = c_{1211} = \\
c_{2111} \,;\, c_{22} = c_{2222} \,;\, c_{23} = c_{2233} = c_{3322} \,;\, c_{24} = c_{2223} = c_{2232} = c_{2322} = c_{3222} \,; \\
c_{25} = c_{2213} = c_{2231} = c_{1322} = c_{3122} \,;\, c_{26} = c_{2212} = c_{2221} = c_{1222} = c_{2122} \,;\, c_{33} = \\
c_{3333} \,;\, c_{34} = c_{3323} = c_{3332} = c_{2333} = c_{3233} \,;\, c_{35} = 3313 = c_{3331} = c_{1333} = c_{3133} \,; \\
c_{36} = c_{3312} = c_{3321} = c_{1233} = c_{2133} \,;\, c_{44} = c_{2323} = c_{2332} = c_{3223} = c_{3232} \,;\, c_{45} = \\
c_{2313} = c_{2331} = c_{3213} = c_{3231} = 1323 = 1332 = c_{3132} = c_{3123} \,;\, c_{46} = c_{2312} = \\
c_{2321} = c_{3212} = c_{3221} = c_{1223} = c_{1232} = c_{2123} = c_{2132} \,;\, c_{55} = c_{1313} = c_{1331} = \\
c_{3113} = c_{3131} \,;\, c_{56} = c_{1312} = c_{1321} = c_{3112} = c_{3121} = c_{1213} = c_{1231} = c_{2113} = \\
c_{2131} \,;\, c_{66} = c_{1212} = c_{1221} = c_{2112} = c_{2121} \,.
\end{gathered} \tag{87}$$

Hence there are only 21 independent constants of the 81 $c_{ijk\ell}$ constants which are determined from the ordinarily elastic constants c_{ij} by replacing

$$1 \text{ by } 11;\ 2 \text{ by } 22;\ 3 \text{ by } 33;\ 4 \text{ by } 23;\ 5 \text{ by } 13;\ 6 \text{ by } 12 \tag{88}$$

and taking all possible permutations of these constants by interchanging them in pairs.

The inverse elastic equations (26) can be written in the simplified form

$$S_{ij} = s_{ijk\ell} T_{k\ell} \,. \tag{89}$$

By expanding these equations and comparing with equations (26) we can establish the relationships

$$\begin{gathered}
s_{11} = s_{1111} \,;\, s_{12} = s_{1122} = s_{2211} \,;\, s_{13} = s_{1133} = s_{3311} \,;\, \frac{s_{14}}{2} = s_{1123} = s_{1132} = s_{2311} = \\
s_{3211} \,;\, \frac{s_{15}}{2} = s_{1113} = s_{1131} = s_{1311} = s_{3111} \,;\, \frac{s_{16}}{2} = s_{1112} = s_{1121} = s_{1211} = s_{2111} \,; \\
s_{22} = s_{2222} \,;\, s_{23} = s_{2233} = s_{3322} \,;\, \frac{s_{24}}{2} = s_{2223} = s_{2232} = s_{2322} = s_{3222} \,;\, \frac{s_{25}}{2} = \\
s_{2213} = s_{2231} = s_{1322} = s_{3122} \,;\, \frac{s_{26}}{2} = s_{2212} = s_{2221} = s_{1222} = s_{2122} \,;\, s_{33} = s_{3333} \,; \\
\frac{s_{34}}{2} = s_{3323} = s_{3332} = s_{2333} = s_{3233} \,;\, \frac{s_{35}}{2} = s_{3313} = s_{3331} = s_{1333} = s_{3133} \,;\, \frac{s_{36}}{2} =
\end{gathered} \tag{90 A}$$

$$\begin{aligned}
&s_{3312} = s_{3321} = s_{1233} = s_{2133} \,;\, \frac{s_{44}}{4} = s_{2323} = s_{2332} = s_{3223} = s_{3232} \,;\, \frac{s_{45}}{4} = s_{2313} = \\
&s_{2331} = s_{3213} = s_{3231} = s_{1323} = s_{1332} = s_{3123} = s_{3132} \,;\, \frac{s_{46}}{4} = s_{2312} = s_{2321} = \\
&s_{3212} = s_{3221} = s_{1223} = s_{1232} = s_{2123} = s_{2132} \,;\, \frac{s_{55}}{4} = s_{1313} = s_{1331} = s_{3113} = \\
&s_{3131} \,;\, \frac{s_{56}}{4} = s_{1312} = s_{1321} = s_{3112} = s_{3121} = s_{1213} = s_{1231} = s_{2113} = s_{2131} \,; \\
&\frac{s_{66}}{4} = s_{1212} = s_{1221} = s_{2112} = s_{2121} \,.
\end{aligned} \tag{90 B}$$

Here again the $s_{ijk\ell}$ elastic constants are determined from the ordinary elastic constants s_{ij} by replacing

1 by 11, 2 by 22, 3 by 33, 4 by 23, 5 by 13, 6 by 12.

However for any number 4, 5, or 6 the elastic compliance s_{ij} has to be divided by two to equal the corresponding $s_{ijk\ell}$ compliance, and if 4, 5 or 6 occurs twice, the divisor has to be 4.

The isothermal elastic compliance of equations (39) can be expressed in tensor form

$$S_{ij} = s^{\Theta}_{ijk\ell}\, T_{k\ell} + \alpha_{ij}\, d\Theta \tag{91}$$

where as before α_{ij} is a tensor of the second rank having the relations to the ordinary coefficients of expansion

$$\alpha_1 = \alpha_{11} \,; \qquad \alpha_2 = \alpha_{22} \,; \qquad \alpha_3 = \alpha_{33} \,; \qquad \frac{\alpha_4}{2} = \alpha_{23} \,;$$
$$\frac{\alpha_5}{2} = \alpha_{13} \,; \qquad \frac{\alpha_6}{2} = \alpha_{12} \,.$$

The heat temperature equation of (35) is written in the simple form

$$dQ = + \,\alpha_{k\ell}\, T_{k\ell}\, \Theta + \rho C_p\, d\Theta. \tag{92}$$

By eliminating $d\Theta$ from (92) and substituting in (91) the adiabatic constants are given in the simple form

$$s^{\sigma}_{ijk\ell} = s^{\Theta}_{ijk\ell} - \frac{\alpha_{ij}\,\alpha_{k\ell}\,\Theta}{\rho C_p}\,. \tag{93}$$

The combination elastic and piezoelectric equations (60) can be written in the tensor form

$$S_{ij} = s^{E}_{ijk\ell} T_{k\ell} + d_{mij} E_m \,; \qquad \delta_n = \frac{\epsilon^{T}_{mn}}{4\pi}\, E_m + d_{nk\ell} T_{k\ell}\,. \tag{94}$$

Here d_{mij} is a tensor of third rank and ϵ^T_{mn} one of second rank. The d_{mij} constants are related to the eighteen ordinary constants d_{ij} by the equations

$$\begin{aligned}
&d_{11} = d_{111}\,;\ d_{12} = d_{122}\,;\ d_{13} = d_{133}\,;\ \frac{d_{14}}{2} = d_{123} = d_{132}\,;\ \frac{d_{15}}{2} = d_{113} = d_{131}\,;\\
&\frac{d_{16}}{2} = d_{112} = d_{121}\,;\ d_{21} = d_{211}\,;\ d_{22} = d_{222}\,;\ d_{23} = d_{233}\,;\ \frac{d_{24}}{2} = d_{223} = d_{232}\,;\\
&\frac{d_{25}}{2} = d_{213} = d_{231}\,;\ \frac{d_{26}}{2} = d_{212} = d_{221}\,;\ d_{31} = d_{311}\,;\ d_{32} = d_{322}\,;\ d_{33} = d_{333}\,;\\
&\frac{d_{34}}{2} = d_{323} = d_{332}\,;\ \frac{d_{35}}{2} = d_{313} = d_{331}\,;\ \frac{d_{36}}{2} = d_{312} = d_{321}\,.
\end{aligned} \tag{95}$$

The tensor equations (94) give a simple method of expressing the piezoelectric equations in an alternate form which is useful for some purposes. This involves relating the stress, strain, and displacement, rather than the applied field strength as in (94). To do this let us multiply through the right hand equation of (94) by the tensor $4\pi\beta^T_{mn}$, obtaining

$$4\pi\beta^T_{mn}\,\delta_n = \epsilon^T_{mn}\beta^T_{mn}E_m + 4\pi d_{nk\ell}\beta^T_{mn}T_{k\ell} \tag{96}$$

where β^T_{mn} is a tensor of the "free" dielectric impermeability obtained from the determinant.

$$\beta^T_{mn} = (-1)^{(m+n)}\,\frac{\Delta^{\epsilon^T}_{mn}}{\Delta^{\epsilon}} \tag{97}$$

where Δ^{ϵ^T} is the determinant

$$\Delta^{\epsilon^T} = \begin{vmatrix} \epsilon^T_{11} & \epsilon^T_{12} & \epsilon^T_{13} \\ \epsilon^T_{12} & \epsilon^T_{22} & \epsilon^T_{23} \\ \epsilon^T_{13} & \epsilon^T_{23} & \epsilon^T_{33} \end{vmatrix} \tag{98}$$

and $\Delta^{\epsilon^T}_{mn}$ the minor obtained from this by suppressing the mth row and nth column. If we take the product $\epsilon^T_{mn}\,\beta^T_{mn}$ for the three values of m, we have as multipliers of E_1, E_2, E_3, respectively

$$\begin{aligned}
\epsilon^T_{11}\,\beta^T_{11} + \epsilon^T_{12}\,\beta^T_{12} + \epsilon^T_{13}\,\beta^T_{13} &= 1\\
\epsilon^T_{21}\,\beta^T_{21} + \epsilon^T_{22}\,\beta^T_{22} + \epsilon^T_{23}\,\beta^T_{23} &= 1\\
\epsilon^T_{31}\,\beta^T_{31} + \epsilon^T_{32}\,\beta^T_{32} + \epsilon^T_{33}\,\beta^T_{33} &= 1.
\end{aligned} \tag{99}$$

But by virtue of equations (97) and (98) it is obvious that the value of each term of (99) is unity. Hence we have

$$E_m = 4\pi\beta^T_{mn}\,\delta_n - (4\pi\, d_{nk\ell}\,\beta^T_{mn})\,T_{k\ell}\,. \tag{100}$$

Since the dummy index n is summed for the values 1, 2, and 3, we can set the value of the terms in brackets equal to

$$g_{mk\ell} = 4\pi\, d_{nk\ell}\, \beta^T_{mn} = 4\pi[d_{1k\ell}\, \beta^T_{m1} + d_{2k\ell}\, \beta^T_{m2} + d_{3k\ell}\, \beta^T_{m3}] \tag{101}$$

and equation (100) becomes

$$E_m = 4\pi\, \beta^T_{mn}\, \delta_n - g_{mk\ell}\, T_{k\ell}\,. \tag{102}$$

Substituting this equation in the first equations of (94) we have

$$S_{ij} = s^D_{ijk\ell}\, T_{k\ell} + g_{nij}\, \delta_n \tag{103}$$

where

$$s^D_{ijk\ell} = s^E_{ijk\ell} - d_{mij}\, g_{mk\ell} = s^E_{ijk\ell} - 4\pi[\beta^T_{mn}\, d_{nk\ell}\, d_{mij}].$$

By substituting in the various values of i, j, k and ℓ corresponding to the 21 elastic constants, the difference between the constant displacement and constant potential elastic constants can be calculated. If equations (102) and (103) are expressed in terms of the $S_1, \cdots, S_6$ strains and $T_1, \cdots, T_6$ stresses, the g_{nij} constants are related to the g_{ij} constants as are the corresponding d_{ij} constants to the d_{nij} constants of equation (95).

