HIGHER ORDER TEMPERATURE COEFFICIENTS OF THE ELASTIC STIFFNESSES AND COMPLIANCES OF ALPHA-QUARTZ

INTRODUCTION

The general theory of the propagation of plane waves in anisotropic media, as derived by Green [1] in 1839, results in three possible types of plane waves for any direction of propagation, each wave having a different velocity and the three directions of vibration being mutually perpendicular.

In 1877 Christoffel [2] wrote the differential equations of motion governing plane waves in terms of strain instead of stress. The six so-called Christoffel moduli Γ_{ik} which are combinations of the 21 stiffnesses $c_{\lambda\mu}$ (λ,μ = 1,2...,6) and the direction cosines of the wave propagation were thereby introduced. In order to describe plane waves in a general triclinic material, only the six so-called Christoffel moduli are required as the strain components perpendicular to the direction of propagation are prohibited by lateral inertia.

The solution of the three second-order differential equations derived by Christoffel leads to three resulting stiffnesses c_m (m = 1, 2, 3) which are related to the velocities of wave propagation and the directions of the displacements which are generally neither parallel nor perpendicular to the direction of the wave propagation.

The resonance frequencies of thickness modes of an infinite crystal plate, based on Christoffel's equations, were derived in 1932 by Koga [3] in closed form, but correspondingly simple solutions for the thickness modes cannot be obtained for a bounded plate. The equations for thickness-shear and flexural vibrations of crystal plates have been solved in a series of papers by Mindlin [4]. Koga's solution, however, can be considered a zero-order approximation, and the resulting stiffness c_m, leading to values of the wave velocity for each of the three thickness modes of motion, approximates frequency expressions close to the values obtained by a higher approximation. The approximate equations can be used to determine the higher order temperature coefficients of the elastic stiffnesses.

The first-order temperature coefficients of the stiffnesses and compliances of alpha-quartz were originally derived by Bechmann [5] in 1934, based on Christoffel's theory, using measured values for the temperature coefficients of frequency of thickness modes of plates and extensional modes of bars in the 20° to 60°C temperature range. These temperature coefficients of the stiffnesses are of interest for practical application. The first-order zero temperature coefficients of frequency of AT- or BT-type quartz plates, for example, can be calculated using these values. The temperature coefficients of the elastic stiffnesses are not linear with temperature in a wider temperature range, and temperature coefficients of higher order have to be taken into consideration by use of a power series. It is sufficient to determine the first three orders of temperature coefficients of frequencies and stiffnesses to obtain satisfactory agreement between measurements and calculations. Difficulties would be encountered, however, if the temperature dependence were described using temperature coefficients of orders higher than three.

A modified theory of elasticity was considered by Laval [6] in 1951, and later by others, proposing that the asymmetrical part of the stress tensor enters into the constitutive relations, thereby increasing the number of elastic constants compared with the classical theory.

Laval's theory of elasticity demands, e.g., for the crystal class D_{2d}, two different stiffnesses c_{44} and c_{77} instead of the elastic-shear stiffness c_{44}. Jaffe and Smith [7] have carried out new measurements on ammonium dihydrogen phosphate by two methods: (1) measurements of the piezoelectric resonances, and (2) measurements using the pulse echo method, both giving the shear elastic stiffnesses directly. Measurements of shear wave velocities by the two simple methods show the velocities of the two waves involving shear between the Y- and Z-axes to be equal well within the experimental error limits.

According to Laval's theory of elasticity the number of elastic constants for the crystal class D_3 is increased by $c_{55} \neq c_{44}$ and c_{17}. Zubov and Firsova [8] carried out a new determination of the elastic stiffnesses of quartz using the increased number of elastic stiffnesses. Their values fall within the limits of accuracy of measurements. The experimental values for the frequency constants of various quartz plates vibrating in thickness modes, and previously used for determination of the elastic stiffnesses given by Bechmann [9], have been recalculated with respect to the new theory. He found that the values for c_{44} and c_{55}, c_{14} and c_{17} are so close and so critical that from an experimental point of view, no conclusions can be drawn nor decisions made as to whether the classical theory or the Laval theory is valid. Recent studies by Mindlin [10] show that the principles of conservation of momentum and energy are not fulfilled by Laval's theory. In the following, determination of the temperature coefficients of the stiffnesses is based on the classical theory of elasticity. Figure 1 shows the measured frequency-temperature behavior of the AT, BT, CT, DT, and RT cuts and, in addition, the so-called optimum angle of an AT cut, so defined that its frequency temperature dependence, in the temperature range $-40°$ to $90°C$, for example, is reduced to a minimum. Table 1 lists the angles of orientation θ for these cuts and the values for their second- and third-order temperature coefficients of frequency b and c respectively.

