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**History** – Piezoelectricity, as distinct from contact and frictional electricity, was discovered at the Sorbonne in 1580 by Pierre and Jacques Curie. Pierre, who 18 years later collaborated with his wife in the discovery of radium, was 21 years old, Jacques 24, when the brothers first demonstrated the piezoelectric effect. In her biography of Pierre, Marie Curie pointed out that the youthful discovery was not an accident but the product of extensive theoretical and experimental study of the symmetry of crystalline matter. Crystallographic and mathematical relations governing piezoelectricity were developed in the few years following the discovery. Crystals studied in this early period included quartz, tourmaline and Rochelle salt (sodium potassium tartrate), which were to become technically important 50 years later. Piezoelectric quartz crystals found some use in electrostatic measurements in connection with studies of radioactivity by Pierre and Marie Curie. The first step toward an engineering application was taken about 1916 in France by Paul Langevin, who constructed an underwater ultrasonic source consisting of a piezoelectric quartz element sandwiched between steel plates; this device was to serve for submarine detection. While piezoelectricity did not become practical for this purpose until many years later, experimentation started during World War I led Walter G. Cady of Wesleyan University (Middletown, Conn.) to recognize the reaction of the mechanical resonance of a vibrating crystal on its electric behaviour, and hence to the invention of frequency control by quartz crystals. Crystal frequency control soon became essential for the growing broadcasting and radio communication industry. During World War II the United States alone used about 50,000,000 quartz crystal elements. The closely related use of piezoelectric crystals in wave filters for multi-channel telephony was largely developed in the Bell Telephone laboratories beginning about 1925. Yet another result of the search for ultrasonic generation in 1917-18 was the observation of the exceptionally high dielectric constant and dielectric hysteresis in Rochelle salt. This behaviour was soon recognized to be a dielectric analogue to ferromagnetism. Since Rochelle salt is known in Europe as Seignette salt, after its discoverer P. Seignette, the phenomenon was termed Seignette electricity by Russian researchers, who led in its study in the early 1930s. After 1945, however, the term ferroelectricity was generally accepted. The ferroelectricity of Rochelle salt is the cause of its very high piezoelectric effect, which led to

a wide use in microphones and phonograph pickups. The growth of these applications came about largely through the efforts of the Brush Development company in Cleveland, O., beginning in 1930. Extensive studies were undertaken in the early 1940s to find water soluble crystals which would approach Rochelle salt in piezo electric effect without its dielectric anomalies and limiting temperature range. These efforts were partly successful, as indicated by the introduction of ammonium dihydrogen phosphate, primarily for sonar applications. Major progress came, however, from an unexpected direction. About 1940, a dielectric constant in excess of 1,000 was found in a refractory material, barium titanate ( $\text{BaTiO}_3$ ). The ferroelectric nature of this compound was recognized by Arthur von Hippel and co-workers at Massachusetts Institute of Technology. Soon afterward it was discovered that treatment in a strong piezoelectric field can permanently reverse the direction of polarity in the crystallites of a ceramic, polycrystalline barium titanate body, and thereby render it strongly piezoelectric. This discovery opened the way for the development of piezoelectric elements comparable with Rochelle salt in sensitivity and with quartz in chemical stability. Ceramic preparation methods made possible shapes and sizes which were unattainable with single crystals. Barium titanate is ferroelectric and piezoelectric only below  $120^\circ\text{C}$ . This limitation was overcome in the 1950s by the discovery of piezoelectric effects in ceramic lead metaniobate,  $\text{PbNb}_2\text{O}_6$ , and lead titanate zirconate,  $\text{Pb}(\text{Ti,Zr})\text{O}_3$ , which are usable at least to  $250^\circ\text{C}$ . By the late 1950s barium titanate and the newer ceramics were dominant in the electroacoustic field in the United States, and novel applications as electric circuit elements were indicated. For frequency control and highly selective electric wave filters, quartz crystals remained unchallenged; dependence on high-quality natural quartz crystals, a near-monopoly of Brazil, however, was alleviated by the development of an industrial process for growing quartz crystals, and crystals of this type became commercially available in 1958.

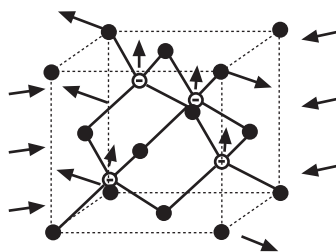
## **THEORETICAL CONSIDERATIONS**

### **Crystallographic and Molecular Considerations**

**Symmetry and Piezoelectric Effect** – Solid matter consists of electrically charged particles disposed in space, the positive and negative charges being in exact balance in an electrically uncharged body. The development of electric surface charges by mechanical deformation is therefore not unexpected. Considerations of symmetry, however, severely limit the conditions under which such charges can appear. The state of mechanical stress or resulting geometric deformation (strain) at any point in a solid is described by a tensor, which does not distinguish between opposite directions, whereas electric polarization and electric