Another variation of the piezoelectric equations which is sometimes employed is one for which the stresses are expressed in terms of the strains and field strength. This form can be derived directly from equations (94) by multiplying both sides of the first equation by the tensor $c^E_{ijk\ell}$ for the elastic constants, where these are defined in terms of the corresponding s^E_{ij} elastic compliances by the equation

$$c^E_{ij} = (-1)^{(i+j)}\, \Delta^{s^E}_{ij} / \Delta^{s^E} \tag{104}$$

where Δ is the determinant

$$\Delta^{s^E} = \begin{vmatrix} s^E_{11} & s^E_{12} & s^E_{13} & s^E_{14} & s^E_{15} & s^E_{16} \\ s^E_{12} & s^E_{22} & s^E_{23} & s^E_{24} & s^E_{25} & s^E_{26} \\ s^E_{13} & s^E_{23} & s^E_{33} & s^E_{34} & s^E_{35} & s^E_{36} \\ s^E_{14} & s^E_{24} & s^E_{34} & s^E_{44} & s^E_{45} & s^E_{46} \\ s^E_{15} & s^E_{25} & s^E_{35} & s^E_{45} & s^E_{55} & s^E_{56} \\ s^E_{16} & s^E_{26} & s^E_{36} & s^E_{46} & s^E_{56} & s^E_{66} \end{vmatrix}$$

and $\Delta^{s^E}_{ij}$ in the minor obtained by suppressing the ith row and jth column. Carrying out the tensor multiplication we have

$$c^E_{ijk\ell}\, S_{ij} = c^E_{ijk\ell}\, s^E_{ijk\ell}\, T_{k\ell} + d_{mij}\, c^E_{ijk\ell}\, E_m\,. \tag{105}$$

As before we find that the tensor product of $c^E_{ijk\ell}\, s^E_{ijk\ell}$ is unity for all values of k and ℓ. Hence equation (105) can be written in the form

$$T_{k\ell} = c^E_{ijk\ell}\, S_{ij} - e_{mk\ell}\, E_m \tag{106}$$

where $e_{mk\ell}$ is the sum

$$e_{mk\ell} = d_{mij}\, c^E_{ijk\ell} \tag{107}$$

summed for all values of the dummy indices i and j. If we substitute the equation (106) in the last equation of (94) we find

$$\delta_n = \frac{\epsilon^S_{mn}}{4\pi} E_m + e_{nij} S_{ij} \tag{108}$$

where ϵ^S_{mn} the clamped dielectric constant is related to the free dielectric constant ϵ^T_{mn} by the equation

$$\epsilon^S_{mn} = \epsilon^T_{mn} - 4\pi[d_{nk\ell}\, e_{mk\ell}]. \tag{109}$$

Expressed in two index piezoelectric constants involving the strains $S_{11} \cdots S_{12}$ and stresses $T_{11} \cdots T_{12}$ the relation between the two and three index piezoelectric constants is given by the equation

$$\begin{aligned}
&e_{11} = e_{111}\,;\ e_{12} = e_{122}\,;\ e_{13} = e_{133}\,;\ e_{14} = e_{123} = e_{132}\,;\ e_{15} = e_{113} = e_{131}\,;\\
&e_{16} = e_{112} = e_{121}\,;\ e_{21} = e_{211}\,;\ e_{22} = e_{222}\,;\ e_{23} = e_{233}\,;\ e_{24} = e_{223} = e_{232}\,;\\
&e_{25} = e_{213} = e_{231}\,;\ e_{26} = e_{212} = e_{221}\,;\ e_{31} = e_{311}\,;\ e_{32} = e_{322}\,;\ e_{33} = e_{333}\,;\\
&e_{34} = e_{323} = e_{332}\,;\ e_{35} = e_{313} = e_{331}\,;\ e_{36} = e_{312} = e_{321}\,.
\end{aligned} \tag{110}$$

Finally, the fourth form for expressing the piezoelectric relation is the one given by equation (53). Expressed in tensor form, these equations become

$$T_{k\ell} = c^D_{ijk\ell}\, S_{ij} - h_{nk\ell}\, \delta_n\,; \quad E_m = 4\pi\beta^S_{mn}\, \delta_n - h_{mij}\, S_{ij} \tag{111}$$

In this equation the three index piezoelectric constants of equation (111) are related to the two index constants of equation (53) as the e constants of (110). These equations can also be derived directly from (106) and (108) by eliminating E_m from the two equations. This substitution yields the additional relations

$$\begin{aligned}
h_{nk\ell} = 4\pi e_{mk\ell}\, \beta^S_{mn}\,; \quad c^D_{ijk\ell} &= c^E_{ijk\ell} + e_{mk\ell}\, h_{mij} = c^E_{ijk\ell}\\
&\quad + 4\pi\, e_{mk\ell}\, e_{nij}\, \beta^S_{mn}
\end{aligned} \tag{112}$$

where

$$\beta^S_{mn} = (-1)^{(m+n)}\, \Delta^{\epsilon S}_{m,n}/\Delta^{\epsilon S}$$

in which

$$\Delta^{\epsilon^S} = \begin{vmatrix} \epsilon_{11}^{S} & \epsilon_{12}^{S} & \epsilon_{13}^{S} \\ \epsilon_{12}^{S} & \epsilon_{22}^{S} & \epsilon_{23}^{S} \\ \epsilon_{13}^{S} & \epsilon_{23}^{S} & \epsilon_{33}^{S} \end{vmatrix}.$$

The four forms of the piezoelectric equations, and the relation between them are given in Table I.

TABLE I

FOUR FORMS OF THE ELASTIC, DIELECTRIC, AND PIEZO ELECTRIC EQUATIONS AND THEIR INTERRELATIONS

Form	Elastic Relation	Electric Relation
1	$S_{ij} = s_{ijk\ell}^{E} T_{k\ell} + d_{mij} E_m$	$\delta_n = \frac{\epsilon_{mn}^{T}}{4\pi} E_n + d_{nk\ell} T_{k\ell}$
2	$S_{ij} = s_{ijk\ell}^{D} T_{k\ell} + g_{nij} \delta_n$	$E_m = 4\pi \beta_{mn}^{T} \delta_n - g_{mk\ell} T_{k\ell}$
3	$T_{k\ell} = c_{ij\ell k}^{E} S_{ij} - e_{mk\ell} E_m$	$\delta_n = \frac{\epsilon_{mn}^{S}}{4\pi} E_m + e_{nij} S_{ij}$
4	$T_{k\ell} = c_{ijk\ell}^{D} S_{ij} - h_{nk\ell} \delta_n$	$E_m = 4\pi \beta_{mn}^{S} \delta_n - h_{mij} S_{ij}$

Form	Relation Between Elastic Constants	Relation Between Piezoelectric Constants	Relation Between Dielectric Constants
1	$s_{ijk\ell}^{D} = s_{ijk\ell}^{E} - d_{mij} g_{mk\ell}$	$g_{mk\ell} = 4\pi \beta_{mn}^{T} d_{nk\ell}$	$\beta_{mn}^{T} = (-1)^{(m+n)} \Delta_{mn}^{\epsilon^T} / \Delta^{\epsilon^T}$
2	$c_{ij}^{E} = (-1)^{(i+j)} \Delta_{ij}^{s^E} / \Delta^{s^E}$	$e_{mk\ell} = d_{mij} c_{ijk\ell}^{E}$	$\epsilon_{mn}^{S} = \epsilon_{mn}^{T} - 4\pi (d_{nk\ell} e_{mk\ell})$
3	$c_{ijk\ell}^{D} = c_{ijk\ell}^{E} + e_{mk\ell} h_{mij}$	$h_{nk\ell} = 4\pi \beta_{mn}^{S} e_{mk\ell}$	$\beta_{mn}^{S} = \beta_{mn}^{T} + \frac{g_{nk\ell} h_{mk\ell}}{4\pi}$
4	$c_{ij}^{D} = (-1)^{(i+j)} \Delta_{ij}^{S^D} / \Delta^{S^D}$	$h_{nk\ell} = g_{nij} c_{ijk\ell}^{D}$	$\beta_{mn}^{S} = (-1)^{(m+n)} \Delta_{mn}^{\epsilon^S} / \Delta^{\epsilon^S}$

5. EFFECT OF SYMMETRY AND ORIENTATION ON THE DIELECTRIC PIEZOELECTRIC AND ELASTIC CONSTANTS OF CRYSTALS

All crystals can be divided into 32 classes depending on the type of symmetry. These groups can be divided into seven general classifications depending on how the axes are related and furthermore all 32 classes can be built out of symmetries based on twofold (binary) axes, threefold (trigonal) axes, fourfold axes of symmetry, sixfold axes of symmetry, planes of reflection symmetry and combinations of axis reflection symmetry besides a simple symmetry through the center. Each of these types of symmetry result in a reduction of the number of dielectric, piezoelectric, and elastic constants.

Since the tensor equation is easily transformed to a new set of axes by the transformaion equations (76) this form is particularly advantageous for determining the reduction in elastic, piezoelectric and dielectric constants. For example consider the second rank tensors $\epsilon_{k\ell}$ and $\alpha_{k\ell}$ for the dielectric constant and the expansion coefficients. Ordinarily for the most general symmetry each tensor, since it is symmetrical, requires six independent coefficients. Suppose however that the X axis is an axis of twofold or binary symmetry, i.e., the properties along the positive Z axis are the same as those along the negative Z axis. If we rotate the axes 180° about the X axis so that $+ Z$ is changed into $- Z$, the direction cosines are

$$\begin{aligned} \ell_1 &= \frac{\partial x_1'}{\partial x_1} = 1\,; & m_1 &= \frac{\partial x_1'}{\partial x_2} = 0\,; & n_1 &= \frac{\partial x_1'}{\partial x_3} = 0 \\ \ell_2 &= \frac{\partial x_2'}{\partial x_1} = 0\,; & m_2 &= \frac{\partial x_2'}{\partial x_2} = -1\,; & n_2 &= \frac{\partial x_2'}{\partial x_3} = 0 \\ \ell_3 &= \frac{\partial x_3'}{\partial x_1} = 0\,; & m_3 &= \frac{\partial x_3'}{\partial x_2} = 0\,; & n_3 &= \frac{\partial x_3'}{\partial x_3} = -1. \end{aligned} \tag{113}$$

The tensor transformation equations for a second rank tensor are

$$\epsilon_{ij}' = \frac{\partial x_i'}{\partial x_k}\frac{\partial x_j'}{\partial x_\ell}\epsilon_{k\ell}\,. \tag{114}$$

Applying (113) to (114) summing for all values of k and l for each value of i, and j we have the six components

$$\epsilon_{11}' = \epsilon_{11}\,;\ \epsilon_{12}' = -\epsilon_{12}\,;\ \epsilon_{13}' = -\epsilon_{13}\,;\ \epsilon_{22}' = \epsilon_{22}\,;\ \epsilon_{23}' = \epsilon_{23}\,;\ \epsilon_{33}' = \epsilon_{33}\,. \tag{115}$$

Since a crystal having the X axis a binary axis of symmetry must have the same constants for a $+Z$ direction as for a $-Z$ direction, this condition can only be satisfied by

$$\epsilon_{12} = \epsilon_{13} = 0. \tag{116}$$

The same condition is true for the expansion coefficients since they form a second rank tensor and hence

$$\alpha_{12} = \alpha_{13} = 0. \tag{117}$$

In a third rank tensor such as d_{ijk}, e_{ijk}, g_{ijk}, h_{ijk}, we similarly find that of the eighteen independent constants

$$\begin{gathered} h_{112} = h_{16}\,;\ h_{113} = h_{15}\,;\ h_{211} = h_{21}\,;\ h_{222} = h_{22}\,; h_{223} = h_{24}\,; \\ h_{233} = h_{23}\,; h_{311} = h_{31}\,; h_{322} = h_{32}\,; h_{323} = h_{34}\,; h_{333} = h_{33}\,. \end{gathered} \tag{118}$$

are all zero. The same terms in the d_{ijk}, e_{ijk}, g_{ijk} tensors are also zero.