CHRISTOFFEL'S THEORY OF PLANE ELASTIC WAVES IN CRYSTALS

Christoffel's theory of the propagation of plane elastic waves in crystals is well known and treated in many papers and text books [11]. It is therefore unnecessary to repeat this theory.

The differential equation for plane waves in anisotropic media is written considering one dimension, that of the propagation s with the direction cosines α_1, α_2, α_3 in the form

$$\rho \frac{\partial^2 \xi}{\partial t^2} - c \frac{\partial^2 \xi}{\partial s^2} = 0 , \tag{1}$$

where c is

$$c = \Gamma_{11}p^2 + \Gamma_{22}q^2 + \Gamma_{33}r^2 + 2\Gamma_{23}qr + 2\Gamma_{31}rp + 2\Gamma_{12}pq \tag{2}$$

and

$$\Gamma_{ik} = \sum_{jl}^{3} c_{ij,kl}\ \alpha_j \alpha_l , \tag{3}$$

the Christoffel stiffnesses, a combination of the stiffnesses c_{ik} and the direction cosines. The constants p, q, r, when normalized by $p^2 + q^2 + r^2 = 1$, are the direction cosines for the displacement ξ_i. To solve Eq. (1) for an infinitely extended plate, the boundary conditions for the free plate

$$\frac{\partial \xi}{\partial s} = 0 \text{ for } s = 0 \text{ and } s = t \text{ (t is the thickness of the plate)}$$

have to be introduced.

When considering the propagation of elastic waves in a piezoelectric material, an additional piezoelectric stress due to the electric field E must be introduced. The elastic properties of an ionic lattice, which cannot be discussed separately, must be considered in conjunction with the theory of piezoelectric and dielectric effects. Because of the coupling of the strain and stress tensors with the vectors of electric field and electric displacement, a slight modification of the elastic stiffnesses $c_{\lambda\mu} = c_{\lambda\mu}^E$ occurs, becoming $c_{\lambda\mu}^{D_s}$, where D_s refers to constant normal displacement. For infinite plates, on the basis of Maxwell's equation, D_{normal} ($= D_s$) and $E_{tangent}$ must be continuous and therefore the related coefficients $c_{\lambda\mu}$ and Γ_{ik} are mixed with $D = 0$ normal to, $E = 0$ parallel to, the wavefront. Consequently, Γ_{ik}^E becomes Γ_{ik}^D, the direction cosines of the displacement change, and the resulting stiffnesses c_m^E become c_m^D. Between the displacement $\xi(p, q, r)$ and the resulting elastic stiffness c, the system of linear equations exists:

$$\begin{aligned} p\Gamma_{11} + q\Gamma_{12} + r\Gamma_{13} &= pc \\ p\Gamma_{12} + q\Gamma_{22} + r\Gamma_{23} &= qc \\ p\Gamma_{13} + q\Gamma_{23} + r\Gamma_{33} &= rc\ . \end{aligned} \tag{3a}$$