field are described by vectors which specify the sense of direction. If a mechanical stress is to produce an electric polarization, a directional quality must therefore be inherent in the body. Conversely, in an isotropic material (i.e., a body without inherent directional quality) mechanical stress or strain caused by an electric field must be equal for opposite directions of the field; this implies a quadratic dependence on the field. This quadratic effect, known as electrostriction, is substantial only in materials of very high dielectric constant, notably ferroelectric materials. A necessary condition for the occurrence of the piezoelectric effect, including the converse linear dependence of stress or strain on electric field, is the absence of a centre of symmetry. Twenty-one of the 32 crystal symmetry classes (see CRYSTALLOGRAPHY) lack this symmetry element, and crystals in all but one of these classes can exhibit piezoelectricity. A qualitative test for presence of piezoelectricity is therefore useful in crystal structure determination. Piezoelectricity has been observed by qualitative tests in about 1,000 crystal species, while more or less complete quantitative data have been taken on about 100 crystals. Sulfates, phosphates, tartrates and various sugars and their derivatives contribute heavily to the latter number. The combination of symmetry planes and axes that is characteristic of any crystal class determines which components of stress and of electric polarization may be linked by piezoelectricity. It must be emphasized, however, that crystallographic symmetry merely states what effects are forbidden; the magnitude of the allowed effects is a matter of empirical observation or of calculation from atomic structure and atomic dynamics. While some principles of such calculations were outlined as early as 1920, the quantitative data available by the early 1960s were almost entirely derived from measurements.

**A Molecular Model** – Symmetry as well as the molecular approach can be illustrated by the simplest crystal structure capable of piezoelectricity. This is the cubic modification of zinc sulfide, ZnS, known as sphalerite or zinc blende. A unit cell of this structure is



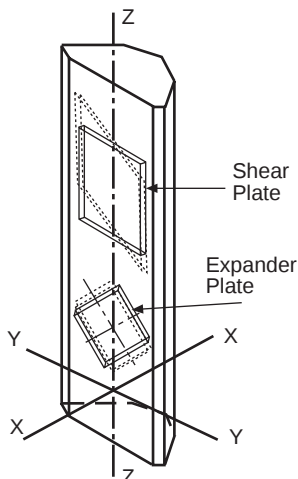
**Fig 1** – Unit cell of cubic zinc sulfide crystal with positive zinc and negative sulfur atoms. Long horizontal arrows indicate applied shearing strain, short vertical arrows the internal electric charge displacement linked to this strain.

shown in fig. 1. It contains only two different atoms, each atom of one kind surrounded by four atoms of the other kind placed at the corners of a tetrahedron. The symmetry class is 43m in the international designation. Compressional stress (stress – force per unit area) applied parallel to an edge of the unit cell will not produce an electric moment since the sulfur atoms (negative) lie in planes halfway between the

zinc atoms (positive), and there is nothing in the nature of the applied stress to disturb this symmetry. If, however, a shearing stress is applied in the horizontal plane, resulting in the shearing strain (displacement per unit length) indicated by long horizontal arrows in fig. 1, then tetrahedral symmetry of the four zinc atoms around each sulfur atom (and vice versa) is disturbed and the sulfur atom is displaced toward the two zinc atoms which have moved apart. The amount of displacement is calculated readily if one postulates that the distance between nearest neighbour atoms remains constant. For a shearing strain of  $1/1000$  (angle of distortion about  $1/20^\circ$ ) the displacement of the sulfur atoms against the zinc atoms in the direction perpendicular to the plane of the shear is  $1/4000$  of the unit cell dimension. The resulting electric polarization is the product of this displacement with the number of sulfur atoms per unit volume and the electric charge per atom. To obtain agreement with the observed piezoelectric effect it is necessary to place a negative charge of one-fourth of an electron on the sulfur and the same positive charge on the zinc. This is in accord with the partially polar character of zinc sulfide. A quantitative theory would have to consider also the distribution of electric charge within each atom.

**Piezoelectricity in Various Crystal Classes** – in zinc sulfide and all other piezoelectric crystals of cubic symmetry, the piezo electric effect of any mechanical stress can be expressed in terms of the single piezoelectric constant relating electric polarization parallel to a cubic axis to strain in the plane perpendicular to this axis. In crystals of lower symmetry, a number of independent piezoelectric constants are needed to describe all possible piezo electric effects. For the triclinic asymmetric crystal class there are 18 independent coefficients. Fortunately, the most important piezoelectric crystals belong to classes having several symmetry elements, and are characterized by only two or three piezoelectric constants. If, starting from class 43m, one of the three axes is made different from the other two, the tetragonal crystal class 42m results, of which ammonium dihydrogen phosphate is an important example. This class has two independent piezoelectric constants. If all three axes are different, the orthorhombic crystal class 22, which includes Rochelle salt, is obtained. The trigonal crystal system includes two very important piezo electric crystals, quartz and tourmaline. The former has three twofold axes of symmetry in addition to the threefold, principal axis; the crystal class is 32, characterized by two piezoelectric constants, one relating compressional stress parallel to a twofold axis with an electric polarization in the same direction, while the second constant relates shearing stress in the plane perpendicular to a twofold axis with polarization parallel to that axis. Tourmaline line, crystal class 3m, has three planes of symmetry intersecting in the threefold axis. Its most important piezoelectric constant relates polarization parallel to this axis to compressional stress in the same direction. It is in the general nature of stress and strain (see ELASTICITY) that a shearing stress or strain can

be resolved into compression or expansion if related to rotated axes. Thus it is possible to obtain piezoelectric response to compressional stresses in the crystals of classes 43m, 42m and 22 if crystal plates are used whose sides are at an angle. The optimum angle is 45°; in this case the effective piezoelectric coefficient for compression is one-half that of the shear coefficient for the original axes. Fig. 2 illustrates this for plates cut from a Rochelle salt crystal. Hydrostatic pressure, however, does not contain an element of shear in any coordinate system and cannot cause a piezoelectric effect in crystals of the three classes mentioned.