In a fourth rank tensor such as $c_{ijk\ell}$, $s_{ijk\ell}$, applying the tensor transformation equation

$$c_{ijk\ell} = \frac{\partial x_i'}{\partial x_m}\frac{\partial x_j'}{\partial x_n}\frac{\partial x_k'}{\partial x_o}\frac{\partial x_\ell'}{\partial x_p} c_{mnop} \tag{119}$$

and the condition (113) we similarly find

$$c_{15} = c_{16} = c_{25} = c_{26} = c_{35} = c_{36} = c_{45} = c_{46} = 0. \tag{120}$$

If the binary axis had been the Y axis the corresponding missing terms can be obtained by cyclically rotating the tensor indices. The missing terms are for the second, third and fourth rank tensors, transformed to two index symbols,

$$\begin{gathered}\epsilon_{23}\,,\ \epsilon_{12}\,;\ h_{11}\,,\ h_{12}\,,\ h_{13}\,,\ h_{15}\,,\ h_{24}\,,\ h_{26}\,,\ h_{31}\,,\ h_{32}\,,\ h_{33}\,,\ h_{35}\,;\\ c_{14}\,,\ c_{16}\,,\ c_{24}\,,\ c_{26}\,,\ c_{34}\,,\ c_{36}\,,\ c_{45}\,,\ c_{55}\,.\end{gathered} \tag{121}$$

Similarly if the Z axis is the binary axis, the missing constants are

$$\begin{gathered}\epsilon_{13}\,,\ \epsilon_{12}\,;\ h_{11}\,,\ h_{12}\,,\ h_{13}\,,\ h_{16}\,,\ h_{21}\,,\ h_{22}\,,\ h_{23}\,,\ h_{26}\,,\ h_{34}\,,\ h_{35}\,;\\ c_{14}\,,\ c_{15}\,,\ c_{24}\,,\ c_{25}\,,\ c_{34}\,,\ c_{35}\,,\ c_{46}\,,\ c_{56}\,.\end{gathered} \tag{122}$$

Hence a crystal of the orthorhombic bisphenoidal class or class 6, which has three binary axes, the X, Y and Z directions, will have the remaining terms,

$$\epsilon_{11}\,,\ \epsilon_{22}\,,\ \epsilon_{33}\,;\ h_{14}\,,\ h_{25}\,,\ h_{36}\,;\ c_{11}\,,\ c_{12}\,,\ c_{13}\,,\ c_{22}\,,\ c_{23}\,,\ c_{33}\,,\ c_{44}\,,\ c_{55}\,,\ c_{66} \tag{123}$$

with similar terms for other tensors of the same rank. Rochelle salt is a crystal of this class.

If Z is a threefold axis of symmetry, the direction cosines for a set of axes rotated 120° clockwise about Z are,

$$\begin{aligned}\ell_1 &= \frac{\partial x_1'}{\partial x_1} = -.5\,; & m_1 &= \frac{\partial x_1'}{\partial x_2} = -.866\,; & n_1 &= \frac{\partial x_1'}{\partial x_3} = 0\\ \ell_2 &= \frac{\partial x_2'}{\partial x_1} = .866\,; & m_2 &= \frac{\partial x_2'}{\partial x_2} = -.5\,; & n_2 &= \frac{\partial x_2'}{\partial x_3} = 0\\ \ell_3 &= \frac{\partial x_3'}{\partial x_1} = 0\,; & m_3 &= \frac{\partial x_3'}{\partial x_2} = 0\,; & n_3 &= \frac{\partial x_3'}{\partial x_3} = 1.\end{aligned} \tag{124}$$

Applying these relations to equations (114) for a second rank tensor, we find for the components

$$\begin{gathered}\epsilon_{11}' = .25\epsilon_{11} + .433\epsilon_{12} + .75\epsilon_{22}\,;\ \epsilon_{12}' = -.433\epsilon_{11} + .25\epsilon_{12} + .433\epsilon_{22}\\ \epsilon_{13}' = -.5\epsilon_{13} - .866\epsilon_{23}\,;\ \epsilon_{22}' = .75\epsilon_{11} - .433\epsilon_{12} + .25\epsilon_{22}\\ \epsilon_{23}' = .866\epsilon_{13} - .5\epsilon_{23}\,;\ \epsilon_{33}' = \epsilon_{33}\,.\end{gathered} \tag{125}$$

For the third and fifth equations, since we must have $\epsilon'_{13} = \epsilon_{13}$; $\epsilon'_{23} = \epsilon_{23}$ in order to satisfy the symmetry relation, the equations can only be satisfied if

$$\epsilon_{13} = \epsilon_{23} = 0. \tag{126}$$

Similarly solving the first three equations simultaneously, we find

$$\epsilon_{12} = 0; \epsilon_{11} = \epsilon_{22} . \tag{127}$$

Hence the remaining constants are

$$\epsilon_{11} = \epsilon_{22} ; \epsilon_{33} . \tag{128}$$

Similarly for third and fourth rank tensors, for a crystal having Z a trigonal axis, the remaining terms are

$$\begin{aligned} &h_{11} , h_{12} = -h_{11} , h_{13} = 0; \; h_{14} , h_{15} , h_{16} = -h_{22} \\ &h_{21} = -h_{22} , h_{22} , h_{23} = 0, h_{24} = h_{15} ; h_{25} = -h_{14} , h_{21} = -h_{11} \\ &h_{31} ; h_{32} = h_{31} ; h_{33} ; h_{34} = 0; \; h_{35} = 0; \; h_{36} = 0 \end{aligned} \tag{129}$$

$$\begin{aligned} &c_{11} ; c_{12} ; c_{13} ; c_{14} ; c_{15} = -c_{25} ; c_{16} = 0 \\ &c_{12} ; c_{22} = c_{11} ; c_{23} = c_{13} ; c_{24} = -c_{14} ; c_{25} ; c_{26} = 0 \\ &c_{13} ; c_{23} = c_{13} ; c_{33} ; c_{34} = 0; \; c_{35} = 0; \; c_{36} = 0 \\ &c_{14} ; c_{24} = -c_{14} ; c_{34} = 0; \; c_{44} ; c_{45} = 0; \; c_{46} = c_{15} \\ &c_{15} = -c_{25} ; c_{25} ; c_{35} = 0; \; c_{45} = 0; \; c_{55} = c_{44} ; c_{56} = c_{14} \\ &c_{16} = 0; \; c_{26} = 0; \; c_{36} = 0; \; c_{46} = c_{25} ; c_{56} = c_{14} ; c_{66} = \tfrac{1}{2} (c_{11} - c_{12}). \end{aligned} \tag{130}$$

If the Z axis is a trigonal axis and the X a binary axis, as it is in quartz, the resulting constants are obtained by combining the conditions (116), (118), (120) with conditions (128), (129), (130) respectively. The resulting second, third and fourth rank tensors have the following terms

$$\begin{aligned} &\epsilon_{11} ; \epsilon_{12} = 0; \; \epsilon_{13} = 0 \\ &\epsilon_{12} = 0; \; \epsilon_{22} = \epsilon_{11} ; \epsilon_{23} = 0 \\ &\epsilon_{13} = 0; \; \epsilon_{23} = 0; \; \epsilon_{33} \end{aligned} \tag{131}$$

$$\begin{aligned} &h_{11} ; h_{12} = -h_{11} ; h_{13} = 0; \; h_{14} ; h_{15} = 0; \; h_{16} = 0 \\ &h_{21} = 0; \; h_{22} = 0; \; h_{23} = 0; \; h_{24} = 0; \; h_{25} = -h_{14} ; h_{26} = -h_{11} \\ &h_{31} = 0; \; h_{32} = 0; \; h_{33} = 0; \; h_{34} = 0; \; h_{35} = 0; \; h_{36} = 0 \end{aligned} \tag{132}$$

$$
\begin{array}{l}
c_{11}\,;\, c_{12}\,;\, c_{13}\,;\, c_{14}\,;\, c_{15} = 0;\;\; c_{16} = 0 \\
c_{12}\,;\, c_{22} = c_{11}\,;\, c_{23} = c_{13}\,;\, c_{24} = -c_{14}\,;\, c_{25} = 0;\;\; c_{26} = 0 \\
c_{13}\,;\, c_{23} = c_{13}\,;\, c_{33}\,;\, c_{34} = 0;\;\; c_{35} = 0;\;\; c_{36} = 0 \\
c_{14}\,;\, c_{24} = -c_{14}\,;\, c_{34} = 0;\;\; c_{44}\,;\, c_{45} = 0;\;\; c_{46} = 0 \\
c_{15} = 0;\;\; c_{25} = 0;\;\; c_{35} = 0;\;\; c_{45} = 0;\;\; c_{55} = c_{44}\,;\, c_{56} = c_{14} \\
c_{16} = 0;\;\; c_{26} = 0;\;\; c_{36} = 0;\;\; c_{36} = 0;\;\; c_{56} = c_{14}\,;\, c_{66} = \tfrac{1}{2}\,(c_{11}-c_{12}).
\end{array}
\tag{133}
$$

5.1 *Second Rank Tensors for Crystal Classes*

The symmetry relations have been calculated for all classes of crystals. For a second rank tensor such as ϵ_{ij}, the following forms are required

Triclinic Classes 1 and 2

$$
\begin{vmatrix}
\epsilon_{11}, & \epsilon_{12}, & \epsilon_{13} \\
\epsilon_{12}, & \epsilon_{22}, & \epsilon_{23} \\
\epsilon_{13}, & \epsilon_{23}, & \epsilon_{33}
\end{vmatrix}
$$

Monoclinic sphenoidal, Y a binary axis, Class 3
Monoclinic domatic, Y a plane of symmetry, Class 4
Monoclinic prismatic, Center of symmetry, Class 5

$$
\begin{vmatrix}
\epsilon_{11}, & 0, & \epsilon_{13} \\
0, & \epsilon_{22}, & 0 \\
\epsilon_{13}, & 0, & \epsilon_{33}
\end{vmatrix}
$$

Orthorhombic
Classes 6, 7, 8

$$
\begin{vmatrix}
\epsilon_{11}, & 0, & 0 \\
0, & \epsilon_{22}, & 0 \\
0, & 0, & \epsilon_{33}
\end{vmatrix}
\tag{134}
$$

Tetragonal, Trigonal
Hexagonal
Classes 9 to 27

$$
\begin{vmatrix}
\epsilon_{11}, & 0, & 0 \\
0, & \epsilon_{11}, & 0 \\
0, & 0, & \epsilon_{33}
\end{vmatrix}
$$

Cubic
Classes 28 to 32

$$
\begin{vmatrix}
\epsilon_{11}, & 0, & 0 \\
0, & \epsilon_{11}, & 0 \\
0, & 0, & \epsilon_{11}
\end{vmatrix}
$$

5.2 *Third Rank Tensors of the Piezoelectric Type for the Crystal Classes*

Triclinic Assymetric (Class 1) No Symmetry

$$
\begin{vmatrix}
h_{11}, & h_{12}, & h_{13}, & h_{14}, & h_{15}, & h_{16} \\
h_{21}, & h_{22}, & h_{23}, & h_{24}, & h_{25}, & h_{26} \\
h_{31}, & h_{32}, & h_{33}, & h_{34}, & h_{35}, & h_{36}
\end{vmatrix}
$$

Triclinic pinacoidal, (center of symmetry) $h = 0$ (Class 2)

Monoclinic Sphenoidal (Class 3) Y is binary axis

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & 0, & h_{16} \\ h_{21}, & h_{22}, & h_{23}, & 0, & h_{25}, & 0 \\ 0, & 0, & 0, & h_{34}, & 0, & h_{36} \end{vmatrix}$$

Monoclinic domatic (Class 4) Y plane is plane of symmetry

$$\begin{vmatrix} h_{11}, & h_{12}, & h_{13}, & 0, & h_{15}, & 0 \\ 0, & 0, & 0, & h_{24}, & 0, & h_{26} \\ h_{31}, & h_{32}, & h_{33}, & 0, & h_{35}, & 0 \end{vmatrix}$$

Monoclinic prismatic (center of symmetry) $h = 0$ (Class 5) (135)

Orthorhombic bisphenoidal (Class 6) X, Y, Z binary axes

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & 0, & 0 \\ 0, & 0, & 0, & 0, & h_{25}, & 0 \\ 0, & 0, & 0, & 0, & 0, & h_{36} \end{vmatrix}$$

Orthorhombic pyramidal (Class 7) Z binary, X, Y, planes of symmetry

$$\begin{vmatrix} 0, & 0, & 0, & 0, & h_{15}, & 0 \\ 0, & 0, & 0, & h_{24}, & 0, & 0 \\ h_{31}, & h_{32}, & h_{33}, & 0, & 0, & 0 \end{vmatrix}$$

Orthorhombic bipyramidal (center of symmetry) $h = 0$ (Class 8)

Tetragonal bisphenoidal (Class 9) Z is quaternary alternating

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & h_{15}, & 0 \\ 0, & 0, & 0, & -h_{15}, & h_{14}, & 0 \\ h_{31}, & -h_{31}, & 0, & 0, & 0, & h_{36} \end{vmatrix}$$

Tetragonal pyramidal (Class 10) Z is quaternary

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & h_{15}, & 0 \\ 0, & 0, & 0, & h_{15}, & -h_{14}, & 0 \\ h_{31}, & h_{31}, & h_{33}, & 0, & 0, & 0 \end{vmatrix}$$

