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THE PHYSICAL CRYSTALLOGRAPHY OF QUARTZ

In order to deal with the problems of designing, developing, and fabricating quartz crystal units, it is necessary to have some familiarity with crystal physics. Only those portions of this very extensive field which are required to design quartz piezoids or to understand their operation will be discussed. For complete treatments of the subject, the reader may consult one or more of the works listed in the bibliography at the end of the book.

ANISOTROPY

Crystals differ from noncrystalline solids (if such materials may be called solids) in that many of the physical properties of the crystal are dependent upon direction in the crystal whereas in a noncrystalline or amorphous material, the properties are independent of direction. For instance, one may speak of the hardness of glass without qualification; but in speaking of the hardness of quartz, the direction must be specified, since this property, like many others, differs in different directions in the crystal. If the coefficients describing the physical properties of a solid differ with direction, the solid is said to be anisotropic. A striking example of anisotropy is the electrical conductivity of quartz, which is about 1000 times greater in one direction than another in the crystal. Except for a few properties such as density, specific heat, melting point, etc., most properties of crystalline materials are direction-dependent. Table 2.1

Table 2.1 Some Anisotropic Properties of Crystals

Elastic modulus and compliance
Thermal conductivity
Electrical conductivity
Coefficient of thermal expansion
Hardness
Solubility
Dielectric constants
Piezoelectric constants
Index of refraction (optical)
Velocity of propagation of longitudinal (sound) waves
Velocity of propagation of shear waves

shows a few of the physical properties of crystals, the values of which, in general, depend upon direction in the crystal.

THE QUARTZ CRYSTAL

Since we are concerned exclusively with quartz in this book, we should first become familiar with the general form of the quartz crystal. The idealized quartz crystal is a hexagonal prism with six cap faces at each end, as shown in Fig. 2.1. The prism faces are designated m-faces and the cap faces are designated R- and r-faces. The R-faces are often called major rhomb faces and the r-faces are called minor rhomb faces. There are, of course, three of each at each end of the complete crystal. These faces betray the trigonal structure of quartz and its threefold symmetry.

Quartz is an enantiomorphic crystal, i.e., it exists in right and left form. The faces designated s and x are rarely seen on crystals, but when present, they enable one to distinguish between right and left quartz. Both kinds of quartz are equally useful for fabricating piezoids, but a distinction is required in processing the material.

Crystals of cultured quartz exhibit the same faces as do crystals of natural quartz, but they are sometimes a little difficult to identify. We will return to this topic after discussing the subject of crystal axes.

CRYSTAL AXES AND AXIAL SYSTEMS

Since the values of the coefficients describing the physical properties of the crystal are in general dependent upon direction, it is necessary

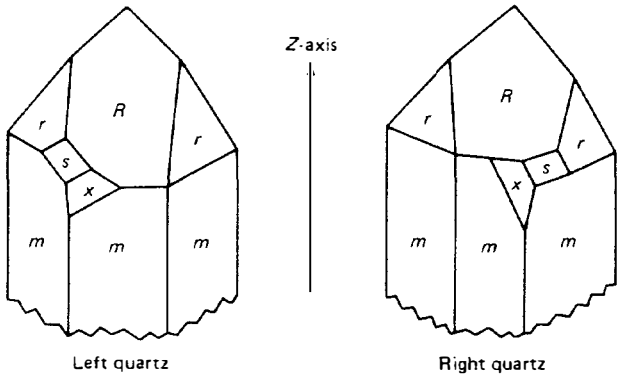

Fig. 2.1. The quartz crystal. Crystals with cap faces on both ends are rare. The *s* and *x* faces are also rare. In right quartz, the *s* and *x* faces occur at the lower-right corner of an *R* face. In left quartz, they occur at the lower-left corner.

to choose reference directions within the crystal for use in specifying their values. Such directions are called the *crystal axes.* It must be very carefully noted that a crystal axis is not a line but a direction in the crystal. The axial directions are chosen to make the description of the crystalline properties as simple as possible. An axis is always chosen with reference to some specific physical property of the crystal, which in turn depends upon the way in which the atoms are arranged within the crystal.

Different axial systems may be used to describe the same crystal, so confusion may result unless it is made quite clear which system is being employed. Furthermore, one axial system may be most convenient for one purpose and another system for another purpose. For example, it is more convenient to use the Bravais-Miller axial system to specify the natural faces and atomic planes in quartz, whereas it is more convenient to use an orthogonal coordinate system for purposes of computations involving the piezoelectric and mechanical properties of the crystal.

The Bravais-Miller (B-M) system of axes consists of a Z-axis (sometimes called the c-axis) and three X-axes (sometimes called a_1, a_2, a_3) which make angles of 120° with each other and which lie in a plane perpendicular to the Z-axis. The B-M system illustrated in Fig. 2.2*a* is applicable to crystals such as quartz which have trigonal symmetry. The use of the B-M system in specifying atomic planes is discussed in the next section.

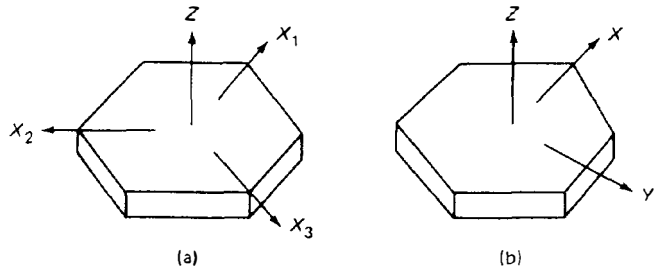

Fig. 2.2. Cross sections of a quartz crystal taken perpendicular to the *Z*-axis, showing (*a*) the B-M system of axes and (*b*) the rectangular system.

The rectangular, or orthogonal, coordinate system of axes is shown in Fig. 2.2*b*. The *Z*-axis in the rectangular system is the same as the *Z*-axis in the B-M system. The *X*-axis of the rectangular system is one of the three *X*-axis of the B-M system. It is immaterial which of the three is chosen since they are identical. The *Y*-axis is perpendicular to both the *Z*- and the *X*-axes. The method of specifying the sense of the *X*-axis will be discussed later.