The secular equation defining the three resulting stiffnesses c_m of a piezoelectric material as a consequence of Eq. (3a) is given by

$$\begin{vmatrix} \Gamma_{11}^{D_s} - c^{D_s} & \Gamma_{12}^{D_s} & \Gamma_{13}^{D_s} \\ \Gamma_{12}^{D_s} & \Gamma_{22}^{D_s} - c^{D_s} & \Gamma_{23}^{D_s} \\ \Gamma_{13}^{D_s} & \Gamma_{23}^{D_s} & \Gamma_{33}^{D_s} - c^{D_s} \end{vmatrix}$$

$$\equiv \begin{vmatrix} \Gamma_{11}^E - c^{D_s} & \Gamma_{12}^E & \Gamma_{13}^E & \Xi_1 \\ \Gamma_{12}^E & \Gamma_{22}^E - c^{D_s} & \Gamma_{23}^E & \Xi_2 \\ \Gamma_{13}^E & \Gamma_{23}^E & \Gamma_{33}^E - c^{D_s} & \Xi_3 \\ \Xi_1 & \Xi_2 & \Xi_3 & -\epsilon_s \end{vmatrix} = 0. \tag{4}$$

The expressions for Γ_{ik}^E and $\Gamma_{ik}^{D_s}$ at constant electric field and constant normal displacement, respectively, in these equations are related by

$$\Gamma_{ik}^{D_s} = \Gamma_{ik}^E + \frac{1}{\epsilon_s} \Xi_i \Xi_k\ . \tag{5}$$

The direction cosines p_τ, q_τ, r_τ ($\tau = 1,2,3$) can be calculated from any two of the three equations (3a), for example, from the second and the third equations of (3a), one obtains

$$p_\tau = \frac{1}{W_\tau} [(\Gamma_{22} - c_\tau)(\Gamma_{33} - c_\tau) - \Gamma_{23}^2],$$

$$q_\tau = \frac{1}{W_\tau} [\Gamma_{13}\Gamma_{23} - \Gamma_{12}(\Gamma_{33} - c_\tau)],$$

$$r_\tau = \frac{1}{W_\tau} [\Gamma_{12}\Gamma_{23} - \Gamma_{13}(\Gamma_{22} - c_\tau)];$$

$$W_\tau = \{[(\Gamma_{22} - c_\tau)(\Gamma_{33} - c_\tau) - \Gamma_{23}^2]^2 + [\Gamma_{13}\Gamma_{23} - \Gamma_{12}(\Gamma_{33} - c_\tau)]^2 + [\Gamma_{12}\Gamma_{23} - \Gamma_{13}(\Gamma_{22} - c_\tau)]^2\}^{1/2}.$$

The effective piezoelectric constant, corresponding to the eigenvalue c_m, is

$$e_m = \sum_i^3 \beta_{im} \cdot \Xi_i ,$$

where the direction cosines β for the displacements follow from Eq. (4). When the components of the third-order piezoelectric tensor are written with three indices, the following conditions hold:

$$e_{n,kl} = e_{n,lk} ,$$

reducing the possible 27 combinations of coefficients to 18. Similarly, when the components of the fourth-order stiffness tensor are written with four indices, the following conditions hold:

$$c_{ij,kl} = c_{ij,lk} = c_{ji,kl} = c_{ji,lk} = c_{kl,ij} = c_{kl,ji} = c_{lk,ij} = c_{lk,ji} ,$$

reducing the 81 possible combinations of the indices to 21. The following table shows the scheme used for converting the double indices i,j (i,j = 1,2,3) to a single index μ (μ = 1, 2 . . . , 6).

ij		μ
11	→	1
22	→	2
33	→	3
23	→	4
31	→	5
12	→	6

The expressions for Christoffel's stiffnesses $\Gamma_{ik} = \Gamma_{ki}$, (i,k = 1,2,3), the piezoelectric stress constants Ξ_l (l = 1,2,3), and the permittivity ϵ_s of a general triclinic crystal as given in Eq. (4) follow from Table 2, e.g.,

$$\Gamma_{11} = c_{11}\alpha_1^2 + c_{66}\alpha_2^2 + c_{55}\alpha_3^2 + 2c_{56}\alpha_2\alpha_3 + 2c_{51}\alpha_3\alpha_1 + c_{16}\alpha_1\alpha_2 . \qquad (6)$$