Response to hydrostatic pressure is also absent in quartz due to a compensation of the effects on the three twofold axes. A piezoelectric effect of hydrostatic pressure is found only in crystals having a single polar axis. These are exactly the same crystals which show true pyroelectric effects. Strong electric response to hydrostatic pressure is found in tourmaline and Lithium sulfate monohydrate (monoclinic, class 2).

## NUMERICAL EXPRESSION OF PIEZOELECTRIC EFFECTS

**Basic Equations** - Piezoelectricity connects an elastic variable, stress or strain, with an electrical variable, electric polarization or electric field. Piezoelectric constants may be defined, to connect either of the two elastic variables with either electric variable. The most useful piezoelectric constants (usually designated by the letter "d") relate electric polarization to the stress causing this polarization. It is found from the requirement of conservation of energy that then the same constant also gives the strain caused by an applied electric field. The vector component of electric field or polarization is indicated by subscripts 1, 2 and 3 for the X, Y and Z axes. The tensor components of stress or strain are indicated by 1, 2 and 3 for compressional components along the axes, while 4, 5 and 6 designate shear in the planes perpendicular to the axis. Thus for a crystal of class 43 m (for example, zinc sulfide) the following relationships are shown:

$$P_1 = d_{14} T_4; P_2 = d_{14} T_5; P_3 = d_{14} T_6 \\ S_4 = d_{14} E_1; S_5 = d_{14} E_2; S_6 = d_{14} E_3$$

where T and E are components of applied stress or electric field, while P and S are components of resulting polarization or strain. For Rochelle salt, class 22, these relationships exist:

$$P_1 = d_{14} T_4; P_2 = d_{25} T_5; P_3 = d_{36} T_6 \\ S_4 = d_{14} E_1; S_5 = d_{25} E_2; S_6 = d_{36} E_3$$

The threefold symmetry of quartz makes the compressional piezoelectric constant  $d_{11}$  also responsible for a shear effect as expressed in the following system of equations:

$$P_1 = d_{11} T_1 - d_{11} T_2 + d_{14} T_4; P_2 = -d_{14} T_5 - 2 d_{11} T_6 \\ S_1 = d_{11} E_1; S_2 = -d_{11} E_1; S_4 = d_{14} E_1; S_5 = -d_{14} E_2; S_6 = -2 d_{11} E_2$$

The strain component  $S_5$  describes a shear in the horizontal plane of fig. 3. The equation indicates that this strain is excited by an electric field in the Y direction. By this relationship, an electric field applied between the surface of a quartz plate cut perpendicular to the Y axis will cause a shearing deformation of the site facets of such a plate.

**Examples** – The units to be used for expressing piezoelectric constants derive from the units employed for elastic stress and electric polarization. For consistency, the electric and elastic units used must lead to the same unit of energy. Preference is given to the metre-kilogram-second system with rationalized electric units. With this choice, the unit of the piezoelectric d-constant becomes the coulomb/newton or metre/volt. Here 1 coulomb = 1 amp. X second and 1 newton = 1kg.-mass X metre/ second<sup>2</sup> = 0.225 lb. = 102 gr. force. The two units are equivalent since 1 newton X metre = 1 joule = 1 volt X coulomb. The values of the piezoelectric coefficients are found to be numerically so extremely small that they are best expressed as multiples of 10<sup>-12</sup>. In Tables I and II this is expressed by giving the unit as the micromicrocoulomb  $\mu\mu C$ ./newton. The dielectric constants are relative, and are to be multiplied by the dielectric constant of empty space  $\epsilon_0$  or 8.85 micromicrofarad ( $\mu\mu f$ ./metre. The meaning of the figures in Table I can be explained by a few practical examples:

1. A force of 10 lb. is exerted on the major face of a quartz plate 1 in. square and 0.1 in. thick cut with its major face perpendicular to an X axis (fig. 3, "X-cut"). The generated charge is:

$$d_{11} \times \text{area} \times \text{stress} = d_{11} \times \text{force} = 23 \times 10 / 0.225 = 102 \mu\mu C$$

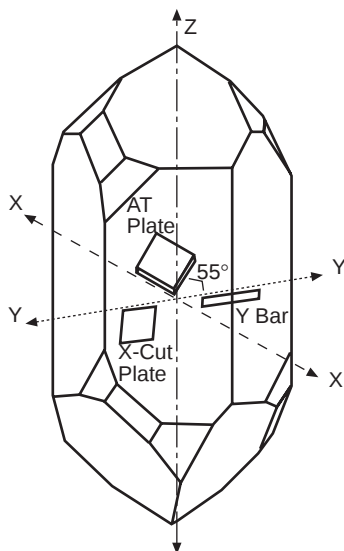
Capacitance = dielectric constant x area/thickness =  $4.5 \times 8.85 \times 0.0254 / .1 = 101 \mu\mu f$ . Generated voltage = charge/capacitance =  $102 / 10.1 = 10.1 V$ .