Tetragonal scalenohedral (Class 11) Z quaternary, X and Y binary

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & 0, & 0 \\ 0, & 0, & 0, & 0, & h_{14}, & 0 \\ 0, & 0, & 0, & 0, & 0, & h_{36} \end{vmatrix}$$

Tetragonal trapezohedral (Class 12) Z quaternary, X and Y binary

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & 0, & 0 \\ 0, & 0, & 0, & 0, & -h_{14}, & 0 \\ 0, & 0, & 0, & 0, & 0, & 0 \end{vmatrix}$$

Tetragonal bipyramidal (center of symmtery) $h = 0$ (Class 13)

Ditetragonal pyramidal (Class 14) Z quaternary, X and Y planes of symmetry

$$\begin{vmatrix} 0 & 0 & 0 & 0 & h_{15} & 0 \\ 0 & 0 & 0 & h_{15} & 0 & 0 \\ h_{31} & h_{31} & h_{33} & 0 & 0 & 0 \end{vmatrix}$$

Ditetragonal bipyramidal (center of symmetry) $h = 0$ (Class 15)

Trigonal pyramidal (Class 16) Z trigonal axis

$$\begin{vmatrix} h_{11} & -h_{11} & 0 & h_{14} & h_{15} & -h_{22} \\ -h_{22} & h_{22} & 0 & h_{15} & -h_{14} & -h_{11} \\ h_{31} & h_{31} & h_{33} & 0 & 0 & 0 \end{vmatrix}$$

Trigonal rhombohedral (Class 17) center of symmetry, $h = 0$

Trigonal trapezohedral (Class 18), Z trigonal, X binary

$$\begin{vmatrix} h_{11} & -h_{11} & 0 & h_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -h_{14} & -h_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

Trigonal bipyramidal (Class 19), Z trigonal, plane of symmetry

$$\begin{vmatrix} h_{11} & -h_{11} & 0 & 0 & 0 & -h_{22} \\ -h_{22} & h_{22} & 0 & 0 & 0 & -h_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

Ditrigonal pyramidal (Class 20) Z trigonal, Y plane of symmetry

$$\begin{vmatrix} 0 & 0 & 0 & 0 & h_{15} & -h_{22} \\ -h_{22} & h_{22} & 0 & h_{15} & 0 & 0 \\ h_{31} & h_{31} & h_{33} & 0 & 0 & 0 \end{vmatrix}$$

Ditrigonal scalenohedral (Class 21) center of symmetry, $h = 0$

Ditrigonal bipyramidal (Class 22) Z trigonal, Z plane of symmetry and Y plane of symmetry

$$\begin{vmatrix} h_{11} & -h_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -h_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

Hexagonal pyramidal (Class 23) Z hexagonal

$$\begin{vmatrix} 0 & 0 & 0 & h_{14} & h_{15} & 0 \\ 0 & 0 & 0 & h_{15} & -h_{14} & 0 \\ h_{31} & h_{31} & h_{33} & 0 & 0 & 0 \end{vmatrix}$$

Hexagonal trapezohedral (Class 24) Z hexagonal, X binary

$$\begin{vmatrix} 0 & 0 & 0 & h_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -h_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}$$

Hexagonal bipyramidal (Class 25) center of symmetry, $h = 0$

Dihexagonal pyramidal (Class 26) X hexagonal Y plane of symmetry

$$\begin{vmatrix} 0, & 0, & 0, & 0, & h_{15}, & 0 \\ 0, & 0, & 0, & h_{15}, & 0, & 0 \\ h_{31}, & h_{31}, & h_{33}, & 0, & 0, & 0 \end{vmatrix}$$

Dihexagonal bipyramidal (Class 27) center of symmetry, $h = 0$

Cubic tetrahedral-pentagonal-dodecahedral (Class 28) X, Y, Z binary

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & 0, & 0 \\ 0, & 0, & 0, & 0, & h_{14}, & 0 \\ 0, & 0, & 0, & 0, & 0, & h_{14} \end{vmatrix}$$

Cubic pentagonal-icositetetrahedral (Class 29) $h = 0$

Cubic, dyakisdodecahedral (Class 30) center of symmetry, $h = 0$

Cubic, hexakistetrahedral (Class 31) X, Y, Z quaternary alternating

$$\begin{vmatrix} 0, & 0, & 0, & h_{14}, & 0, & 0 \\ 0, & 0, & 0, & 0, & h_{14}, & 0 \\ 0, & 0, & 0, & 0, & 0, & h_{14} \end{vmatrix}$$

Cubic, hexakis-octahedral (Class 32) center of symmetry, $h = 0$

This third rank tensor has been expressed in terms of two index symbols rather than the three index tensor symbols, since the two index symbols are commonly used in expressing the piezoelectric effect. The relations for the h and e constants are

$$h_{i4}, h_{i5}, h_{i6} \text{ are equivalent to } h_{i23}, h_{i13}, h_{i12} \tag{136}$$

in three index symbols, whereas for the d_{ij} and g_{ij} constants we have the relations

$$\frac{d_{i4}}{2}, \frac{d_{i5}}{2}, \frac{d_{i6}}{2} \text{ are equivalent to } d_{i23}, d_{i13}, d_{i12} \tag{137}$$

Hence the d_i relations for classes 16, 18, 19, and 22 will be somewhat different than the h symbols given above. These classes will be

$$\begin{aligned}
&\text{Class 16} \quad \begin{vmatrix} d_{11} & -d_{11} & 0 & d_{14} & d_{15} & -2d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & -d_{14} & -2d_{11} \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{vmatrix} \\
&\text{Class 18} \quad \begin{vmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix} \\
&\text{Class 19} \quad \begin{vmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & -2d_{22} \\ -d_{22} & d_{22} & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix} \\
&\text{Class 22} \quad \begin{vmatrix} d_{11} & -d_{11} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{vmatrix}
\end{aligned} \tag{138}$$

5.3 *Fourth Rank Tensors of the Elastic Type for the Crystal Classes*

Triclinic System (Classes 1 and 2) 21 moduli

$$\begin{vmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{12} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{13} & c_{23} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{14} & c_{24} & c_{34} & c_{44} & c_{45} & c_{46} \\ c_{15} & c_{25} & c_{35} & c_{45} & c_{55} & c_{56} \\ c_{16} & c_{26} & c_{36} & c_{46} & c_{56} & c_{66} \end{vmatrix} \tag{139}$$

The *s* tensor is entirely analogous

Monoclinic System (Classes 3, 4 and 5) 12 moduli

$$\begin{vmatrix} c_{11} & c_{12} & c_{13} & 0 & c_{15} & 0 \\ c_{12} & c_{22} & c_{23} & 0 & c_{25} & 0 \\ c_{13} & c_{23} & c_{33} & 0 & c_{35} & 0 \\ 0 & 0 & 0 & c_{44} & 0 & c_{46} \\ c_{15} & c_{25} & c_{35} & 0 & c_{55} & 0 \\ 0 & 0 & 0 & c_{46} & 0 & c_{66} \end{vmatrix}$$

The *s* tensor is entirely analogous

Rhombic System (Classes 6, 7 and 8) 9 moduli	$\begin{matrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{13} & c_{23} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{matrix}$	The s tensor is entirely analogous
Tetragonal system, Z a fourfold axis (Classes 9, 10, 13) 7 moduli	$\begin{matrix} c_{11} & c_{12} & c_{13} & 0 & 0 & c_{16} \\ c_{12} & c_{11} & c_{13} & 0 & 0 & -c_{16} \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ c_{16} & -c_{16} & 0 & 0 & 0 & c_{66} \end{matrix}$	The s tensor is entirely analogous
Tetragonal system, Z a fourfold axis, X a twofold axis (Classes 11, 12, 14, 15) 6 moduli	$\begin{matrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{66} \end{matrix}$	The s tensor is entirely analogous
Trigonal system, Z a twofold axis, (Classes 16, 17) 7 moduli	$\begin{matrix} c_{11} & c_{12} & c_{13} & c_{14} & -c_{25} & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & c_{25} & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{44} & 0 & c_{25} \\ -c_{25} & c_{25} & 0 & 0 & c_{44} & c_{14} \\ 0 & 0 & 0 & c_{25} & c_{14} & \frac{c_{11} - c_{12}}{2} \end{matrix}$	The s tensor is analogous except that $s_{46} = 2s_{25}$, $s_{56} = 2s_{14}$, $s_{66} = 2(s_{11} - s_{12})$

Trigonal system, Z a trigonal axis, X a binary axis (Classes 18, 20, 21) 6 moduli	$\begin{matrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & c_{14} \\ 0 & 0 & 0 & 0 & c_{14} & \frac{c_{11} - c_{12}}{2} \end{matrix}$	The s tensor is analogous except that $s_{56} = 2s_{14}$, $s_{66} = 2(s_{11} - s_{12})$
Hexagonal system, Z a sixfold axis, X a twofold axis (Classes 19, 22, 23, 24, 25, 26, 27) 5 moduli	$\begin{matrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{c_{11} - c_{12}}{2} \end{matrix}$	The s tensor is analogous except $s_{66} = 2(s_{11} - s_{12})$
Cubic system (Classes 28, 29, 30, 31, 32) 3 moduli	$\begin{matrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{matrix}$	The s tensor is entirely analogous
Isotropic bodies, 2 moduli	$\begin{matrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{c_{11} - c_{12}}{2} & & \\ 0 & 0 & 0 & 0 & \frac{c_{11} - c_{12}}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{c_{11} - c_{12}}{2} \end{matrix}$	The s tensor analogous except last three diagonal terms are $2(s_{11} - s_{12})$

5.4 *Piezoelectric Equations for Rotated Axes*

Another application of the tensor equations for rotated axes is in determining the piezoelectric equations of crystals whose length, width, and thickness do not coincide with the crystallographic axes of the crystal. Such oriented cuts are useful for they sometimes give properties that cannot be obtained with crystals lying along the crystallographic axes. Such properties may be higher electromechanical coupling, freedom from coupling to undesired modes of motion, or low temperature coefficients of frequency. Hence in order to obtain the performance of such crystals it is necessary to be able to express the piezoelectric equations in a form suitable for these orientations. In fact in first measuring the properties of these crystals a series of oriented cuts is commonly used since by employing such cuts the resulting frequencies, and impedances can be used to calculate all the primary constants of the crystal.

The piezoelectric equations (111) are

$$T_{k\ell} = c^{D}_{ijk\ell} S_{ij} - h_{nk\ell}\delta_n \, ; \quad E_m = 4\pi\beta^{S}_{mn}\delta_n - h_{mij}S_{ij} \, . \qquad (111)$$

The first equation is a tensor of the second rank, while the second equation is a tensor of the first rank. If we wish to transform these equations to another set of axes x', y', z', we can employ the tensor transformation equations

$$\begin{aligned} T'_{k\ell} = \frac{\partial x'_k}{\partial x_k}\frac{\partial x'_\ell}{\partial x_\ell} T_{k\ell} &= \frac{\partial x'_k}{\partial x_k}\frac{\partial x'_\ell}{\partial x_\ell} \\ &\quad \cdot \left[c^{D}_{11k\ell}S_{11} + 2c^{D}_{12k\ell}S_{12} + 2c^{D}_{13k\ell}S_{13} + c^{D}_{22k\ell}S_{22}\right. \\ &\quad \left. + 2c^{D}_{23k\ell}S_{23} + c^{D}_{33k\ell}S_{33}\right] - \frac{\partial x'_k}{\partial x_k}\frac{\partial x'_\ell}{\partial x_\ell}\left[h_{1k\ell}\delta_1 + h_{2k\ell}\delta_2 + h_{3k\ell}\delta_3\right] \qquad (140) \\ E'_m &= 4\pi \frac{\partial x'_m}{\partial x_m}\left[\beta^{S}_{m1}\delta_1 + \beta^{S}_{m2}\delta_2 + \beta^{S}_{m3}\delta_3\right] - \frac{\partial x'_m}{\partial x_m} \\ &\quad \cdot \left[h_{m11}S_{11} + 2h_{m12}S_{12} + 2h_{m13}S_{13} + h_{m22}S_{22} + 2h_{m23}S_{23} + h_{m33}S_{33}\right]. \end{aligned}$$