THE Z-AXIS AND OPTICAL TWINNING

The principle, or *Z*-axis (also called the optic axis and the *c*-axis) in quartz is an axis of threefold symmetry. This means that all the physical properties repeat each 120° as the crystal is rotated about the *Z*-axis. If a beam of plane-polarized light is passed through the crystal in the direction of the *Z*-axis, the plane of polarization is rotated by 15 to 45° for each millimeter of quartz traversed. The exact amount of rotation depends on the color of the light and the temperature of the quartz. This phenomenon is called optical rotation and it forms the basis of a number of optical instruments. It has no special significance in the field of piezoelectricity.

In some specimens of quartz the plane of polarization is rotated one way and in other specimens the rotation is in the opposite sense. The crystal is said to be right-hand (or simply right) quartz if the plane of polarization is rotated clockwise as seen by an observer looking through the quartz toward the source of light. Left quartz produces the opposite rotation. Both types of quartz may be used in

fabricating piezoids, but some attention must be given to the hand in cutting certain types of piezoids.

Most crystals of natural quartz are composed partially of left and partially of right quartz. Such crystals are said to be *optically twinned*. The presence of optical twinning can be detected by inspection with polarized light or by etching a surface with hydrofluoric acid or ammonium bifluoride. Due to anisotropy the rate at which the acid attacks the quartz is different in different directions. Consequently, small etch pits having the form of a shingled roof begin to develop. The etch pits have different orientations in the two parts of the crystal and therefore reflect light differently, revealing the boundary between the right and left portions. Figure 2.3 illustrates the appearance of a Z-section of twinned quartz after etching.

Piezoids can be fabricated from either right or left quartz, but it is usually not permissible to have both types present in the same one. For this reason it is necessary to inspect the quartz carefully to ensure that no twin boundaries are present. Cultured quartz is usually free of optical twinning. The seed crystals are carefully selected to be free of twinning and other defects, since any defect present is usually propagated through the crystal as it grows.

THE X-AXIS AND ELECTRICAL TWINNING

The X-axes in quartz are parallel to a line bisecting the angles between adjacent prism faces. The X-axis is also called the *electrical axis*. More precisely it is a polar axis, since electric polarization

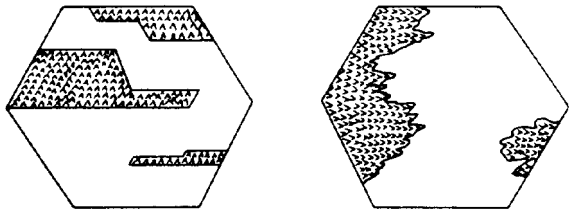

Fig. 2.3. (*a*) Optical twinning and (*b*) electric twinning. The boundaries between optical twins are usually straight lines. The boundary between electrical twins are usually irregular.

occurs in this direction upon mechanical strain. Only those crystals having one or more polar axes display the phenomenon of piezoelectricity.

If a plate of quartz is cut in such a way that the major surfaces are perpendicular to the X-axis, the resulting piezoid is called an X-cut. If the plate is subjected to mechanical compression, a positive charge is developed on one side and an equal negative charge on the other. These charges are readily observed by placing conducting films on each side of the plate and connecting these to a direct-current vacuum-tube voltmeter. If the input capacitance of the meter is low, potential differences of several volts result from the application of a pressure of a few newtons per square centimeter.

The sign of the charge developed alternates between positive and negative at successive corners of the crystal. Following the IEEE standards, the positive X-direction is chosen to be the direction in which a positive strain produces a positive charge. A positive strain is defined to be the extension resulting from tension. By this definition, that end of the X-axis is positive where a negative charge is developed by compression.

Quartz crystals are often electrically twinned. Electric twinning consists of a reversal of the X-axis. In an electrically twinned crystal compression produces a positive charge on one side of the twin boundary and a negative charge on the other. Electric twinning (also known as *Dauphiné twinning*) usually occurs in irregular patches within the crystal; and the boundaries, revealed by etching, do not conform to any geometric pattern, as illustrated in Fig. 2.3*b*.

At temperatures above 573°C, called the *Curie*, or *inversion*, temperature, quartz exists in a hexagonal form called *beta quartz*. The sense of the polar axis is lost when the crystal changes from the alpha to the beta phase. When the crystal is cooled through the inversion temperature, it returns to the alpha phase, but the sense of the polar axis is usually opposed in different parts of the crystal, i.e., the crystal is electrically twinned. Electrical twinning can be induced in quartz at temperatures below the inversion temperature by mechanical stress. It is therefore important that thermal and mechanical stresses be avoided in processing quartz for piezoelectrical applications.

Cultured quartz is usually free of electrical twinning, but it may occur if the seed crystal is twinned or if undue stress is exerted on the crystal during or after growth. A twinned crystal can often be identified by a "shingled" appearance on the $+X$-surface.

THE Y-AXIS

The Y-axis is not a polar axis in quartz and no electric polarization results from an extensional strain in the Y-direction. It will be seen later, however, that a shear stress applied to a Y-cut quartz plate does result in electric polarization. This relationship forms the basis of a number of important types of quartz piezoids.

SPECIFICATION OF ATOMIC PLANES IN CRYSTALS

In order to describe the position of a given set of parallel atomic planes in a crystal, a coordinate system is required. In crystals of cubic symmetry such as the alkali halides (NaCl, KCl, etc.), the ordinary XYZ coordinate system is used. The directions of the coordinate axes are chosen to be parallel to the natural cleavage planes. Any plane in the crystal must intercept at least one of the coordinate axes. In case the plane is parallel to the axis, it is said to intersect it at the point of infinity. The Miller indices of the plane is a set of three numbers which are the smallest integers proportional to the reciprocals of the intercepts of the plane with the X-, Y-, and Z-axes, respectively.

Suppose, for example, we imagine a plane to intercept the X-axis at a distance $2a$ from the origin. Let it intercept the Y-axis at $3a$ and the Z-axis at $1a$. The reciprocals of these three numbers are, respectively, $1/2a$, $1/3a$, $1/1a$. Multiplying each of the numbers by $6a$, we arrive at the set of numbers 3, 2, 6. These numbers, written (326) and read "three, two, six," are the Miller indices of the plane.