2. A plate of Rochelle salt 1 cm. long, 2 mm wide and 0.5 mm thick, mounted at one end, is subjected to shearing stress by application of 10 grams of force in the width direction at the free end. The generated charge is:

$$d_{14} \times \text{area} \times \text{stress} = d_{14} \times \text{force} \times \text{length} / \text{thickness} = 350 \times 10 / (102 \times 0.05) = 700 \mu\mu C$$

Capacitance =  $550 \times 8.85 \times 0.01 \times 2 / .5 = 200 \mu\mu f$ . Voltage =  $700 / 200 = 3.5 V$ .

3. A voltage of 1,000 is applied to an ammonium dihydrogen phosphate plate 1 cm. square and 1 mm. thick, with its major face perpendicular to the Z axis. The resulting shear deformation (change in angle between the X and Y axes) is:  $S_6 = d_{36} \text{ voltage} / \text{thickness} = 0.000048 \text{ radians} = 0.16 \text{ minutes}$ .



**Fig. 3 – Quartz crystal with 3 most important piezoelectric elements**  
X-cut is used for expansion or contraction in thickness direction on application of electric field in X direction; Y-bar expands and contracts in length when field applied in X direction. AT plate shows shear in side faces when field applied in thickness direction; it excels in low temperature variation on resonance frequency

These typical examples show that the electric charges generated are quite small but the voltages very substantial. Conversely mechanical displacements caused by piezoelectric effects are minute, but due to the high elastic stiffness of crystals the forces created can be large.

## FERROELECTRICITY

**Ferroelectric Crystals** – Inspection of Table I shows Rochelle salt to be superior to the other listed crystals in the value of its piezoelectric constant  $d_{14}$ . At the

same time, the dielectric constant is also in the order of 100 times higher than that of ordinary solids. The high values of these two constants are a result of the ferroelectricity of Rochelle salt. This term designates a dielectric phenomenon analogous to ferromagnetism in magnetic materials (see Magnetism). The basic condition for either phenomenon is a co-operative molecular effect. In magnetism it involves the electron spins associated with certain metallic elements, while in the dielectric case it involves electric dipoles which may be permanent or may be induced by local electric fields. Consideration of the value of the electrical charge and typical interatomic distances indicates that ferroelectricity should be a more widespread phenomenon than ferromagnetism. Extensive studies of dielectric properties of solids in the late 1950s indeed produced numerous examples of ferroelectric materials, especially among organic salt type compounds, but none of these latter were found to approach Rochelle salt in piezoelectric effects. Characteristic of ferroelectrics is the formation of “domains”; i.e., regions within each crystal which have a spontaneous electric polarization. Under the influence of an applied electric field these domains may reverse their orientation; this effect can contribute substantially to the dielectric constant. In most ferroelectrics a characteristic temperature, the Curie point, is observed above which domain structure disappears. The dielectric constant reaches particularly high values near this temperature. In the case of Rochelle salt, the Curie temperature occurs at 24° C, and thus a very high dielectric constant is found in the room-temperature range. This high dielectric constant may be said to enhance the piezoelectric effect, the origin of which, in Rochelle salt, as in other crystals containing asymmetrical organic molecules, is inherent in the molecular structure.

**Barium titanate.** – Barium titanate,  $\text{BaTiO}_3$ , and related compounds including lead titanate,  $\text{PbTiO}_3$ , calcium titanate,  $\text{CaTiO}_3$ , and lead zirconate,  $\text{PbZrO}_3$ , belong to a simple crystal structure type, the perovskite type, which is cubic and has a centre of symmetry in the ideal case. This cubic symmetry is actually found for barium titanate above 120° C.; below this temperature barium titanate is tetragonal with a polar symmetry, class 4mm. The transition from cubic to tetragonal near 120° C. is a Curie point with a peak dielectric

| Crystal                              | Piezoelectric Constants * | Dielectric Constants# |
|--------------------------------------|---------------------------|-----------------------|
| Rochelle Salt (30° C)                | $d_{14} + 550$            | 350                   |
|                                      | $d_{26} - 54$             | 9.2                   |
|                                      | $d_{36} + 12$             | 9.5                   |
| Quartz                               | $d_{11} + 2.3$            | 4.5                   |
|                                      | $d_{14} - 0.7$            | 4.5                   |
| Ammonium dihydrogen phosphate (ADP)  | $d_{14} - 1.5$            | 56                    |
|                                      | $d_{26} + 48$             | 15.5                  |
| Potassium dihydrogen phosphate (KDP) | $d_{14} + 1.3$            | 42                    |
|                                      | $d_{26} + 21$             | 21                    |
| Tourmaline                           | $d_{15} + 3.6$            | 6.3                   |
|                                      | $d_{22} - 0.3$            | 6.3                   |
|                                      | $d_{31} + 0.3$            | 7.1                   |
|                                      | $d_{33} + 1.8$            | 7.1                   |
| Zinc blende (ZnS)                    | $d_{14} - 3.2$            | 9                     |
| Barium titanate crystal              | $d_{11} - 34$             | 170                   |
|                                      | $d_{23} + 86$             | 170                   |
|                                      | $d_{15} + 392$            | 2900                  |
| Barium titanate ceramic              | $d_{11} - 78$             | 1700                  |
|                                      | $d_{23} + 190$            | 1700                  |
|                                      | $d_{15} + 260$            | 1450                  |