These equations express the new stresses and fields in terms of the old strains and displacements. To complete the transformation we need to express all quantities in terms of the new axes. For this purpose we employ the tensor equations

$$S_{ij} = \frac{\partial x_i}{\partial x'_i}\frac{\partial x_j}{\partial x'_j} S'_{ij} \, ; \qquad \delta_n = \frac{\partial x_n}{\partial x'_n}\delta'_n \qquad (141)$$

where $\frac{\partial x_i}{\partial x'_i}$ are the direction cosines between the old and new axes. It is obvious that $\frac{\partial x'_i}{\partial x_i} = \frac{\partial x_i}{\partial x'_i}$ and the relations can be written

$$
\begin{aligned}
\ell_1 &= \frac{\partial x_1'}{\partial x_1} = \frac{\partial x_1}{\partial x_1'}; & \ell_2 &= \frac{\partial x_1}{\partial x_2'}; & \ell_3 &= \frac{\partial x_1}{\partial x_3'} \\
m_1 &= \frac{\partial x_2}{\partial x_1'}; & m_2 &= \frac{\partial x_2}{\partial x_2'}; & m_3 &= \frac{\partial x_2}{\partial x_3'} \\
n_1 &= \frac{\partial x_3}{\partial x_1'}; & n_2 &= \frac{\partial x_3}{\partial x_2'}; & n_3 &= \frac{\partial x_3}{\partial x_3'}.
\end{aligned}
\tag{142}
$$

Hence substituting equations (141) in equations (140) the transformation equations between the new and old axes become

$$
\begin{aligned}
T_{k\ell}' &= c_{ijk\ell}^{D} \frac{\partial x_k'}{\partial x_k} \frac{\partial x_\ell'}{\partial x_\ell} \frac{\partial x_i}{\partial x_i'} \frac{\partial x_j}{\partial x_j'} S_{ij}' - h_{mk\ell} \frac{\partial x_k'}{\partial x_k} \frac{\partial x_\ell'}{\partial x_\ell} \frac{\partial x_n}{\partial x_n'} \delta_n' \\
E_m' &= 4\pi\beta_{mn}^{S} \frac{\partial x_m'}{\partial x_m} \frac{\partial x_n}{\partial x_n'} \delta_n' - h_{mij} \frac{\partial x_m'}{\partial x_m} \frac{\partial x_i}{\partial x_i'} \frac{\partial x_j}{\partial x_j'} S_{ij}'.
\end{aligned}
\tag{143}
$$

These equations then provide means for determining the transformation of constants from one set of axes to another.

As an example let us consider the case of an ADP crystal, vibrating longitudinally with its length along the x_1' axis, its width along the x_2' axis and its thickness along the x_3' axis, which is also the x_3 axis, and determine the elastic, piezoelectric and dielectric constants that apply for this cut when x_1' is $\Theta = 45°$ from x_1. Under these conditions

$$
\begin{aligned}
\ell_1 &= \frac{\partial x_1'}{\partial x_1} = \frac{\partial x_1}{\partial x_1'} = \cos\theta; & \ell_2 &= \frac{\partial x_2'}{\partial x_1} = \frac{\partial x_1}{\partial x_2'} = -\sin\theta; \\
& & \ell_3 &= \frac{\partial x_3'}{\partial x_1} = \frac{\partial x_1}{\partial x_3'} = 0 \\
m_1 &= \frac{\partial x_1'}{\partial x_2} = \frac{\partial x_2}{\partial x_1'} = \sin\theta; & m_2 &= \frac{\partial x_2'}{\partial x_2} = \frac{\partial x_2}{\partial x_2'} = \cos\theta; \\
& & m_3 &= \frac{\partial x_3'}{\partial x_2} = \frac{\partial x_2}{\partial x_3'} = 0 \\
n_1 &= \frac{\partial x_1'}{\partial x_3} = \frac{\partial x_3}{\partial x_1'} = 0; & n_2 &= \frac{\partial x_2'}{\partial x_3} = \frac{\partial x_3}{\partial x_2'} = 0; \\
& & n_3 &= \frac{\partial x_3'}{\partial x_3} = \frac{\partial x_3}{\partial x_3'} = 1.
\end{aligned}
\tag{144}
$$

Since ADP belongs to the orthorhombic bisphenoidal (Class 6), it will have the dielectric, piezoelectric and elastic tensors shown by equations (134), (135), (139). Applying equations (143) and (144) to these tensors it is readily shown that the stresses for $\Theta = 45°$ are given by the equations expressed in two index symbols

$$\begin{aligned}
T_1' &= \frac{(c_{11}^D + c_{12}^D + 2c_{66}^D)}{2} S_1' \\
&\qquad + \frac{(c_{11}^D + c_{12}^D - 2c_{66}^D)}{2} S_2' + c_{13}^D S_3' - h_{36}\delta_3' \\
T_2' &= \frac{(c_{11}^D + c_{12}^D - 2c_{66}^D)}{2} S_1' \\
&\qquad + \frac{(c_{11}^D + c_{12}^D + 2c_{66}^D)}{2} S_2' + c_{13}^D S_3' + h_{36}\delta_3' \qquad (145) \\
T_3' &= c_{13}^D S_1' + c_{13}^D S_2' + c_{33} S_3' \\
T_4' &= c_{44}^D S_4' + h_{14}\delta_2' ; \qquad E_1 = -h_{14} S_5' + 4\pi[\beta_{11}\delta_1'] \\
T_5' &= c_{44}^D S_5' - h_{14}\delta_1' ; \qquad E_2 = h_{14} S_1' + 4\pi[\beta_{11}\delta_2'] \\
T_6' &= \frac{(c_{11}^D - c_{12}^D)}{2} S_6' ; \qquad E_3 = -h_{36}[S_1' - S_2'] + 4\pi[\beta_{33}\delta_3'].
\end{aligned}$$

For a long thin longitudinally vibrating crystal all the stresses are zero except the stress T_1' along the length of the crystal. Hence it is more advantageous to use equations which express the strains in terms of the stresses since all the stresses can be set equal to zero except T_1'. All the strains are then dependent functions of the strain S_1' and this only has to be solved for. Furthermore, since plated crystals are usually used to determine the properties of crystals, and the field perpendicular to a plated surface is zero, the only field existing in a thin crystal will be E_3' if the thickness is taken along the x_3' or Z' axis. Hence the equations that express the strains in terms of the stresses and fields are more advantageous for calculating the properties of longitudinally vibrating crystals. By orienting such crystals with respect to the crystallographic axis, all of the elastic constants except the shear elastic constants can be determined. All of the piezoelectric and dielectric constants can be determined from measurements on oriented longitudinally vibrating crystals.

For such measurements it is necessary to determine the appropriate elastic, piezoelectric, and dielectric constants for a crystal oriented in any direction with respect to the crystallographic axes. We assume that the length lies along the x_1' axis, the width along the x_2' axis and the thickness along the x_3' axis. Starting with equations of the form

$$\begin{aligned}
S_{ij} &= s_{ijkl}^E T_{kl} + d_{ijm} E_m \\
\delta_n &= \frac{\epsilon_{mn}^T}{4\pi} E_m + d_{nkl} T_{kl}
\end{aligned} \qquad (146)$$

and transforming to a rotated system of axes whose direction cosines are given by (142), the resulting equation becomes

$$\begin{aligned} S'_{ij} &= s^{E}_{ijk\ell}\frac{\partial x'_i}{\partial x_i}\frac{\partial x'_j}{\partial x_j}\frac{\partial x_k}{\partial x'_k}\frac{\partial x_\ell}{\partial x'_\ell}T'_{k\ell} + d_{ijm}\frac{\partial x'_i}{\partial x_i}\frac{\partial x'_j}{\partial x_j}\frac{\partial x_m}{\partial x'_m}E'_m\,, \\ \delta'_n &= \frac{\epsilon^{T}_{mn}}{4\pi}\frac{\partial x'_n}{\partial x_n}\frac{\partial x_m}{\partial x'_m}E'_m + d_{nk\ell}\frac{\partial x'_n}{\partial x_n}\frac{\partial x_k}{\partial x'_k}\frac{\partial x_\ell}{\partial x'_\ell}T'_{k\ell}\,. \end{aligned} \tag{147}$$

All the stresses except T'_{11} can be set equal to zero and all the fields except E'_3 vanish. Furthermore, all the strains are dependently related to S'_{11}. Hence for a thin longitudinal crystal the equation of motion becomes

$$\begin{aligned} S'_{11} &= s^{E}_{ijk\ell}\frac{\partial x'_1}{\partial x_i}\frac{\partial x'_1}{\partial x_j}\frac{\partial x_k}{\partial x'_1}\frac{\partial x_\ell}{\partial x'_1}T'_{11} + d_{ijm}\frac{\partial x'_1}{\partial x_i}\frac{\partial x'_1}{\partial x_j}\frac{\partial x_m}{\partial x'_3}E'_m\,, \\ \delta'_3 &= \frac{\epsilon^{T}_{mn}}{4\pi}\frac{\partial x'_3}{\partial x_n}\frac{\partial x_m}{\partial x'_3}E'_3 + d_{nk\ell}\frac{\partial x'_3}{\partial x_n}\frac{\partial x_k}{\partial x'_1}\frac{\partial x_\ell}{\partial x'_1}T'_{11}\,. \end{aligned} \tag{148}$$

In terms of the two index symbols for the most general type of crystal, we have

$$\begin{aligned} s^{E'}_{1111} = s^{E'}_{11} &= s^{E}_{11}\ell_1^4 + (2s^{E}_{12} + s^{E}_{66})\ell_1^2m_1^2 + (2s^{E}_{13} + s^{E}_{55})\ell_1^2n_1^2 \\ &\quad + 2(s^{E}_{14} + s^{E}_{56})\ell_1^2m_1n_1 + 2s^{E}_{15}\ell_1^3n_1 + 2s^{E}_{16}\ell_1^3m_1 + s^{E}_{22}m_1^4 \\ &\quad + (2s^{E}_{23} + s^{E}_{44})m_1^2n_1^2 + 2s^{E}_{24}m_1^3n_1 + 2(s^{E}_{25} + s^{E}_{46})m_1^2\ell_1n_1 \\ &\quad + 2s^{E}_{26}m_1^3\ell_1 + s^{E}_{33}n_1^4 + 2s^{E}_{34}n_1^3m_1 + 2s^{E}_{35}n_1^3\ell_1 \\ &\quad + 2(s^{E}_{36} + s^{E}_{45})n_1^2\ell_1m_1 \\ d'_{111} = d'_{11} &= d_{11}\ell_3\ell_1^2 + d_{12}\ell_3m_1^2 + d_{13}\ell_3n_1^2 + d_{14}\ell_3m_1n_1 + d_{15}\ell_3\ell_1n_1 \\ &\quad + d_{16}\ell_3\ell_1m_1 + d_{21}m_3\ell_1^2 + d_{22}m_3m_1^2 + d_{23}m_3n_1^2 + d_{24}m_3m_1n_1 \\ &\quad + d_{25}n_3\ell_1n_1 + d_{26}m_3\ell_1m_1 + d_{31}n_3\ell_1^2 + d_{32}n_3m_1^2 + d_{33}n_3n_1^2 \\ &\quad + d_{34}n_3m_1n_1 + d_{35}n_3\ell_1n_1 + d_{36}n_3\ell_1m_1 \\ \epsilon^{T'}_{33} &= \epsilon^{T}_{11}\ell_3^2 + 2\epsilon^{T}_{12}\ell_3m_3 + 2\epsilon^{T}_{13}\ell_3n_3 + \epsilon^{T}_{22}m_3^2 + 2\epsilon^{T}_{23}m_3n_3 + \epsilon^{T}_{33}n_3^2 \end{aligned} \tag{149}$$

Hence by cutting 18 crystals with independent direction cosines 9 elastic constants and 6 relations between the remaining twelve constants can be determined. All of the piezoelectric constants and all of the dielectric constants can be determined from these measurements. These constants can be measured by measuring the resonant and antiresonant frequencies and the capacity at low frequencies. The resonant frequency f_R is determined by the formula

$$f_R = \frac{1}{2\ell}\sqrt{\frac{1}{\rho s^{E'}_{11}}} \tag{150}$$

for any long thin crystal vibrating longitudinally. Hence when the density is known, $s_{11}^{E'}$ can be calculated from the resonant frequency and the length of the crystal. Using the values of $s_{11}^{E'}$ obtained for 15 independent orientations enough data is available to solve for the constants of the first of equations (149). The capacities of the different crystal orientations measured at low frequencies determine the dielectric constant $\epsilon_{33}^{T'}$ and six orientations are sufficient to determine the six independent dielectric constants ϵ_{mn}^{T}. The separation between resonance and antiresonance $\Delta f = f_A - f_R$ determines the piezoelectric constant d'_{11} according to the formula

$$d'_{11} \doteq \frac{\pi}{2}\sqrt{\frac{\Delta f}{f_R}}\sqrt{\frac{\epsilon_{33}^{T'}}{4\pi}\, s_{11}^{E'}}\,. \tag{151}$$

The values of d'_{11} measured for 18 independent orientations are sufficient to determine the eighteen independent piezoelectric constants.