This scheme reduces considerably for quartz which belongs to the trigonal crystal class D_3. The stiffnesses c_{11}, c_{33}, c_{12}, c_{13}, c_{44}, c_{14} are finite. The following relationships hold: $c_{22} = c_{11}$, $c_{55} = c_{44}$, $c_{66} = \frac{1}{2}(c_{11} - c_{12})$, $c_{13} = c_{23}$ and $-c_{24} = c_{56} = c_{14}$. Further, $c_{15} = c_{16} = c_{25} = c_{26} = c_{35} = c_{36} = 0$. The piezoelectric constants are zero except $e_{11} = -e_{12} = -e_{26}$ and $e_{14} = -e_{25}$. For the dielectric constants $\epsilon_{22} = \epsilon_{11}$ and $\epsilon_{12} = \epsilon_{13} = \epsilon_{21} = \epsilon_{23} = \epsilon_{31} = \epsilon_{32} = 0$ hold. The scheme of the Christoffel stiffnesses Γ_{ik}, the piezoelectric stress constants Ξ_l, and the permittivity ϵ_s reduces for the trigonal crystal class D_3, which includes alpha-quartz, to the scheme shown in Table 3.

Considering the eigenfrequencies $\omega = 2\pi f$ of an infinitely extended plate vibrating in thickness modes, introducing $c = \frac{\rho\omega^2}{k^2}$, and taking into account the boundary conditions $\cos\frac{kt}{2} = 0$

having the solution $\frac{kt}{2} = \frac{n\pi}{2}$, the frequency in first approximation is

$$f_m^{(n)} = \frac{n}{2t}\sqrt{\frac{c_m^{D_s}}{\rho}}\,, \quad (m = 1, 2, 3) \tag{7}$$

where n is an odd integer. Correction terms, due to the piezoelectric effect and coupling with flexural modes, are omitted. The frequency $f_m^{(n)}$ for the nth overtone for mode m is determined by the eigenvalue $c_m^{D_s}$, the thickness of the plate t, and the density ρ. For practical purposes it is more convenient to consider the frequency constant $N = f \cdot t$, rather than the frequency, as the frequency f and the thickness t are the measured quantities. Generally, three solutions for the frequency f_m $(m = 1, 2, 3)$ of the thickness vibrations and their overtones exist for each individual plate and in the following are designated as modes A, B, and C. Mode A is essentially the thickness-extensional mode while B and C are essentially thickness-shear modes. The frequencies for each plate always follow in the sequence $f_A > f_B > f_C$.

The equation for the temperature behavior of the frequency can be developed in the following power series

$$\frac{f - f_o}{f_o} = \frac{\Delta f}{f_o} = \sum_{n=1}^{3} Tf^{(n)} (T - T_o)^n , \tag{8}$$

where

$$Tf^{(n)} = \frac{1}{n!\, f_o}\left(\frac{\partial^n f}{\partial T^n}\right)_{T = T_o}, \tag{8a}$$

$Tf^{(n)}$ $(n = 1, 2, 3)$ being designated a, b, and c respectively. T is the variable temperature and T_o the reference temperature.

The relationships between the first-order temperature coefficients of frequency $Tf^{(1)}$ and the first-order temperature coefficients of the stiffnesses $Tc_{\lambda\mu}^{(1)}$ are given by

$$2Tf^{(1)} = Tc^{(1)} - T\rho^{(1)} - 2Tt^{(1)}; \tag{9}$$

the relations for the second-order temperature coefficients of frequency and stiffnesses are

$$\begin{aligned} 2\left[Tf^{(2)} - \tfrac{1}{2}(Tf^{(1)})^2\right] &= Tc^{(2)} - T\rho^{(2)} - 2Tt^{(2)} \\ &\quad -\tfrac{1}{2}\left[(Tc^{(1)})^2 - (T\rho^{(1)})^2 - 2(Tt^{(1)})^2\right]; \end{aligned} \tag{10}$$

and for the third-order

$$\begin{aligned} 2\left[Tf^{(3)} - Tf^{(2)}Tf^{(1)} + 1/3(Tf^{(1)})^3\right] &= Tc^{(3)} - T\rho^{(3)} - 2Tt^{(3)} \\ &\quad - \left[Tc^{(2)}Tc^{(1)} - T\rho^{(2)}T\rho^{(1)} - 2Tt^{(2)}Tt^{(1)}\right] \\ &\quad + 1/3\left[(Tc^{(1)})^3 - (T\rho^{(1)})^3 - 2(Tt^{(1)})^3\right], \end{aligned} \tag{11}$$

where $T\rho = -(2\alpha_x + \alpha_z)$ and α_x and α_z are the expansion coefficients. Tt is the temperature coefficient of the thickness of the plate. The essential term in these equations is the temperature coefficient of the eigenvalue Tc determined by Eqs. (9) to (11); however, the terms resulting from the dimensions of the plate may be considered as corrections.