As another example, consider a plane which intersects the X-axis at $1a$, the Y-axis at $3a$ and is parallel to the Z-axis. The intercepts are $1a$, $3a$, and ∞, respectively. The reciprocals are $1/1a$, $1/3a$, 0. Multiplying each of these numbers by $3a$ gives the Miller indices (310). The plane is called the *three, one, zero plane*. Any plane parallel to

this plane is also a (310) plane, so that the Miller indices of a plane do not refer to any particular plane of atoms but to all members of a set of parallel atomic planes.

In order to specify planes in a crystal such as quartz, it is necessary to use the Bravais-Miller indices and the trigonal axial system. The Z- axis and the three X- axes form a coordinate system. Any plane in the crystal intersects each of the four coordinate axes including the point at infinity when the plane is parallel to one of the axes. The Bravais-Miller indices then constitute a set of four numbers which are the smallest integers that are proportional to the reciprocals of the intercepts of the plane with the $X_{\bar{1}}$, $X_{\bar{2}}$, $X_{\bar{3}}$, and Z-axes respectively.

As an illustration of the use of the B-M indices to describe a crystal face or plane, consider the m, or prism, face of a crystal of quartz. Figure 2.4 is intended to show a Z-section i.e., a surface normal to the Z-axis. The m planes are therefore perpendicular to the plane of the page. If we call a the unit distance along the X-axes, the intercepts of plane 1 with the $X_{\bar{1}}$, $X_{\bar{2}}$, $X_{\bar{3}}$, and Z-axes are a, ∞, $-a$, and ∞, respectively. The B-M indices are therefore proportional to the numbers $1/a$, 0, $1/-a$, and 0 or 1, 0, -1, and 0. The B-M indices are therefore (1 0 -1 0). In the B-M system the algebraic sum of the first three indices must be zero, so that writing the third digit is superfluous and it is often replaced by a dot. The B-M indices of the plane are then (10.0). The plane we have just studied is marked 1 in Figure 2.4. The other m-faces, marked 2 and 3, have different indices which can be determined in the same way. When a

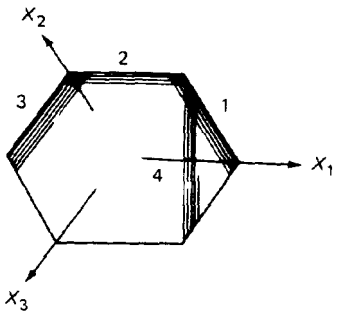

Fig. 2.4. A Z-section of a crystal of quartz. The Z-axis is perpendicular to the page.

minus sign appears in the B-M indices it is usually written by putting the minus sign above the numeral. Hence, the B-M indices for the planes marked 3 which are (−1 1 . 0) becomes ($\bar{1}$1.0).

All the other atomic planes may be specified in the same way. For example, the set of planes normal to the X-axis which are designated as 4 in Fig. 2.4 intercept the axes at $a/2$, $-a$, $-a$, and ∞, respectively. Therefore, the B-M indices of these planes are (21.0). Although the X-planes do not form a natural face in quartz, they are important because a number of piezoids are prepared with their surfaces parallel to these planes. In fact, the first piezoelectric devices made by the Curies were X-cut plates of quartz.

The B-M indices for each of the three m, R, r, s, and x natural faces are given in Table 2.2.

The plane perpendicular to the optic or Z-axis is designated the (00.3) plane. It is not a natural face. The AT-cut is oriented with respect to one of the r-faces with which it makes a dihedral angle of about 3°. Another important set of planes which do not form a natural face are the (20.3) planes which make an angle of about 49° with the Z-axis and are used in orienting the BT-cut. Similarly, the (12.2) planes are used in orienting the IT- and SC-cuts.

Tables of many atomic planes which are useful as reference planes by which to orient quartz piezoids are given by Heising.[1] A few of the more commonly used planes are listed in Table 11.2.

The enantiomorphic nature of quartz makes it necessary to consider the hand of the crystal in setting up a coordinate system. Fortunately the values of the coefficients of all the physical properties and the mathematical relationships between them become identical

Table 2.2 The B-M Indices of the Natural Faces in Quartz

	m	R	r	s	x
1	(10.0)	(01.1)	(10.1)	(11.1)	(51.1)
2	(0$\bar{1}$.1)	($\bar{1}$0.1)	($\bar{1}$1.1)	(1$\bar{2}$.1)	($\bar{6}$5.1)
3	($\bar{1}$1.0)	(1$\bar{1}$.1)	(0$\bar{1}$.1)	($\bar{2}$1.1)	(1$\bar{6}$.1)

[1] R. A. Heising, *Quartz Crystals for Electrical Circuits.* New York: Van Nostrand, 1946, p. 105.

if a right-hand coordinate system is used for right crystals and a left-hand coordinate system with left crystals. For this reason the IRE (now IEEE) Standards Committee has recommended that the following conventions be used with quartz crystals.

1. A right-hand coordinate system is used to describe the physical properties of a crystal of right quartz and a left-hand system for left quartz.
2. In a right-hand coordinate system a positive rotation is one which appears counterclockwise when observed from the positive end of the axis of rotation.

Because of the peculiar screwlike nature of the structure of quartz, it is immaterial which end of the Z-axis is chosen as positive. This is analogous to the easily confirmed observation that a right-hand screw is not changed to a left-hand screw by simply looking at it from the opposite end.

CULTURED QUARTZ

Most of the quartz used in the quartz crystal industry today (1980) is man-made or cultured quartz. (The term *artificial quartz* is to be avoided, since all quartz is crystalline SiO_2, whether crystallized in nature or in a factory.) Although the cost of cultured quartz per kilogram is generally higher than that of natural quartz, the cost per crystal unit is usually less. And in any case, the supply of natural quartz is inadequate to meet the demands of the industry. The cost per unit is less with cultured than with natural quartz because less labor and skill are required in orientation and cutting; little or no waste results from twinning and other defects; and the stones are grown to such size and shape that the minimum amount of quartz is wasted in cutting.