\* Unit is micromicrocoulomb / newton  
# Relative to air

Table II

| Material                            | Upper temperature limit (° C) | Field direction | Force direction | Effective piezoelectric constant (d) (coulomb/newton) | Young's modulus (Y) (Newton/m <sup>2</sup> ) | Dielectric constant (K) | Electro-mechanical coupling factor (k) | Density (kg/m <sup>3</sup> ) | Elastic wave velocity (m/sec) |
|-------------------------------------|-------------------------------|-----------------|-----------------|-------------------------------------------------------|----------------------------------------------|-------------------------|----------------------------------------|------------------------------|-------------------------------|
| Quartz                              | 550                           | X               | X               | $2.3 \times 10^{-12}$                                 | $8.0 \times 10^{10}$                         | 4.5                     | 0.10                                   | $2.65 \times 10^3$           | 5400                          |
|                                     |                               | X               | Y               | $2.3 \times 10^{-12}$                                 | $8.0 \times 10^{10}$                         | 4.5                     | 0.10                                   |                              | 5400                          |
| Ammonium dihydrogen phosphate (ADP) | 120                           | Z               | 4.5° XY         | $24 \times 10^{-12}$                                  | $1.9 \times 10^{10}$                         | 15.5                    | 0.29                                   | $1.80 \times 10^3$           | 3250                          |
|                                     |                               | X               | 4.5° YZ         | $290 \times 10^{-12}$                                 | $1.8 \times 10^{10}$                         | 350                     | 0.68                                   | $1.77 \times 10^3$           | 3200                          |
| Rochelle salt (30° C)               | 45                            | Y               | 4.5° ZX         | $27 \times 10^{-12}$                                  | $1.0 \times 10^{10}$                         | 9.2                     | 0.30                                   |                              | 2400                          |
|                                     |                               | Z               | Z               | $190 \times 10^{-12}$                                 | $10.6 \times 10^{10}$                        | 1700                    | 0.52                                   | $5.7 \times 10^3$            | 4300                          |
| Barium titanate ceramic             | 100                           | Z               | X               | $78 \times 10^{-12}$                                  | $11.0 \times 10^{10}$                        | 1700                    | 0.22                                   |                              | 4400                          |
|                                     |                               | Z               | Z               | $140 \times 10^{-12}$                                 | $7.1 \times 10^{10}$                         | 450                     | 0.60                                   | $7.6 \times 10^3$            | 3100                          |
| Lead titanate zirconate (45/55)     | 300                           | Z               | X               | $57 \times 10^{-12}$                                  | $8.7 \times 10^{10}$                         | 450                     | 0.26                                   |                              | 3400                          |
|                                     |                               | Z               | Z               | $250 \times 10^{-12}$                                 | $6.7 \times 10^{10}$                         | 1200                    | 0.64                                   | $7.5 \times 10^3$            | 3000                          |
| Lead strontium titanate zirconate   | 300                           | Z               | X               | $105 \times 10^{-12}$                                 | $8.1 \times 10^{10}$                         | 1200                    | 0.30                                   |                              | 3300                          |
|                                     |                               | Z               | Z               | $80 \times 10^{-12}$                                  | $6.0 \times 10^{10}$                         | 225                     | 0.42                                   |                              | 3200                          |
| Lead metaniobate                    | 500                           | Z               | Z               | $11 \times 10^{-12}$                                  | $6.0 \times 10^{10}$                         | 225                     | 0.04                                   | $6.0 \times 10^3$            | 3200                          |
|                                     |                               | Z               | X               |                                                       |                                              |                         |                                        |                              |                               |

constant as high as 10,000. Below this temperature a barium titanate crystal is found to consist of domains having electric polarity in different directions but always parallel to a cube axis. Each of these domains is a true tetragonal crystal having definite piezoelectric coefficients. The multidomain crystal is, in crystallographic terms, a multiple twin. The piezoelectric properties of such a crystal will depend on the domain distribution; reproducible data are found only if uniform domain orientation is induced by a maintained external electric field: Domain reversal may be caused by moderate applied fields such as 100 v./mm. This phenomenon has been applied in electric data storage.

Domain reversal by applied electric fields makes it possible to induce a resultant over-all polarization in polycrystalline ceramic masses of barium titanate crystallites. Due to forces acting between the crystals, the electric polarization of the ceramic is more stable than that of the single crystal. Barium titanate and ceramics of related structure have thus become major practical piezoelectric materials.