The elastic stiffnesses, the resulting elastic stress constants, and the first-order temperature coefficient of frequency have been calculated using a Burroughs 220 computer as a function of the orientation angles ϕ and θ for quartz in the interval

$$-90^\circ \leq \theta \leq +90^\circ, \qquad 0^\circ \leq \phi \leq +30^\circ .$$

The intervals of calculation were $\Delta\theta = 1^\circ$ and $\Delta\phi = 1^\circ$. The orientation of a plate is shown in Fig. 2. The direction cosines α_i (i = 1, 2, 3) defining the normal of the plate are given by

$$\begin{aligned} \alpha_1 &= \sin\phi\cos\theta \\ \alpha_2 &= \cos\phi\cos\theta \\ \alpha_3 &= \sin\theta \end{aligned}$$

when the Z-axis is chosen as the axis of the polar coordinate system and the angle ϕ is taken from the X-axis. Figure 3 shows the frequency constants N_m in kc·mm, the first-order temperature coefficient of frequency $Tf_m^{(1)}$ in $10^{-6}/^\circ C$ and the piezoelectric stress constant e_m in 10^4 esu cm^{-2}, as plotted for modes A, B, and C corresponding to m = 1, 2, 3. The IRE notation [13] was used in these curves and throughout this report in describing a generally rotated plate as shown in Fig. 2 for the RT cut. By use of this notation, the Y cut is defined as $\phi = 0^\circ$, $\theta = 0^\circ$; an AT cut by $\phi = 0^\circ$, $\theta = 35^\circ$; the BT cut as $\phi = 0^\circ$, $\theta = -49^\circ$. The curves in Fig. 3 are plotted for the azimuth $\phi = 0^\circ$, 6°, 12°, 18°, 24°, and 30°. From these curves three dimensional models have been made which are shown in Figs. 4-12.

METHODS AND EQUIPMENT FOR MEASUREMENTS

The measurements carried out included: 1) frequency measurements of the three modes of vibration at room temperature, and 2) frequency-temperature dependence of these three modes in an extended temperature range.

The frequency range for these three modes of vibration were approximately 4 to 8 Mc with $f_A > f_B > f_C$. Most of the crystals were excited in a CI Meter Type TS 330/TSM. A Heegner oscillator [12] was used sometimes to excite modes whose activity was too low for excitation in the CI Meter. The frequencies were determined with a Hewlett-Packard Counter, Model 524B.

The apparatus used for measuring the dependence of crystal frequency on temperature included: 1) a small aluminum cylinder having two cavities, with a canned crystal unit inserted in one of the cavities and a thermocouple in the other; 2) a calibrated precision bridge to determine the temperature; 3) a wire heating element which was wound around the aluminum cylinder; and 4) a well-insulated Dewar flask containing liquid nitrogen.

Measurements of the frequency-temperature behavior were conducted as follows: in order to obtain a very low initial temperature, the cylinder containing the crystal and a thermocouple were lowered into the flask containing liquid nitrogen. After the temperature within the two cavities approximated the temperature of liquid nitrogen, the liquid nitrogen was removed and the flask containing the cylinder was sealed to stabilize the temperature within the flask at the desired temperature. By means of the heating element described above and controlled by a variac, the temperature was gradually increased and frequency readings were taken at 5°C intervals over the temperature range of approximately -196° to $+170^\circ C$.