The remaining six elastic constants can be determined by measuring long thin crystals in a face shear mode of motion. Since this is a contour mode of motion, the equations are considerably more complicated than for a longitudinal mode and involve elastic constants that are not constant field or constant displacement constants. It can be shown[5] that the fundamental frequency of a crystal with its length along x_1, width (frequency determining direction) along x_2 and thickness (direction of applied field) along x_3, will be

$$f = \frac{1}{2\ell_w}\sqrt{\frac{c_{22}^{c,E} + c_{66}^{c,E} \pm \sqrt{(c_{22}^{c,E} - c_{66}^{c,E})^2 + 4c_{26}^{c,E^2}}}{2\rho}} \tag{152}$$

where the contour elastic constants are given in terms of the fundamental elastic constants by

$$c_{22}^{c,E} = \frac{s_{11}^{E} s_{66}^{E} - s_{16}^{E^2}}{\Delta}; \qquad c_{26}^{c,E} = \frac{s_{12}^{E} s_{16}^{E} - s_{11}^{E} s_{26}^{E}}{\Delta}; \qquad c_{66}^{c,E} = \frac{s_{11}^{E} s_{22}^{E} - s_{12}^{E^2}}{\Delta} \tag{153}$$

where Δ is the determinant

$$\Delta = \begin{vmatrix} s_{11}^{E}, & s_{12}^{E}, & s_{16}^{E} \\ s_{12}^{E}, & s_{22}^{E}, & s_{26}^{E} \\ s_{16}^{E}, & s_{26}^{E}, & s_{66}^{E} \end{vmatrix} \tag{154}$$

Since all of the constants except s_{12}^{E} and s_{66}^{E} can be determined by measurements on longitudinal crystals and the value of $(2s_{12}^{E} + s_{66}^{E})$ has been de-

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[5] This is proved in a recent paper "Properties of Dipotassium Tartrate (DKT) Crystals," *Phys. Rev., Nov., 1946.*

termined, the measurement of the lowest mode of the face shear crystal gives one more relation and hence the values of s_{12}^E and s_{66}^E can be uniquely determined.

Similar measurements with crystals cut normal to x_1 and width along x_3 and with crystals cut normal to x_2 and width along x_1 determine the constants s_{44}^E, s_{23}^E and s_{55}^E, s_{13}^E respectively. The equivalent constants are obtained by adding 1 to each subscript 1, 2, 3 or 4, 5, 6 for the first crystal with the understanding that $3 + 1 = 1$ and $6 + 1 = 4$. For the second crystal 2 is added to each subscript.

Finally the remaining three constants can be determined by measuring the face shear mode of three crystals that have their lengths along one of the crystallographic axes and their width (frequency determining axis) 45° from the other two axes.

Any symmetry existing in the crystal will cut down on the number of constants and hence on the number of orientations to determine the fundamental constants.

6. TEMPERATURE EFFECTS IN CRYSTALS

In section 2 a general expression was developed for the effects of temperature and entropy on the constants of a crystal. Two methods were given, one which considers the stresses, field, and temperature differentials as the independent variables, and the second which considers the strains, displacements and entropy as the independent variables. In tensor form the 10 equations for the first method take the form

$$\begin{aligned} T_{k\ell} &= c_{ijk\ell}^{D,\sigma} S_{ij} - h_{nk\ell}^{\sigma} \delta_n - \lambda_{k\ell}^{S,D}\, dQ \\ E_m &= -h_{mij}^{\sigma} S_{ij} + 4\pi\beta_{mn}^{S,\sigma} \delta_n - q_m^{S,D}\, dQ \\ d\Theta &= -\Theta\lambda_{ij}^{S,D} S_{ij} - \Theta q_n^{S,D} \delta_n + \frac{dQ}{\rho C_v^D} \end{aligned} \tag{155}$$

The piezoelectric relations have already been discussed for adiabatic conditions assuming that no increments of heat dQ have been added to the crystal.

If now an increment of heat dQ is suddenly added to any element of the crystal, the first equation shows that a sudden expansive stress is generated proportional to the constant $\lambda_{k\ell}^{S,D}$ which has to be balanced by a negative stress (a compression) in order that no strain or electric displacement shall be generated. This effect can be called the stress caloric effect. The second equation of (155) shows that if an increment of heat dQ is added to the crystal an inverse field E_m has to be added if the strain and surface charge are to remain unchanged. This effect may be called the field caloric effect. Finally the third equation of (155) shows that there is a reciprocal effect in which a stress or a displacement generates a change in temperature even in the absence of added heat dQ. These effects can be called the strain temperature and charge temperature effects.

The second form of the piezoelectric equations given by (58) are more familiar. In tensor form these can be written

$$\begin{aligned} S_{ij} &= s^{E,\Theta}_{ijk\ell} T_{k\ell} + d^{\Theta}_{mij} E_m + \alpha^{E}_{ij}\, d\Theta \\ \delta_n &= d^{\Theta}_{nk\ell} T_{k\ell} + \frac{\epsilon^{T,\Theta}_{mn}}{4\pi} E_m + p^{T}_{n}\, d\Theta \\ dQ = \Theta\, d\sigma &= \Theta \alpha^{E}_{k\ell} T_{k\ell} + \Theta p^{T}_{m} E_m + \rho C^{E}_{p}\, d\Theta \end{aligned} \tag{156}$$

The α^E_{ij} are the temperature expansion coefficients measured at constant field. In general these are a tensor of the second rank having six components. The constants p^T_n are the pyroelectric constants measured at displacements which relate the increase in polarization or surface charge due to an increase in temperature. They are equal to the so-called "true" pyroelectric constants which are the polarizations at constant volume caused by an increase in temperature plus the "false" pyroelectric effect of the first kind which represents the polarization caused by a uniform temperature expansion of the crystal as its temperature increases by $d\Theta$. As mentioned previously it is more logical to call the two effects the pyroelectric effects at constant stress and constant strain. By eliminating the stresses from the first of equations (156) and substituting in the second equation it is readily shown that

$$p^{S}_{n} = p^{T}_{n} - \alpha^{E}_{ij} e^{\Theta}_{nij} \tag{157}$$

Hence the difference between the pyroelectric effect at constant stress and the pyroelectric effect at constant strain is the so-called "false" pyroelectric effect of the first kind $\alpha^E_{ij} e^{\Theta}_{nij}$.

The first term on the right side of the last equation is called the heat of deformation, for it represents the heat generated by the application of the stresses $T_{k\ell}$. The second term is called the electrocaloric effect and it represents the heat generated by the application of a field. The last term is p times the specific heat at constant pressure and constant field.

The temperature expansion coefficients α^E_{ij} form a tensor of the second rank and hence have the same components for the various crystal classes as do the dielectric constants shown by equation (134).

The pyroelectric tensor p^T_n and p^S_n are tensors of the first rank and in general will have three components p_1, p_2, and p_3. In a similar manner to that used for second, third and fourth rank tensors it can be shown that the various crystal classes have the following components for the first rank tensor p_n.

Class 1: components p_1, p_2, p_3.
Class 3: Y axis of binary symmetry, components 0, p_2, 0 (158)
Class 4: components p_1, 0, p_3.

Classes 7, 10, 14, 16, 20, 23, and 26: components 0, 0, p_3; and Classes 2, 5, 6, 8, 9, 11, 12, 13, 15, 17, 18, 19, 21, 22, 24, 25, 27, 28, 29, 30, 31, and 32: components 0, 0, 0, i.e., $p = 0$.

For a hydrostatic pressure, the stress tensor has the components

$$T_{11} = T_{22} = T_{33} = -p = \text{pressure}; \qquad T_{12} = T_{13} = T_{23} = 0 \quad (159)$$

Hence the displacement equations of (156) can be written in the form

$$\delta_n = \frac{\epsilon_{mn}^{T,\Theta}}{4\pi} E_m - d_n^{\Theta} p + p_n^{T}\, d\Theta \qquad (160)$$

where

$$d_n^{\Theta} p = d_{n11}^{\Theta} T_{11} + d_{n22}^{\Theta} T_{22} + d_{n33}^{\Theta} T_{33}$$

that is the contracted tensor $d_{nkk} T_{kk}$. This is a tensor of the first rank which has the same components as the pyroelectric tensor p_n for the various crystal classes.

7. SECOND ORDER EFFECTS IN PIEZOELECTRIC CRYSTALS

We have so far considered only the conditions for which the stresses and fields are linear functions of the strains and electric displacements. A number of second order effects exist when we consider that the relations are not linear. Such relations are of some interest in ferroelectric crystals such as Rochelle salt. A ferroelectric crystal is one in which a spontaneous polarization exists over certain temperature ranges due to a cooperative effect in the crystal which lines up all of the elementary dipoles in a given "domain" all in one direction. Since a spontaneous polarization occurs in such crystals it is more advantageous to develop the equations in terms of the electric displacement rather than the external field. Also heat effects are not prominent in second order effects so that we develop the strains and potentials in terms of the stresses and electric displacements D. By means of McLaurin's theorem the first and second order terms are in tensor form

$$\begin{aligned} S_{ij} &= \frac{\partial S_{ij}}{\partial T_{kl}} T_{kl} + \frac{\partial S_{ij}}{\partial \delta_n} \delta_n + \frac{1}{2!}\left[\frac{\partial^2 S_{ij}}{\partial T_{kl} \partial T_{qr}} T_{kl} T_{qr} \right. \\ &\qquad \left. + 2 \frac{\partial^2 S_{ij}}{\partial T_{kl} \partial \delta_n} T_{kl} \delta_n + \frac{\partial^2 S_{ij}}{\partial \delta_n \partial \delta_0} \delta_n \delta_0 \right] + \cdots \text{higher terms} \\ E_m &= \frac{\partial E_m}{\partial T_{kl}} T_{kl} + \frac{\partial E_m}{\partial \delta_n} \delta_n + \frac{1}{2!}\left[\frac{\partial^2 E_m}{\partial T_{kl} \partial T_{qr}} T_{kl} T_{qr} \right. \\ &\qquad \left. + 2 \frac{\partial^2 E_m}{\partial T_{kl} \partial \delta_n} T_{kl} \delta_n + \frac{\partial^2 E_m}{\partial \delta_n \partial \delta_0} \delta_n \delta_0 \right] + \cdots \text{higher terms} \end{aligned} \qquad (161)$$

whereas before $\delta = D/4\pi$.