GROWTH OF CULTURED QUARTZ

Alpha quartz is grown from water solution. It is not possible to grow crystals of alpha quartz from the melt as is done with germanium,

silicon, and other crystals. The melting point of SiO_2 is above 1700°C. Above 573°C, which is called the Curie temperature, SiO_2 exists as beta quartz, which has a hexagonal instead of a trigonal structure. When a crystal of beta quartz is cooled through the Curie temperature to become alpha quartz, very large thermal stresses occur and the crystal often shatters. Even if it does not break, the crystal usually becomes electrically twinned.

Cultured quartz is grown in large, very strong autoclaves which are typically 3 to 5 m long and half a meter or more in diameter with walls 10 to 15 cm thick. They are mounted, usually underground, in a vertical position and surrounded with heating coils and thermal insulation. The electric power to the heating elements is controlled by a computer programmed to establish the proper thermal gradients in the autoclave and to change them as the growth proceeds.

The seed crystals are mounted in racks somewhat like the rungs of a ladder. Pure silica, in chunks having a volume of a few cubic centimeters, provides the nutrient for the crystals. It is placed in the bottom of the autoclave, which is then filled nearly full of water to which is added some alkaline material such as sodium carbonate. Naturally the purest materials are required as is great care with cleanliness. The quality of the product is critically dependent on these factors as well as on the growing conditions.

The autoclave is sealed and the temperature is raised to approximately 350°C. The liquid expands until it fills the autoclave and exerts pressures of the order of 1000 atm on its walls. At these temperatures the solubility of SiO_2 is quite appreciable and, as in the usual case, increases with the temperature.

The lower end of the autoclave where the nutrient is placed is maintained at a higher temperature than the upper end where the seed crystals are located. The solution, which is saturated at the higher temperature, rises by convection to the cooler region, where it becomes supersaturated and SiO_2 is deposited on the seed crystals. Consequently, crystalline quartz grows at the expense of the pure silica nutrient.

The crystal grows most rapidly in the Z-direction where the rate is typically 0.5 mm/day. Thus a Y-bar of cultured quartz having dimensions 2 × 3 × 15 cm can be grown in about 1 month. Figure 2.5 shows a typical Y-bar of cultured quartz.

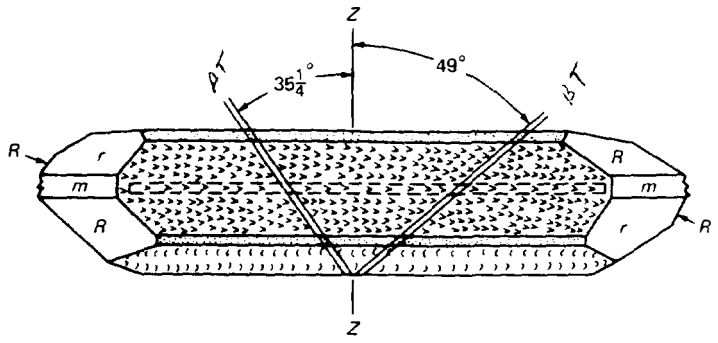

Fig. 2.5. Sketch of a specimen of cultured quartz grown in *Y*-bar form for use in fabricating AT- and BT-cut piezoids. The specimen is right-hand quartz with the positive end of the *X*-axis directed upward. The position of the seed crystal is indicated by the dotted lines. Compare the natural faces with those of Fig. 2.1. The lines sloping left from the *Z*-axis indicate the saw-cut position for cutting AT-cut plates. The lines sloping right are for the BT-cut.

ORIENTATION

Stones to be fabricated into AT- and BT-cut plates are usually grown in the form of *Y*-bars. Typically the seed crystal consists of a bar of quartz having a length of about 15 cm in the *Y*-direction, a width of 5 to 10 mm in the *X*-direction, and a thickness of 2 to 3 mm in the *Z*-direction. The seeds are usually cut from right-hand quartz, although this is of no particular importance except convenience. The final crystal has the form of a long bar with its maximum dimension in the *Y*-direction and its minimum dimension in the *X*-direction. The seed crystals are carefully selected to avoid twinning and other defects which could be propagated through the crystal as it grows.

Only two steps are required to obtain an accurately oriented AT- or BT-cut wafer using cultured quartz. This is very much simpler than the corresponding process using natural quartz, especially if most or all of the natural faces are absent. The first step is to grind a flat surface on the bar perpendicular to the *X*-axis. The bar is then mounted on this surface with the *X*-axis in a vertical position. The second step is to set the saw to cut parallel to the *X*-axis and at the correct angle with respect to the *Z*-axis. The correct angular position is achieved by the use of x-ray diffraction. The (10.1) planes which are parallel to the minor rhomb face (*r*) make an angle of 38°13′

with the *Z*-axis. The AT-cut makes an angle of approximately 35°15′ with the *Z*-axis. Therefore, the dihedral angle between the (10.1) planes and the AT-cut is about 2°58′ (the exact value depending on the frequency and temperature range over which the unit is to be used). This is the angle which is measured by x-ray diffraction.

The BT-cut makes an angle of about −49° with the *Z*-axis. The rotation is in the opposite sense from that of the AT-cut. The (20.3) planes make an angle of 49°44′ with the *Z*-axis and are commonly used for orienting the BT-cut.

DEFECTS IN QUARTZ

Although cultured quartz has largely replaced natural quartz in the piezoelectric industry, the latter is still preferred for a few applications where the highest performance is required. Significant differences do exist between natural and cultural quartz and, indeed, between samples of natural quartz, although very sophisticated techniques are required to demonstrate them. These differences are associated with crystalline imperfections which are primarily impurity atoms, interstitial atoms, and lattice vacancies.

It is well known that some specimens of natural quartz are smoky or straw-colored. It has long been known, too, that some specimens of natural quartz are darkened by exposure to x-rays or gamma radiation. The development of smokiness is accompanied by changes in the elastic constants resulting in changes in the resonant frequencies which, in BT-cut plates, may be as great as 0.02 percent. At one time this change of frequency was considered as a method of adjusting the frequency of quartz crystal units. The idea was soon abandoned because some samples of quartz do not darken nor do their elastic constants change with exposure to radiation. Furthermore, the smokiness and frequency changes are both reversible by heating the quartz to a temperature of about 200°C. If the quartz is heated in a dark room, a flash of light may be observed as the temperature passes through the temperature at which the smokiness disappears. Although this phenomenon, called thermoluminescence, is well understood and is the basis of a dosimeter used to monitor exposure to radiation, it would take us too far into the physics of solids to

discuss it further. It may be said, however, that crystalline defects are responsible for the effect.