**Ferroelectric Ceramics** – In barium titanate and other ferro electric ceramics that have been rendered polar by treatment in a strong electric direct-current field such as 50,000 v. per inch, is found an over-all symmetry comprising a polar axis and all planes intersecting in this axis. This leads to three independent piezoelectric constants,  $d_{33}$ ,  $d_{31}$  and  $d_{15}$ . It is usually found that a compression parallel to the 3-axis causes electric polarization opposite to that originally applied in the poling process, while compression at right angles to this axis causes the polarization to increase. The effect of axial compression is predominant so that a decrease of polarization also results from hydrostatic pressure. The shear piezoelectric constant  $d_{15}$  has values even larger than  $d_{33}$  but this shear effect does not have such wide applications. In the ferroelectric oxide ceramics the phenomenon of ferroelectricity does not merely enhance the piezoelectric effect, but is its basis. No piezoelectric effects are present above the Curie point. The asymmetry of the single crystal below the Curie point which permits piezoelectricity is a direct result of ferroelectricity. Further, the possibility of rendering a ceramic polar depends on reversal of ferroelectric domains.

**High-Temperature Ferroelectric** – Substantial variations in the properties of barium titanate ceramics have been obtained by modification of their composition. In some cases this has involved solid solution formation, with such elements as calcium and strontium replacing barium, or zirconium replacing titanium. A principal effect of such substitutions is a shift in the Curie point. More subtle changes in electric properties are obtained by additives, such as rare-earth oxides, from other columns of the periodic system. Additions in the range of 1% may destroy the ability of barium titanate ceramics to accept permanent polarization, but advantageous dielectric properties for capacitor applications have resulted. Solid solutions of lead titanate and lead zirconate, also of the perovskite structure type, are found to possess

piezoelectric properties generally similar to those of barium titanate. Lead titanate zirconate compositions, in addition to having high Curie points (300° to 400° C.), have a higher electromechanical coupling than barium titanate. A wide range of electric properties can be achieved by the controlled variation of composition in the preparation of lead titanate zirconate. Further perovskite-type ferroelectrics of potential technical interest are obtained by partial substitution of potassium or lead for sodium in sodium niobate (columbate),  $\text{NaNbO}_3$ . Lead metaniobate,  $\text{PbNb}_2\text{O}_6$  is of promise for high-temperature applications in view of its high Curie point (570° C.) and is of theoretical interest as a prototype of a new crystal structure.

## PREPARATION AND MEASUREMENT METHODS

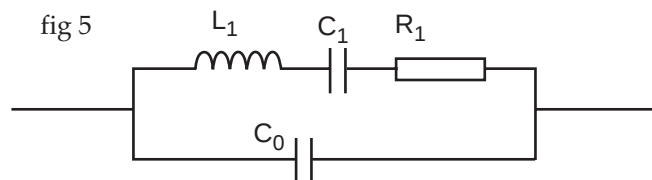
**Preparation of Crystals** – The manufacture of useful piezoelectric bodies from piezoelectric crystals depends on the services of the geologist and mineralogist in locating suitable high-quality single crystals of the minerals quartz and tourmaline. In the case of quartz the absence of crystallographic twinning is essential. This requirement has limited the supply of commercial piezoelectric quartz to a few locations, notably Brazil and Madagascar. Water-soluble crystals such as Rochelle salt and ammonium di-hydrogen phosphate are grown from their solutions, under closely controlled conditions of temperature, with the use of seed crystals of definite shape and orientation. The art of crystal growing has been extended also to quartz. The solvent in this case is water with the addition of an alkali under supercritical conditions such as a temperature of 400° C. and a pressure of 1,000 atmospheres. To obtain the desired piezoelectric action, piezoelectric elements have to be cut from the natural or grown crystal to close tolerances of dimensions and orientation in regard to the crystal axes. In case of quartz crystal oscillators for precision frequency control, dimensional stability may have to be more than one billionth of an inch and dimensional accuracy closer than one minute of arc. The methods for cutting and finishing quartz oscillator plates are akin to those used in manufacture of precision optics.

**Preparation of Ceramics** – Piezoelectric ceramics are obtained by methods generally applied in preparing electric insulator ceramics, but closer control over impurities usually is required. The addition of fluxes can affect the electric properties undesirably. After a ceramic firing process the ferroelectric bodies are given closely adhering electrodes, usually in the form of a fired-on silver preparation, and subjected to high direct-current voltage for a period of time as long as one hour. Usually this takes place at an elevated temperature, preferably close to the Curie point.

**Direct Measurement methods** – The most direct method of determining the piezoelectric effect of a crystal body is the measurement of the electric charge generated upon application or removal of a mechanical force. Such measurements are convenient on the

piezoelectric ceramics showing high piezoelectric effect and good insulation resistance. The method requires considerable skill when applied to piezoelectric crystals of only moderate piezoelectric effect. In such cases application of an oscillatory force of unknown magnitude and amplification of the resulting alternating current piezoelectric signal may be employed. Other methods depend on the converse piezoelectric effect. A static method uses strain gauges to study the deformation resulting from an applied high direct-current voltage. Small oscillatory displacements resulting from the application of alternating voltage may be detected as frequency modulation if the vibration is applied to the plate of a tuning condenser in a high-frequency circuit.