In this equation the linear partial differentials have already been discussed and are given by the equations

$$\frac{\partial S_{ij}}{\partial T_{k\ell}} = s^D_{ijk\ell}\,; \quad \frac{\partial S_{ij}}{\partial \delta_n} = \frac{\partial E_n}{\partial T_{ij}} = g_{ijn}\,; \quad \frac{\partial E_m}{\partial \delta_n} = 4\pi\beta^T_{mn} \tag{162}$$

where $s^D_{ijk\ell}$ are the elastic compliances of the crystal at constant displacement, g_{ijn} the piezoelectric constants relating strain to electric displacement $/4\pi$, and β^T_{mn} the dielectric "impermeability" tensor measured at constant stress. We designate the partial derivatives

$$\begin{aligned} &\frac{\partial S_{ij}}{\partial T_{k\ell}\partial T_{qr}} = N^D_{ijk\ell qr}\,; \quad \frac{\partial^2 S_{ij}}{\partial T_{k\ell}\partial \delta_m} = \frac{\partial^2 E_m}{\partial T_{k\ell}\partial T_{qr}} = M^D_{ijk\ell n} \\ &\frac{\partial^2 S_{ij}}{\partial \delta_n \partial \delta_0} = \frac{\partial^2 E_n}{\partial T_{ij}\partial \delta_0} = Q^D_{ijno}\,; \quad \frac{\partial^2 E_m}{\partial \delta_n \partial \delta_0} = O^D_{mno} \end{aligned} \tag{163}$$

The tensors N, M, Q, and O are respectively tensors of rank 6, 5, 4 and 3 whose interpretation is discussed below. Introducing these definitions equations (161) can be written in the form

$$\begin{aligned} S_{ij} &= T_{k\ell}[s^D_{ijk\ell} + \tfrac{1}{2}N^D_{ijk\ell qr}T_{qr} + M^D_{ijk\ell n}\delta_n] + \delta_n[g_{ijn} + \tfrac{1}{2}Q^D_{ijno}\delta_0] \\ E_m &= T_{k\ell}[g_{mk\ell} + \tfrac{1}{2}M^D_{ijk\ell n}T_{qr} + Q^D_{k\ell mn}\delta_n] + \delta_n[4\pi\beta^T_{mn} + \tfrac{1}{2}O^D_{mno}\delta_0] \end{aligned} \tag{164}$$

Written in this form the interpretation of the second order terms is obvious. $N^D_{ijk\ell qr}$ represents the nonlinear changes in the elastic compliances $s^D_{ijk}{}^\ell$ caused by the application of stress T_{qr}. Since the product of $N_{ijk\ell qr}T_{qr}$ represents a contracted fourth rank tensor, there is a correction term for each elastic compliance. The tensor $M^D_{ijk\ell n}$ can represent either the nonlinear correction to the elastic compliances due to an applied electric displacement D_n or it can represent the correction to the piezoelectric constant g_{ijn} due to the stresses $T_{k\ell}$. By virtue of the second equation of (162), the second equivalence of (163) results. The fourth rank tensor $\frac{1}{2}Q^D_{ijno}$ represents the electrostrictive effect in a crystal for it determines the strains existing in a crystal which are proportional to the square of the electric displacement. Twice the value of the electrostrictive tensor $\frac{1}{2}Q^D_{ijno}$, which appears in the second equation of (164) can be interpreted as the change in the inverse dielectric constant or "impermeability" constant. Since a change in dielectric constant with applied stress causes a double refraction of light through the crystal, this term is the source of the piezo-optical effect in crystals. The third rank tensor O^D_{mno} represents the change in the "impermeability" constant due to an electric field and hence is the source of the electro-optical effect in crystals.

These equations can also be used to discuss the changes that occur in ferroelectric type crystals such as Rochelle Salt when a spontaneous polarization occurs in the crystal. When spontaneous polarization occurs, the dipoles of the crystal are lined up in one direction in a given domain. For Rochelle salt this direction is the $\pm X$ axis of the crystal. Now the electric displacement D_x is equal to

$$\delta_x = \frac{D_x}{4\pi} = \frac{E_x}{4\pi} + P_{x_0} + P_{x_D} = \frac{E_x \epsilon_0}{4\pi} P_{x_D} \tag{165}$$

where P_{x_0} is the electronic and atomic polarization, and P_{x_D} the dipole polarization The electronic and atomic polarization is determined by the field and hence can be combined with the field through the dielectric constant ϵ_0, which is the temperature independent part of the dielectric constant. When the crystal becomes spontaneously polarized, a field E_x will result, but this soon is neutralized by the flow of electrons through the surface and volume conductance of the crystal and in a short time $E_x = 0$. Hence for any permanent changes occurring in the crystal we can set

$$\delta_x = \frac{D_x}{4\pi} = P_{x_D} = \text{dipole polarization} \tag{166}$$

which we will write hereafter as P_1.

In the absence of external stresses the direct effects of spontaneous polarization are a spontaneous set of strains introduced by the product of the spontaneous polarization by the piezoelectric constant, and another set produced by the square of the polarization times the appropriate electrostrictive components. For example, Rochelle salt has a spontaneous polarization P_1 along the X_1 axis between the temperatures $-18°$C to $+24°$C. The curve for the spontaneous polarization as a function of temperature is shown by Fig. 6.[6] The only piezoelectric constant causing a spontaneous strain will be $g_{14/2} = g_{123}$. Hence the spontaneous polarization causes a spontaneous shearing strain

$$S_4 = g_{14} P_x = 120 \times 10^{-8} \times 760 = 9.1 \times 10^{-4} \tag{167}$$

if we introduce the experimentally determined values. Since S_4 is the cosine of 90° plus the angle of distortion, this would indicate that the right angled axes of a rhombic system would be distorted 3.1 minutes of arc. This is the value that should hold for any domain. For a crystal with several domains, the resulting distortion will be partly annulled by the different signs of the polarization and should be smaller. Mueller[7] measured an angle of 3′45″ at 0°C for one crystal. This question has also been

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[6] This has been measured by measuring the remanent polarization, when all the domains are lined up. See "The Dielectric Anomalies of Rochelle Salt," H. Mueller, *Annals of the N. Y. Acad. Science,* Vol. XL, Art. 5, page 338, Dec. 31, 1940.

[7] "Properties of Rochelle Salt," H. Mueller, *Phys. Rev.*, Vol. 57, No. 9, May 1, 1940.

investigated by the writer and Miss E. J. Armstrong by measuring the temperature expansion coefficients of the Y and Z axes and comparing their average with the expansion coefficient at 45° from these two axes. The difference between these two expansion coefficients measures the change in angle between the Y and Z axes caused by the spontaneous shearing strains. The results are shown by Fig. 7. Above and below the ferroelectric region, the expansion of the 45° crystal coincides with the average expansion of the Y and Z axes measured from 25°C as a reference temperature. Between the Curie temperatures a difference occurs indicating that the Y and Z crystallographic axes are no longer at right angles. The difference in expansion per unit length at 0°C (the maximum point) corresponds to 1.6×10^{-4} cm per cm. This represents an axis distortion of 1.1 minutes of arc. Correspondingly smaller values are found at other temperatures in agreement with the smaller spontaneous polarization at other temperatures. It was also found that practically the same curve resulted for either 45° axis, indicating that the mechanical bias put on by the optometer used for measuring expansions introduced a bias determining the direction of the largest number of domains.

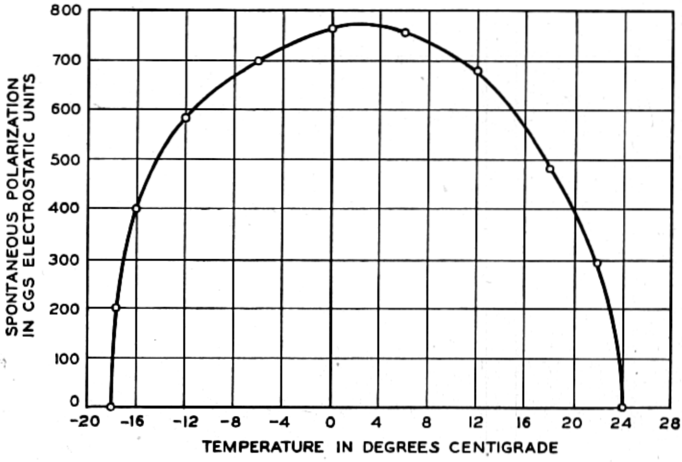

Fig. 6.—Spontaneous polarization in Rochelle Salt along the X axis.

The second order terms caused by the square of the spontaneous polarization is given by the expression

$$S_{ij} = Q^D_{ij11} P_1^2 \tag{168}$$

Since Q is a fourth rank tensor the possible terms for an orthorhombic bisphenoidal crystal (the class for Rochelle salt) are

$$S_{11} = Q^D_{1111} P_1^2 ; \quad S_{22} = Q^D_{2211} P_1^2 ; \quad S_{33} = Q^D_{3311} P_1^2 \tag{169}$$

In an effort to measure these effects, careful measurements have been made of the temperature expansions of the three axes *X*, *Y* and *Z*. The results are shown by Table II. On account of the small change in dimension from the standard curve it is difficult to pick out the spontaneous components by plotting a curve. By expressing the expansion in the form of the equation

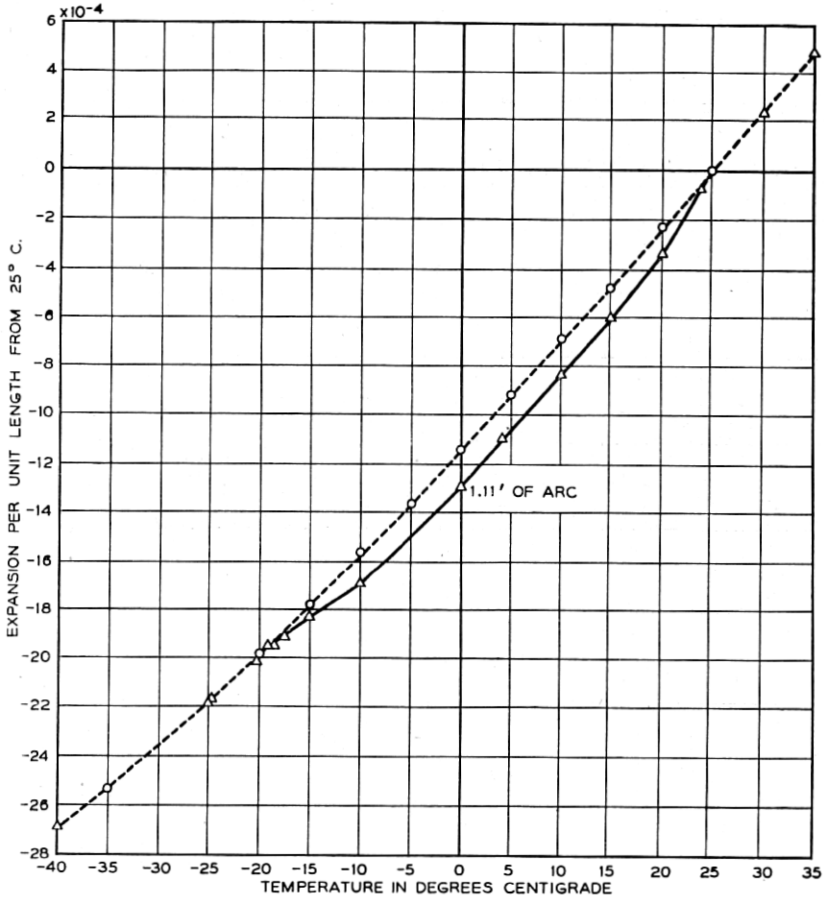

Fig. 7.—Temperature expansion curve along an axis 45° between Y and Z as a function of temperature.

$$\frac{\Delta L}{L} = a_1(T\text{-}25) + a_2(T\text{-}25)^2 + a_3(T\text{-}25)^3 \qquad (170)$$

TABLE II

MEASURED TEMPERATURE EXPANSIONS FOR THE THREE CRYSTALOGRAPHIC AXES

Temperature Expansion			Expansion		Expansion
in °C.	× 10⁻⁴ X Axis	Temperature in °C.	× 10⁻⁴ Y Axis	Temperature in °C.	× 10⁻⁴ Z Axis
39.6	10.2	+35.0	4.45	+34.9	+4.9
38.7	9.46	30.3	2.5	29.9	2.5
35.2	6.96	25.25	0.2	25.05	+.05
30.2	3.63	23.9	−0.42	24.0	−.5
27.2	1.41	22.9	−0.88	19.95	−2.62
26.2	0.71	19.35	−2.4	14.95	−5.11
25.15	0.06	14.9	−4.25	+9.75	−7.55
24.0	−0.71	10.0	−6.25	+4.9	−9.9
23.0	−1.39	5.4	−8.18	0	−12.31
21.8	−2.37	+0.3	−10.15	−6.35	−15.3
16.0	−6.5	−9.7	−13.98	−10.5	−17.29
15.2	−7.05	−16.3	−16.41	−15.0	−19.42
4.9	−14.12	−20.85	−17.94	−18.0	−20.86
+0.3	−17.28	−25.1	−19.22	−23.2	−23.08
−4.7	−20.3	−30.3	−20.8	−25.1	−23.96
−10.7	−24.0	−35.0	−22.23	−31.1	−26.59
−15.3	−26.6	−39.7	−23.54	−35.0	−28.28
−20.7	−30.2	−53.2	−27.60	−40.0	−30.4
−25.7	−32.7				
−30.1	−35.2				
−34.7	−37.85				
−40.7	−41.25				
−45.0	−44.0				
−50.5	−47.0				

and evaluating the constants by employing temperatures outside of the ferroelectric range, a normal curve was established. For the X, Y, and Z axes these relations are

$$\frac{\Delta L}{L} = 69.6 \times 10^{-6}(T\text{-}25) + 7.4 \times 10^{-8}(\mathrm{T}\text{-}25)^2 - 3.13 \times 10^{-10}(\mathrm{T}\text{-}25)^3 \qquad (X \text{ direction})$$

$$\frac{\Delta L}{L} = 43.7 \times 10^{-6}(\mathrm{T}\text{-}25) + 8.16 \times 10^{-8}(\mathrm{T}\text{-}25)^2 - 3.60 \times 10^{-10}(\mathrm{T}\text{-}25)^3 \qquad (Y \text{ direction}) \tag{171}$$

$$\frac{\Delta L}{L} = 49.4 \times 10^{-6}(T\text{-}25) + 1.555 \times 10^{-8}(T\text{-}25)^2 - 2.34 \times 10^{-10}(T\text{-}25)^3 \qquad (Z \text{ direction})$$