Some impurities may be removed from quartz by placing the quartz in a strong electric field at elevated temperatures. Quartz which has been treated in this way is called *swept* quartz, since the impurity ions have been swept out by the electric field. Swept quartz is used in some very critical applications.

It seems likely that natural quartz grew at relatively low temperatures over very long periods of time. Cultured quartz, on the other hand, is grown at elevated temperatures in short periods of time. It is unavoidable that the number of interstitial atoms and lattice dislocations must increase as the growing temperature is increased. Consequently, the quality of cultured quartz is somewhat dependent upon the conditions under which it is grown.

The differences of growth conditions are reflected in the quality factor Q of the resonators made from the quartz. The presence of certain imperfections which produce absorption bands in the infrared absorption spectrum of the crystal have been correlated with the degradation of the Q of the resonator. Consequently infrared measurements are sometimes used to select quartz of superior quality for use in the most critical applications.

SYMMETRY RELATIONS IN CRYSTALS

Some properties of crystals are not unlike the corresponding properties in noncrystalline materials; for instance, density and specific heat. Such properties are called scalar quantities. Most physical properties, however, are dependent upon direction in the crystal. These are called tensor quantities.

The speed of propagation of a sound wave in a glass rod is independent of the direction in which the rod was cut from the original piece of glass. However, the speed of sound in a similar rod cut from a crystal of quartz is dependent upon the orientation of the rod relative to the crystallographic axes of the quartz. Thus, whereas a given physical property has only one value in a noncrystalline or amorphous material, it may have two or more in a crystalline material. It might be thought that the values of the coefficients in different directions would all be independent of each other, but they

are not. Symmetry conditions in the crystal impose definite restrictions on both the number of independent coefficients and their values.

As an example of the restrictions imposed by symmetry conditions, we may consider the index of refraction of light in quartz. The index of refraction is the ratio of the velocity of light in vacuum to the velocity in the medium. A ray of yellow light traveling in the Z-direction in quartz travels at such a velocity that the index of refraction is 1.544. The index of refraction for light of the same color traveling in a direction perpendicular to the Z-direction is 1.553. A crystal, such as quartz, which has two indices of refraction, is said to be birefringent.

In the same way, the dielectric constant of quartz is different for fields applied parallel and perpendicular to the Z-axis. The value for fields in the Z- direction $k_{\parallel} = 4.60$, whereas the value for fields in the perpendicular direction $k_{\perp} = 4.51$.

The peculiar nature of crystals requires a special type of mathematics for use in solving problems involving their anisotropic properties. Matrix algebra is the mathematical tool best suited for the purpose. Since it is necessary to make some use of matrix algebra in designing quartz crystal units, a brief introduction to this very useful branch of mathematics will be given. A more complete treatment with further applications to problems of piezoid design has been given by Bond.[2]

THE ELEMENT OF MATRIX ALGEBRA

Matrix algebra is a branch of mathematics which is especially useful for handling sets of linear algebraic equations. Consider, for example, the set of linear equations

$$\begin{aligned} y_1 &= a_{11}x_1 + a_{12}x_2 + a_{13}x_3 \\ y_2 &= a_{21}x_1 + a_{22}x_2 + a_{23}x_3 \\ y_3 &= a_{31}x_1 + a_{32}x_2 + a_{33}x_3 \end{aligned} \tag{1}$$

[2] Walter L. Bond, "The Mathematics of the Physical Properties of Crystals," *B.S.T.J.*, 22: 1-72 (1943).

in which the y's are variables and the a_{ij}'s are constant coefficients. The equation above is written in matrix notation as

$$y = ax \tag{2}$$

where y is written for the array $\begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix}$, x for the array $\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$

and a for the matrix $\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$

Expression (2) is made formally equal to expression (1) by defining an operation called matrix multiplication. Written out in full, (2)

$$\text{becomes} \begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} \tag{3}$$

Matrix multiplication consists of forming the sum of the products obtained by multiplying the terms in the rows of a by the corresponding terms in the column of x. Mechanically this is readily done by moving a finger of the left hand across the rows of a while a finger of the right hand moves down the column of x performing the multiplication at each step and accumulating the sum mentally. Computer programs are readily prepared for performing the operation. By defining multiplication in this way, (3) is made formally equivalent to (1).

The value of matrix algebra is due to the ease with which it permits handling large sets of simultaneous equations. For example, it can be used to "solve" sets of simultaneous equations of the following type.

Let Eq. (1) above be represented by

$$y = ax \tag{4}$$

and let

$$x = bz \tag{5}$$

represent the set

$$\begin{aligned} x_1 &= b_{11}z_1 + b_{12}z_2 + b_{13}z_3 \\ x_2 &= b_{21}z_1 + b_{22}z_2 + b_{23}z_3 \\ x_3 &= b_{31}z_1 + b_{32}z_2 + b_{33}z_3 \end{aligned} \tag{6}$$

The x's may be eliminated and the y's expressed in terms of the z's by writing formally

$$y = abz \tag{7}$$

where bz is substituted for x in (4). It must be noted that the substitution must be made in the particular order, for ab is not equivalent to ba. Matrix multiplication is *not* commutative.