**Resonance Measurement Method** – The most accurate measurements of piezoelectric constants depend on the electric effects in piezoelectric bodies vibrating near their principle mechanical resonance frequencies. Applied to small crystals or crystal fragments, resonance is employed in the most sensitive test for presence of piezoelectricity, the click test. In this the tester listens to the transients occurring in an oscillator circuit when it is swept over resonances of the crystals. When the electrical impedance of a crystal is measured as function of frequency, it is found that the apparent capacitance increases to very high values as the resonance is approached. At this point the impedance is a pure resistance, then becomes inductive. With a further increase of frequency, the impedance becomes once more a pure resistance but at a much higher resistance level, and then it returns to capacitive. This behaviour can be represented by an equivalent electric circuit (fig. 5). In this circuit,  $C_0$  represents the capacitance of the crystal if the piezoelectric effect were suppressed.  $L_1$  and  $C_1$  are related to the mass and



elastic compliance of the crystal, multiplied by a factor representing the piezoelectric effect.  $R_1$  represents the mechanical damping of the crystal. The ratio of the inductive impedance to  $R_1$  is given by the mechanical quality factor which is the reciprocal of the mechanical damping factor. This quality factor may be as high as 1,000,000 in practical quartz crystal oscillators. The ratio of capacitances  $C_1/C_0$  is a direct measure of the strength of the piezoelectric effect involved in the elastic resonance under study. It is found to be related to the piezoelectric d-constants by equations of the type

$$C_1/C_0 = fd^2 Y / Ke_0$$

Where  $Y$  is Young's elastic modulus,  $K$  is the dielectric constant  $\epsilon_0$  is the dielectric constant of empty space and  $f$  is a numerical factor related to the amplitude distribution of the elastic mode;

it is near 0.8 for typical fundamental modes This capacitance ratio represents the amount of sharing of

electric and elastic energy through the piezoelectric effect. The square root of the capacitance ratio is proportional to the electromechanical coupling factor  $k$  defined by

$$k = \sqrt{Y/K \epsilon_0}$$

The most convenient way of obtaining the coupling factor and hence the piezoelectric constant is by the measurement of the two frequencies at which the impedance of the crystal is a pure resistance. The frequency of low resistance is the resonance frequency and the frequency of high resistance is the antiresonance. For an elongated bar the product of the fundamental frequency and length is one-half the elastic wave velocity. Extremely accurate values of the elastic modulus,  $Y$ , are obtained by the relation wave velocity =  $\sqrt{Y/\text{density}}$

Table II lists the important piezoelectric operating parameters of some crystals and ceramics. The data for ceramics are only representative, since small variations in composition or processing, either intentional or fortuitous, can cause substantial changes in operating parameters. Only piezoelectric effects of compression or expansion forces, as distinct from shear forces, are considered. The table comprises cases where the electric field and force are parallel as well as those where they are at right angles. For quartz, the same coefficients hold for both cases since  $d_{12} = -d_{11}$ . Young's modulus is much lower for the water-soluble crystals than for ceramics or quartz, but for calculation of wave velocity this is largely compensated by the lower density of the soluble crystals. The enormous spread in the piezoelectric d-constants is somewhat balanced by the analogous spread of dielectric constants, so that the listed electromechanical coupling coefficients are comprised within one order of magnitude. It is noteworthy that electromechanical coupling coefficients in excess of 0.4 are found only in ferroelectric materials. The ideal piezoelectric would approach the value 1 for this coefficient.

## APPLICATIONS

**Mechanical Measurements**– The crystals and ceramics listed in Table II are those which have found major application. Minor but continuing use in measurement instruments is made of tourmaline and lithium sulfate. Ethylene diamine tartrate (EDT) and neutral potassium tartrate (DKT) crystals were produced in sizable quantities around 1950 but failed to establish themselves on a competitive basis. Potassium dihydrogen phosphate has found some application for an electro-optic effect closely related to piezoelectricity.

All the methods of observing the piezoelectric effect have become the basis of applications of this effect in the field of electro mechanical measurement, electroacoustics, electric voltage sources and frequency controlling devices. The most immediate application is in the measurement of force or pressure.

Here, however, a major limitation is encountered as a result of the dielectric leakage current which gradually neutralizes the voltage generated by application of a force. Piezoelectric effects are therefore not suitable for measurement of constant or slowly changing pressures such as barometric pressure. The compactness and high mechanical resonance frequency of piezoelectrics gives them, however, unique advantages for dynamic pressure studies, as in blast gauges and accelerometers for the analysis of rapidly changing states of motion.