The difference between the normal curves and the measured values in the Curie region is shown plotted by the points of Fig. 8. The solid and dashed curves represent curves proportional to the square of the spontaneous polarization and with multiplying constants adjusted to give the best fits for the measured points. These give values of Q^D_{1111}, Q^D_{2211}, Q^D_{3311} equal to

$$Q^D_{1111} = -86.5 \times 10^{-12}; \qquad Q^D_{2211} = +17.3 \times 10^{-12}; \qquad Q^D_{3311} = -24.2 \times 10^{-12} \quad (172) \tag{172}$$

Another effect noted for Rochelle salt is that some of the elastic constants suddenly change by small amounts at the Curie temperatures. This is a consequence of the tensor $M^D_{ijk\ell n}$, for if a spontaneous polarization P occurs, a sudden change occurs in some of the elastic constants as can be seen from the first of equations (164). The second equation of (164) shows that this same tensor causes a nonlinear response in the piezoelectric constant. Since a change in the elastic constant is much more easily determined than a nonlinear change in the piezoelectric constant, the first effect is the only one definitely determined experimentally. Since all three crystallographic axes are binary axes in Rochelle salt, it is easily shown that the only terms that can exist for a fifth rank tensor are terms of the types

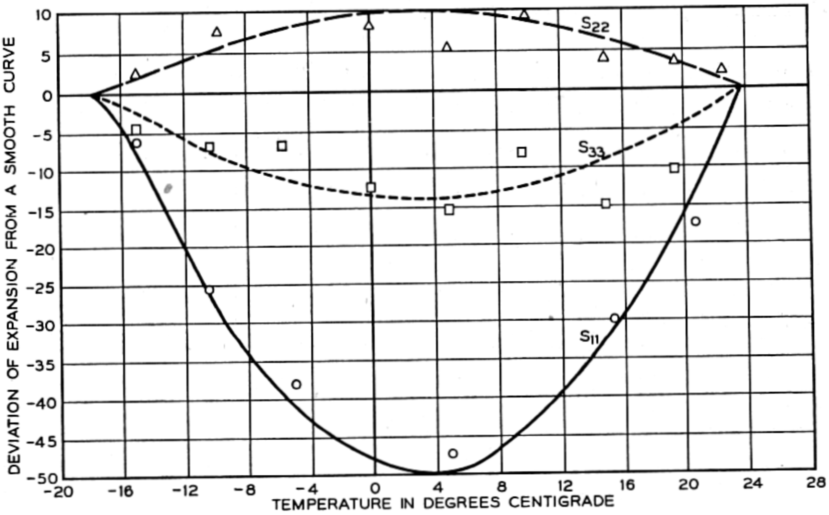

Fig. 8.—Spontaneous electrostrictive strain in Rochelle Salt along the three crystallographic axes.

$$M^D_{11123}\ ; \quad M^D_{12223}\ ; \quad M^D_{12333} \tag{173}$$

with permutations and combinations of the indices. Hence when a spontaneous polarization P_1 occurs, the elastic constants become

$$s^D_{ijk\ell} - M^D_{ijk\ell 1}P_1 \tag{174}$$

Comparing these with the relation of (90) we see that the spontaneous polarization has added the elastic constants

$$
\begin{aligned}
s_{14}^{D} &= \frac{(M_{11231}^{D} + M_{11321}^{D} + M_{23111}^{D} + M_{32111}^{D})P_1}{2} \\
s_{24}^{D} &= \frac{(M_{22231}^{D} + M_{22321}^{D} + M_{23221}^{D} + M_{32221}^{D})P_1}{2} \\
s_{34}^{D} &= \frac{(M_{23331}^{D} + M_{32331}^{D} + M_{33321}^{D} + M_{33231}^{D})P_1}{2} \\
s_{56}^{D} &= \frac{\begin{array}{l}(M_{12151}^{D} + M_{13211}^{D} + M_{31121}^{D} + M_{31211}^{D} \\ \qquad + M_{12131}^{D} + M_{12311}^{D} + M_{21131}^{D} + M_{21311}^{D})P_1\end{array}}{2}
\end{aligned}
\tag{175}
$$

between the two Curie points. Hence while the spontaneous polarization P_1 exists, the resulting elastic constants are

$$
\begin{vmatrix}
s_{11}, & s_{12}, & s_{13}, & s_{14}, & 0, & 0 \\
s_{12}, & s_{22}, & s_{23}, & s_{24}, & 0, & 0 \\
s_{13}, & s_{23}, & s_{33}, & s_{34}, & 0, & 0 \\
s_{14}, & s_{24}, & s_{34}, & s_{44}, & 0, & 0 \\
0, & 0, & 0, & 0, & s_{55}, & s_{56} \\
0, & 0, & 0, & 0, & s_{56}, & s_{66}
\end{vmatrix}
\tag{176}
$$

Comparing this to equation (139) which shows the possible elastic constants for the various crystal classes, we see that between the two Curie points, the crystal is equivalent to a monoclinic sphenoidal crystal (Class 3) with the X axis the binary axis. Outside the Curie region the crystal becomes orthorhombic bisphenoidal. This interpretation agrees with the temperature expansion curves of Fig. 7.

The sudden appearance of the polarization P_1 will affect the frequency of a 45° X-cut crystal, for with a crystal cut normal to the X axis and with the length of the crystal at an angle Θ with the Y axis, the value of the elastic compliance s_{22}' along the length is

$$
\begin{aligned}
s_{22}^{D\prime} = s_{22}^{D} \cos^4 \Theta + 2s_{24}^{D} \cos^3 \Theta \sin \Theta + (2s_{23}^{D} + s_{44}^{D}) \sin^2 \Theta \cos^2 \Theta \\
+ 2s_{34}^{D} \sin^3 \Theta \cos \Theta + s_{33}^{D} \sin^4 \Theta
\end{aligned}
\tag{177}
$$

Hence for a crystal with its length 45° between the Y and Z axes, elastic compliance becomes

$$
s_{22}^{\prime D} = \frac{s_{22}^{D} + 2(s_{24}^{D} + s_{23}^{D} + s_{34}^{D}) + s_{44}^{D} + s_{33}^{D}}{4} \tag{178}
$$

For a 45° X-cut crystal we would expect a sudden change in the value of s'^{D}_{22} as the crystal becomes spontaneously polarized between the two Curie points due to the addition of the s^{D}_{24} and s^{D}_{34} elastic compliances. Such a change has been observed for Rochelle salt[8] as shown by Fig. 9 which shows the frequency constant of a nonplated crystal for which the elastic compliances s^{D}_{ij} should hold.

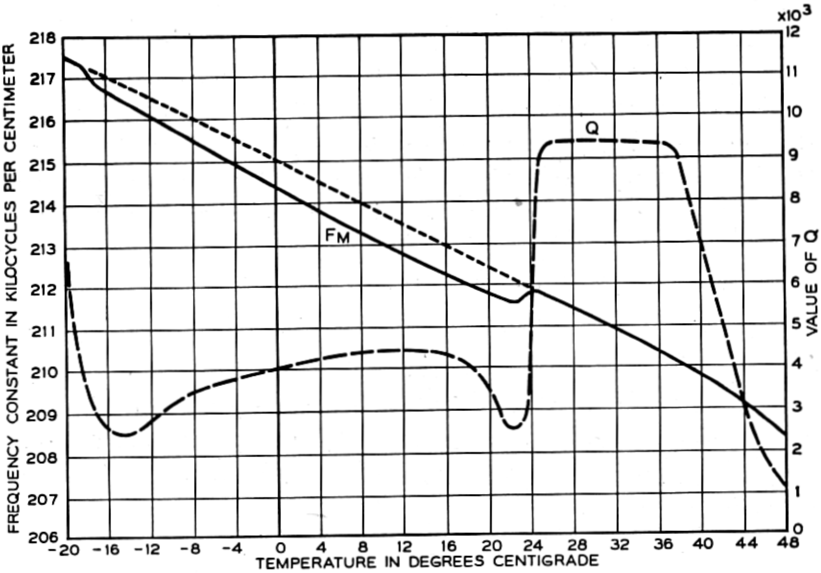

Fig. 9.—Frequency constant and Q of an unplated 45°X cut Rochelle Salt crystal plotted as a function of temperature.

Hence the sudden change in the elastic constant is a result of the two second order terms $s^{D}_{24} + s^{D}_{34}$, which are caused by the spontaneous polarization. The value of the sum of these two terms at the mean temperature of the Curie range, 3°C is

$$s^{D}_{24} + s^{D}_{34} = 4.1 \times 10^{-14}\ \mathrm{cm}^2/\mathrm{dyne} \tag{179}$$

Crystals cut normal to the Y and Z axes should not show a spontaneous change in their frequency characteristic since the spontaneous terms s_{14}, s_{24}, s_{34} and s_{56} do not affect the value of Young's modulii in planes normal to Y and Z. Experiments on a 45° Y-cut Rochelle salt crystal do not show a spontaneous change in frequency at the Curie temperature, although there is a large change in the temperature coefficient of the elastic compliance between the two Curie points. This is the result of third order term and is

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[8] "The Location of Hysteresis Phenomena in Rochelle Salt Crystals," W. P. Mason, *Phys. Rev.*, Vol. 50, p. 744–750, October 15, 1940.

not considered here. The spontaneous s_{56} constant affects the shear constant s'_{66} for crystals rotated about the X axis and could be detected experimentally. No experimental values have been obtained.

The effects of spontaneous polarization in the second equation of (164) are of two sorts. For an unplated crystal, a spontaneous voltage is generated on the surface, which, however, quickly leaks off due to the surface and volume leakage of the crystal. The other effects are that the spontaneous polarization introduces new piezoelectric constants through the tensor $Q^D_{k\ell mn}$, changes the dielectric constants through the tensor O^D_{mno} and introduces a stress effect on the piezoelectric constants through the tensor $M^D_{k\ell mqr}$. Since piezoelectric constants are not as accurately measured as elastic constants, the first effect has not been observed. The additional piezoelectric constants introduced by the tensor $Q^D_{k\ell mn}$ are shown by equation (180)

$$\begin{matrix} g_{11} & g_{12} & g_{13} & g_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & g_{25} & g_{26} \\ 0 & 0 & 0 & 0 & g_{35} & g_{36} \end{matrix} \qquad (180)$$

Since the only constants for the Rochelle salt class, the orthorhombic bisphenoidal, are g_{14}, g_{25}, g_{36}, this shows that between the two Curie points the crystal becomes monoclinic sphenoidal, with the X axis being the binary axis. The added constants are, however, so small that the accuracy of measurement is not sufficient to evaluate them. From the expansion measurements of equation (172) and the spontaneous polarization values, three of them should have maximum values of

$$g_{11} = -6.6 \times 10^{-8}; \qquad g_{12} = +1.3 \times 10^{-8}; \qquad g_{13} = -1.8 \times 10^{-8} \qquad (181)$$

These amount to only 6 per cent of the constant g_{14}, and hence they are not easily evaluated from piezoelectric measurements.

The effect of the tensor O^D_{mno} is to introduce a spontaneous dielectric constant ϵ_{23} between the Curie temperatures so that the dielectric tensor becomes

$$\begin{matrix} \epsilon_{11}, & 0, & 0 \\ 0, & \epsilon_{22}, & \epsilon_{23} \\ 0, & \epsilon_{23}, & \epsilon_{33} \end{matrix} \qquad (182)$$

As discussed at length by Mueller[9] this introduces a spontaneous birefringence for light passing through the crystal along the X, Y and Z axes which adds to the birefringence already present.

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[9] "Properties of Rochelle Salt I and IV," *Phys. Rev.* 47, 175 (1935); 58, 805 November 1, 1940.