Written out in full, (7) becomes

$$\begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} \begin{pmatrix} z_1 \\ z_2 \\ z_3 \end{pmatrix} \tag{8}$$

In "solving" (8), the product ab is first formed. The product of ab is a square matrix, the ij term of which is found by forming the product of the ith row of a with the jth column of b. Carrying out the multiplication in this way results in the matrix

$ab =$

$$\begin{pmatrix} a_{11}b_{11}+a_{12}b_{21}+a_{13}b_{31} & a_{11}b_{12}+a_{12}b_{22}+a_{13}b_{32} & a_{11}b_{13}+a_{12}b_{23}+a_{13}b_{33} \\ a_{21}b_{11}+a_{22}b_{21}+a_{23}b_{31} & a_{21}b_{12}+a_{22}b_{22}+a_{23}b_{32} & a_{21}b_{13}+a_{22}b_{23}+a_{23}b_{33} \\ a_{31}b_{11}+a_{32}b_{21}+a_{33}b_{31} & a_{31}b_{12}+a_{32}b_{22}+a_{33}b_{32} & a_{31}b_{13}+a_{32}b_{23}+a_{33}b_{33} \end{pmatrix}$$

Finally the product ab is multiplied into z giving

$$\begin{aligned} y_1 &= (a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31})z_1 + (a_{11}b_{12} + a_{12}b_{22} + a_{13}b_{32})z_2 + \\ &\quad (a_{11}b_{13} + a_{12}b_{23} + a_{13}b_{33})z_3 \\ y_2 &= (a_{21}b_{11} + a_{22}b_{21} + a_{23}b_{31})z_1 + (a_{21}b_{12} + a_{22}b_{22} + a_{23}b_{32})z_2 + \\ &\quad (a_{21}b_{13} + a_{22}b_{23} + a_{23}b_{33})z_3 \\ y_3 &= (a_{31}b_{11} + a_{32}b_{21} + a_{33}b_{31})z_1 + (a_{31}b_{12} + a_{32}b_{22} + a_{33}b_{32})z_2 + \\ &\quad (a_{31}b_{13} + a_{32}b_{23} + a_{33}b_{33})z_3 \end{aligned}$$

In the last set of equations the x's have been eliminated and the y's are expressed in terms of the z's.

A square matrix is one having equal numbers of rows and columns. In a square matrix the diagonal from upper left to lower right is called the major diagonal. A matrix consisting of 1's on the major diagonal with all other terms zero is called the identity matrix I. Multiplying any matrix by I leaves the matrix unchanged. I in matrix algebra is therefore analogous to unity in ordinary algebra. The reciprocal matrix A^{-1} is defined by

$$A\,A^{-1} = I$$

The matrix equation $Y = AX$ can be considered to be solved for X by writing

$$A^{-1}Y = A^{-1}AX = IX = X$$

Rules for computing the reciprocal matrix may be found in books on the subject of matrix algebra. A simple method involves the following four steps.

1. Interchange rows and columns.
2. Replace each term by the determinant of its minor. (The minor of a given term is the remainder of the matrix after the row and column containing the given term have been removed.)
3. Multiply alternate terms by 1 and -1 starting with 1 in the upper-left-hand-corner.
4. Divide each term by the determinant of the original matrix.

To illustrate these steps, we compute the reciprocal of the matrix A where

$$A = \begin{pmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 2 & 8 & 4 \end{pmatrix}$$

The application of step 1 gives

$$\begin{pmatrix} 1 & 4 & 2 \\ 2 & 5 & 8 \\ 3 & 6 & 4 \end{pmatrix}$$

Step 2 gives

$$\begin{pmatrix} -28 & -16 & -3 \\ 4 & -2 & -6 \\ 22 & 4 & -3 \end{pmatrix}$$

Step 3 gives

$$\begin{pmatrix} -28 & 16 & -3 \\ -4 & -2 & 6 \\ 22 & -4 & -3 \end{pmatrix}$$

Finally, using step 4,

$$A^{-1} = \begin{pmatrix} -28/30 & 16/30 & -3/30 \\ -4/30 & -2/30 & 6/30 \\ 22/30 & -4/30 & -3/30 \end{pmatrix}$$

It can readily be shown that

$$A^{-1}A = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = I$$

The reciprocal matrix can be considered to be the solution of the original matrix, for if $I = AX$, then $X = A^{-1}I$. It follows therefore that the reciprocal matrix is defined only for a square matrix. The calculation of the reciprocal of a large matrix can be quite tedious, but computer programs are available for computing A^{-1} for any matrix.

ROTATION OF AXES

One of the principle applications of matrix algebra to the physics of crystals is that of determining the values of the coefficients of the physical properties for any given direction in the crystal. This is especially important in the design of piezoids, which must often be oriented in such a way that the directions of the electric fields and wave propagation are not parallel to the crystallographic axes. With the aid of matrix algebra it is possible to compute the value of any

coefficient provided only that the corresponding values are known for the directions of the crystallographic axes.

To illustrate how this is done, we first show how to find the components of a vector in a new coordinate system given the components in the original system. Let the vector **V** have the components V_x, V_y, V_z in the right-hand coordinate system XYZ. Then let the coordinate system be rotated about the X axis by an angle θ forming the new coordinate system $XY'Z'$.

It is easy to see from Fig. 2.6 that the components of the vector V' in the new system expressed in terms of the components of V in the old system are

$$\begin{aligned} V'_x &= V_x \\ V'_y &= V_y \cos\theta + V_z \sin\theta \\ V'_z &= -V_y \sin\theta + V_z \cos\theta \end{aligned} \tag{9}$$

In matrix notation the set of equations above may be written as

$$V' = aV$$

where a is the matrix

$$a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & c & s \\ 0 & -s & c \end{pmatrix} \quad \text{in which} \quad \begin{aligned} c &= \cos\theta \\ s &= \sin\theta \end{aligned} \tag{10a}$$

The matrix a may be thought of as performing a rotation of the vector **V** by an angle θ about the X axis.

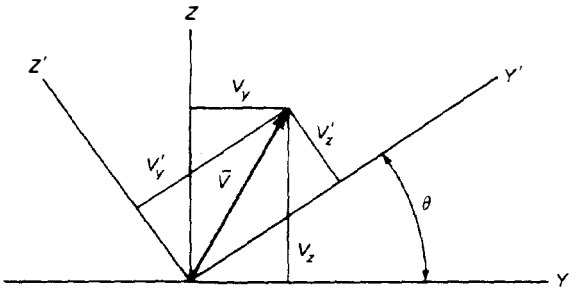

Fig. 2.6. Coordinate system XYZ rotated by an angle θ to form a new coordinate system $XY'Z'$.

In the same way the matrix

$$b = \begin{pmatrix} c & 0 & -s \\ 0 & 1 & 0 \\ s & 0 & c \end{pmatrix} \quad \text{in which} \quad \begin{matrix} c = \cos\psi \\ s = \sin\psi \end{matrix} \tag{10b}$$

performs a rotation of angle ψ about the Y axis. The matrix

$$c = \begin{pmatrix} c & s & 0 \\ -s & c & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{in which} \quad \begin{matrix} c = \cos\phi \\ s = \sin\phi \end{matrix} \tag{10c}$$

performs a rotation of ϕ about the Z axis.