**Phonograph Pickup** – Devices translating electric energy into mechanical energy and vice versa are known as electromechanical transducers. Most transducers involve compressional rather than shear piezoelectric effects. The largest use of piezo electric elements in terms of units manufactured is in phonograph pickups. In these, the piezoelectric element transforms the mechanical energy picked up by the phonograph needle into an electrical signal. In the period from about 1938 to 1958 Rochelle salt phonograph pickup elements supplied approximately nine-tenths of the whole phonograph industry of the United States. Beginning in the early 1950s ceramic piezoelectric elements became increasingly important. They are free of temperature and atmospheric humidity problems and are well adapted to light-weight construction. Major requirements for a phonograph pickup element are high mechanical compliance and high voltage output. In both these respects lead titanate zirconate offers considerable advantage over barium titanate. In a widely used arrangement, two piezoelectric plates are combined into a sandwich which is subjected to bending forces. The piezoelectric effect used links the field in the thickness direction to elastic stress along the length. The size may be as small as 0.5 X 0.06 X 0.02 in. for the sandwich, and the standard voltage output is typically one volt for five to ten grams stylus pressure. The two component elements may be connected either in series or in parallel. In either case connections are made so that the outputs of the two elements add when one is compressed and the other is expanded as occurs in bending. An alternative arrangement, in which torque is applied to a combination of two shear-sensitive elements, has been very successful with Rochelle salt but is not feasible with piezoelectric ceramics. Torque in the crystal sandwich is caused by the lateral movement of the stylus. A vertical stylus movement in the same arrangement causes bending of the crystal sandwich. This has been used in one type of stereophonic crystal pickup which contains a sandwich of one Rochelle salt “shear” plate and one “expander” plate (see fig. 2). Separate electrical connections from the two plates carry signals proportional, respectively, to the horizontal and vertical excursions of the record groove.

**Acoustics and Ultrasonics** – Other applications of piezoelectric transducers are in the fields of sound transmission and reception. They have been especially successful in acoustic underwater sound devices because piezoelectric solids are much better matched

acoustically to water than to air. Thus, comparatively simple matching structures or none at all are required for piezoelectric underwater transducers. While much of the use of piezoelectric crystals has been for military underwater sound purposes, increasing peacetime uses of sound energy in liquids developed after about 1950. Ultrasonic cleaning devices, operating at frequencies from 10 kHz. to 100 kHz., have been particularly successful. For this frequency range, resonating bars have convenient lengths of 0.5 to 5 in. To obtain reasonably large values of capacitance, bars with the electric field perpendicular to the length direction are usually preferred even when, as in the case of the ceramics, the piezo electric effect for length-wise mechanical action is the weaker one. For frequencies above 100 kHz, thickness resonance of plates with mechanical and electrical action in the thickness direction is preferred. The conditions for elastic vibrations of bars and plates are different- the data of Table II refer to bars and are only approximately applicable to plates in thickness vibration. The principal materials used in underwater sound transducers are ammonium dihydrogen phosphate, barium titanate and lead titanate zirconate. (See also ULTRA-SONICS.)

**Frequency Control** – The major application of piezo-electric quartz crystals is for electric frequency control. Quartz combines exceptional chemical and mechanical stability with very unusual elastic properties. While most materials show a steady decrease in the elastic moduli with temperature, some of the elastic moduli of quartz show the opposite trend. By cutting plates from quartz crystals at certain orientations and dimensions, a high degree of compensation for these temperature coefficients can be obtained. The piezo-electric coupling of quartz, while not very large, is entirely adequate to cause a reaction of the quartz crystal on the electric driving circuit. This reaction can force the circuit to oscillate at an exact frequency determined by the quartz crystal. Quartz crystal oscillators have been built to operate at frequencies from 1kHz or less to approximately 100 MHz. The largest number are in the communication range from five to ten MHz. For this range the most important type of quartz crystal oscillator is the AT cut (SC6 fig. 3). By applying an electric field in the thickness direction, this plate is excited to transverse vibrations travelling in the thickness direction. To obtain fundamental resonance (one half standing wave) at eight MHz, the thickness should be about 0.008 in. The orientation of the AT cut is chosen so as to minimize the temperature dependence of the resonant frequency over a wide operating range, such as—55 to +90°C. Stability within 0.005% may be obtained without temperature control of the crystal.

A frequency constant to 1 part per 1,000,000,000 over many months has been obtained through ~the use of extremely carefully prepared quartz oscillators, maintained at constant temperature. Liquid helium boiling at constant pressure is especially suitable, because at such very low temperatures any gradual changes in elastic properties are suppressed. Such

“quartz clocks” are more constant than the rotation of the earth itself.

**Wave Filters** — Closely related to frequency control is the mechanical wave filter application of piezoelectric crystals. In this case the remarkable impedance properties of the crystal near a resonance point are used to provide passage of an electric signal that falls within a prescribed band of frequencies, while other frequencies are rejected. The width of the frequency pass-band is related to the range of frequency at which the crystal impedance is inductive and thus to the capacitance ratio ( $C_1/C_0$ ) (see above, Resonance Measurement methods). In quartz crystals, unless associated with additional inductors, this pass-band is limited to the order of 1% of the centre frequency of the band. Nevertheless, quartz crystal filters are of great importance in separating the voice channels in multichannel telephony, in which carrier frequencies range from 65 to 200 kHz. Piezoelectric ceramics are intrinsically less stable than quartz. Nevertheless, modifications of barium titanate and lead titanate zirconate have been found which combine a high piezoelectric coupling coefficient, and hence a high band width, with sufficient stability for intermediate frequency filtering—usually at 455 kHz—in radio receivers. The search for new and improved piezoelectric materials is part of the expanding field of solid state physics. Its practical aim is the development of devices and circuit components of smaller size, greater ruggedness and increased temperature and frequency operating range. See also ELECTRICITY, CONDUCTION OF.