To illustrate the application of the method we may consider any vector property of the crystal such as electric induction, magnetic induction, or thermal or electric conductivity. We use the first to illustrate the procedure.

In an isotropic material the electric induction **D** is related to the electric-field intensity **E** by the equation $\mathbf{D} = k\,\mathbf{E}$, where k is called the dielectric constant. **D** and **E** are parallel. In an anisotropic material, such as quartz, **D** and **E** are not necessarily parallel and in general each component of **D** depends on all three components of **E**. We therefore have for the components of the induction **D** in terms of the components of the electric field **E**,

$$\begin{aligned} D_x &= k_{11}E_x + k_{12}E_y + k_{13}E_z \\ D_y &= k_{21}E_x + k_{22}E_y + k_{23}E_z \\ D_z &= k_{31}E_x + k_{32}E_y + k_{33}E_z \end{aligned} \tag{11}$$

or in matrix notation

$$D = kE$$

Both **D** and **E** being vectors, are rotated according to the rules developed above, so that for a rotation of axes by the matrix a we have

$$D' = aD \quad \text{and} \quad E' = aE \quad \text{and} \quad a^{-1}E' = a^{-1}aE = E$$

$$D' = a\,k\,E = a\,k\,a^{-1}\,E'$$

so that $D' = k'E'$ where $k' = a\,k\,a^{-1}$

The convenience and brevity of the notation above should not be permitted to obscure the physical picture of the operation.

A very important and powerful application of the rotation of axes is involved in investigating the effects of crystal symmetry. For example, we will show that of the nine possible terms in the matrix for the dielectric constant of quartz, all but three are zero and two of these are equal. The same result can be obtained for any other vector property.

The Z-axis in quartz is, as we have seen, an axis of three fold symmetry. A rotation of 120° about the Z-axis must, therefore, leave all the physical properties unchanged. As an example we will perform such a rotation on the dielectric matrix [Eq. (11)]. For a rotation of 120° about the Z-axis, we have from Eq. (10c),

$$a = \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad a^{-1} = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The k matrix is, of course,

$$k = \begin{pmatrix} k_{11} & k_{12} & k_{13} \\ k_{21} & k_{22} & k_{23} \\ k_{31} & k_{32} & k_{33} \end{pmatrix}$$

the $k' = aka^{-1}$ matrix for a rotation of 120° about the Z axis is then

$$k' = \begin{pmatrix} 1/4\,k_{11} - \sqrt{3}/4\,k_{21} & \sqrt{3}/4\,k_{11} - 3/4\,k_{21} & -1/2\,k_{13} + \sqrt{3}/2\,k_{23} \\ +\sqrt{3}/4\,k_{12} + 3/4\,k_{22} & +1/4\,k_{12} - \sqrt{3}/4\,k_{22} & \\ \sqrt{3}/4\,k_{11} + 1/4\,k_{21} & 3/4\,k_{11} + \sqrt{3}/4\,k_{21} & -\sqrt{3}/2\,k_{13} - 1/2\,k_{23} \\ -3/4\,k_{12} - \sqrt{3}/4\,k_{22} & +\sqrt{3}/4\,k_{12} + 1/4\,k_{22} & \\ -1/2\,k_{31} + \sqrt{3}/2\,k_{32} & -\sqrt{3}/2\,k_{31} - 1/2\,k_{32} & k_{33} \end{pmatrix}$$

Since any rotation which is compatible with symmetry conditions must leave the values of the coefficients unchanged, it follows that

k_{11} must be equal to k'_{11}, $k_{12} = k'_{12}$, etc. These relations lead to a set of nine simultaneous equations which are satisfied if and only if

$$k_{21} = k_{13} = k_{31} = k_{12} = k_{23} = k_{32} = 0$$
$$\text{and} \quad k_{11} = k_{22} \qquad k'_{33} = k_{33}$$

We thus find that quartz has only two independent dielectric constants, k_{11} and k_{33}, i.e., the values perpendicular and parallel, respectively, to the Z-axis. To prove that k_{33} is indeed not equal to k_{11} it is necessary to perform another rotation of 180° about either the X- or Y-axis. This operation, which is also compatible with the symmetry of quartz, is carried out in the same way and leads to the result that the dielectric matrix for quartz is

$$k = \begin{pmatrix} k_{11} & 0 & 0 \\ 0 & k_{11} & 0 \\ 0 & 0 & k_{33} \end{pmatrix}$$

The dielectric matrix for quartz thus contains only three nonzero terms and two of these are equal. A similar matrix describes the thermal and electric conductivities and all other vector properties of quartz. The fact that many of the possible coefficients are zero is a consequence of the symmetry conditions in the crystal and fortunate for the individual who finds it necessary to make computations which involve the physical properties of crystalline materials.

THE DIELECTRIC CONSTANT AND THERMAL EXPANSION

As illustrations of the use of the matrix algebra we will compute the dielectric constant and thermal expansion coefficient for an arbitrary direction in the quartz crystal. To do so we need only compute the values in the YZ-plane, since the value of any vector quantity is constant in the XY-plane in quartz.

We will determine the dielectric constant in the thickness direction of a quartz plate whose normal makes an angle θ with the Z-axis by performing a rotation about the X-axis. We have already seen that $D' = k'E'$, where $k' = a\,k\,a^{-1}$. The matrix which performs a rotation

about the X-axis is given by Eq. (10a). Its reciprocal can be computed by the recipe given on page 28. The required operation is therefore

$$k' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & c & s \\ 0 & -s & c \end{pmatrix} \begin{pmatrix} k_{11} & 0 & 0 \\ 0 & k_{11} & 0 \\ 0 & 0 & k_{33} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & c & -s \\ 0 & s & c \end{pmatrix}$$

where $c = \cos\theta$ and $s = \sin\theta$.

Carrying out the indicated operations gives

$$k' = \begin{pmatrix} k_{11} & 0 & 0 \\ 0 & k_{11}c^2 + k_{33}s^2 & (k_{33} - k_{11})sc \\ 0 & (k_{33} - k_{11})sc & k_{11}s^2 + k_{33}c^2 \end{pmatrix}$$

If $\theta = 0$ the matrix k' reduces to the matrix k and if $\theta = 90°$, the result is to interchange the Y- and Z-axes. The meaning is obvious geometrically.

In order to interpret the significance of the terms in the k' matrix, it is necessary to recall the significance of a matrix which is simply a table of the coefficients of the terms in a set of linear equations. The term k_{ij} relates the induction in the i direction with the electric field in the j direction. The terms $k'_{12} = k'_{21} = k'_{13} = k'_{31} = 0$ imply that no electric displacement is induced in the X'-direction by components of an electric field in the Y'- and Z'-directions and that no electric displacement in the Y'- or Z'-directions is produced by a field in the X'-direction.

The term $k'_{22} = k_{11} \cos^2\theta + k_{33} \sin^2\theta$ indicates that the electric displacement in the Y'-direction depends on both k_{11} and k_{33} as well as the angle θ. The same is true of k'_{33}.

The terms $k'_{23} = k'_{32} = (k_{33} - k_{11}) \sin\theta \cos\theta$, which is not always zero, implies that a field in the Y'-direction may produce a displacement in the Z'-direction, and vice versa. It is a bit surprising at first to find a component of electric displacement at right angles to the electric field which produces the displacement. This, of course, does not occur in isotropic materials. But in a crystalline dielectric the resultant of the displacement may not be parallel to the electric field;

it may be said to "follow the grain of the crystal" somewhat as a nail tends to follow the grain of the wood.

We now compute the effective dielectric constant for an AT-cut plate in which the plate normal makes an angle of (approximately) 55° with the Z-axis. The component of the dielectric constant k' in the direction normal to the plate is given by

$$k'_{33} = k_{11} \sin^2 55° + k_{33} \cos^2 55°$$

Since[3] $k_{11} = 4.51$ and $k_{33} = 4.60$, the value of the effective dielectric constant for the AT-cut plate is

$$k'_{33} = 4.54$$

Later we will have occasion to use this value in calculating the static capacitance of the crystal unit.

It is of interest to calculate the value of k'_{32}, which yields the component of the displacement in the Y'-direction. It has the value

$$\begin{aligned} k'_{32} &= (k_{33} - k_{11}) \sin 55° \cos 55° \\ &= 0.042 \end{aligned}$$

The Z'-component of the displacement is large compared with the Y'-component because the values of k_{11} and k_{33} are so nearly equal. Consequently, the orthogonal component may usually be disregarded in computing the effective dielectric constant in quartz. This may not be possible in other crystals in which the values are much different. In the example of the AT-cut, the displacement makes an angle arctan (0.042/4.54), which is about 0.5°, with the direction of the electric field.

Exactly the same procedure is followed in calculating other vector-vector properties such as the electrical and thermal conductivities. Again it is found that the direction of current flow is not necessarily

[3] The dielectric constants of alpha quartz at 20°C are $k_{33} = k_{\parallel} = 4.60 \pm 0.01$ and $k_{11} = k_{\perp} = 4.51 \pm 0.01$. Virgil E. Bottom, "Dielectric Constants of Quartz," *J. Appl. Phys.*, 43 (4): 1493–1495 (1972).

parallel to the applied field nor is the direction of heat flow necessarily parallel to the temperature gradient.

The linear coefficient of thermal expansion for an arbitrary direction in a crystal is calculated in a slightly different way, since temperature is a scalar quantity. By a proper choice of axes (which in quartz is the usual XYZ axial system) the linear coefficients of thermal expansion can be expressed in the form

$$\alpha = \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix}$$

The change $\Delta \mathbf{L}$ in a vector $\mathbf{L}$ resulting from unit temperature change (Fig. 2.7) may be expressed in matrix notation by

$$\Delta L = \alpha L$$

Since both $\mathbf{L}$ and $\Delta \mathbf{L}$ are vectors they transform as

$$L' = aL \qquad \text{and} \qquad \Delta L' = a \Delta L$$

where[4]

$$a = (\cos\phi \sin\theta, \sin\phi \sin\theta, \cos\theta)$$

is the matrix of the coordinates of the vector L. Hence $\Delta L' = \alpha' L'$, where $\alpha' = a \alpha a^{-1}$.

Carrying out the indicated operation,

$$\begin{pmatrix} \cos\phi \sin\theta, \sin\phi \sin\theta, \cos\theta \end{pmatrix} \quad \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix} \quad \begin{pmatrix} \cos\phi \sin\theta \\ \sin\phi \sin\theta \\ \cos\theta \end{pmatrix}$$

we have

$$\alpha'_{\theta,\phi} = \alpha_{11} \cos^2 \phi \sin^2\theta + \alpha_{22} \sin^2 \phi \sin^2 \theta + \alpha_{33} \cos^2 \theta$$

[4] The IEEE (or IRE) notation is used in the equations above, whereas the Bond notation is used in Eqs. (87) and (92). This accounts for the difference in the value of θ for the AT-cut. See Fig. 8.1.

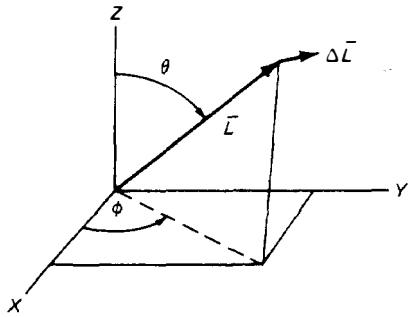

Fig. 2.7. The effect of thermal expansion is to change L to L + Δ L.

In quartz $\alpha_{11} = \alpha_{22}$ so the expression above reduces to

$$\alpha'_\theta = \alpha_{11} \sin^2 \theta + \alpha_{33} \cos^2 \theta$$

In the case of the AT-cut plate in which $\theta = 55°$ (see footnote 4), the linear coefficient of thermal expansion in the thickness direction is

$$\alpha_{\theta = 55°} = (14.3 \sin^2 55° + 7.8 \cos^2 55°) \times 10^{-6} \text{ per } °C$$
$$= 12.2 \times 10^{-6} \text{ per } °C$$