DETERMINATION OF TEMPERATURE COEFFICIENTS OF STIFFNESSES AND COMPLIANCES OF ALPHA-QUARTZ

A large number of crystals vibrating in fundamental thickness modes and oriented at different angles have been investigated with respect to their frequencies and temperature behavior at USAELRDL. In this report the IRE rotational symbol (yxwl)$\phi\theta$ is used to describe a generally rotated plate* [13]. Figure 2 shows schematically the orientation angles ϕ and θ for double-rotated quartz plates and, particularly, for the so-called RT cut having an orientation of $\phi = 15°$ and $\theta = -34°30'$. Most of the crystals were oriented at negative θ angles and various ϕ angles. The plates were square and had a length and width of approximately 0.5 **inches,** their edges were bevelled, and the blanks mounted in HC-6 holders. The plate thicknesses were adjusted so that in all cases, mode B was calibrated at the 5-mc frequency.** Some crystals oriented at positive angles of θ and at about $\phi = 20°$ were also investigated. The orientation $\phi = 20°$, $\theta = 34°20'$ is known as the IT cut† [14] when vibrating in the C mode. Several crystal plates with the orientation (xy)θ ($\theta = 0°$ to $60°$ at $10°$ intervals), (rotated X cuts) have been made at USAELRDL.

The values for the frequency constant N of the three fundamental modes A, B, and C were calculated using Eq. (4) and the recently published values for $c_{\lambda\mu}$ of quartz [9]. The elastic stiffnesses are given in Table 4 (mks units are used throughout this report), together with a new determination of the stiffnesses by Mindlin and Gazis [15]. Although the formulae on which the determination by Mindlin and Gazis is based do not include the piezoelectric and thermoelectric terms, they do account for mechanical coupling. The values derived by Mindlin and Gazis coincide most closely with the stiffnesses given by Bechmann [9] for both constant electric field and entropy and constant electric displacement and entropy.

The measured crystals had large electrode separations in order to obtain closer agreement between the measured and observed values.

The values for the temperature coefficients of the elastic stiffnesses $Tc_{\lambda\mu}$ are dependent on the accuracy of the measurements of the temperature coefficients of frequency **Tf**. It is well known that the temperature coefficients of frequency depend slightly on: state of the plate measured, e.g., the form of the plate (circular or square); the electrode size (ratio $\frac{\phi_e}{t}$ where ϕ_e is the diameter of the electrode and t is the thickness of the plate); the electrode separation (whether an air gap or plated blank is used); the order of overtone which changes the zero angles for the first-order zero temperature coefficients $Tf^{(1)}$; the bevelling of the plate which is necessary to avoid coupling with other modes which gives rise to errors; and the drive level of the resonator. Further, there are slight differences between the temperature coefficients of natural and synthetic quartz. Finally, the temperature coefficients of the stiffnesses are dependent on the approximation of the solution of the equations on which the determination is based.

Some previous investigations of the frequency-temperature behavior of double-rotated quartz crystals were conducted by Saunders and Hammond [16] based on the earlier calculation by Bechmann [5].

The frequency-temperature dependence of the quartz blanks mentioned was measured in the temperature range $-196°$ to $+170°$C. All blanks used for frequency-temperature measurements were plated. The resulting frequency curve was developed in a power series with respect to the reference temperature $T_o = 25°$C up to the third order. The first-, second-, and third-order temperature coefficients of frequency a, b, and c of a number of these crystals, which were used for the determination of the temperature coefficients of the stiffnesses, are also listed in Table 5.

*From this rotational symbol, the appropriate coordinate transformation can be easily derived [29].

**Most of these crystals were fabricated by McCoy Electronics Company, Mount Holly Springs, Pa. The accuracy of the orientation angle was better than 10′ for the ϕ angle and better than 5′ for the θ angle, according to the manufacturer.

†These IT-cut crystals were furnished through the courtesy of Scientific Radio Products, Inc., Loveland, Colorado.

This table gives some of the measured and calculated values for the first-, second-, and third-order temperature coefficients a, b, and c, respectively, for modes A, B, and C. Crystals marked * indicate that the temperature coefficients of frequency of all three modes A, B, C have been measured. The calculation of the values for $Tc\lambda_{\mu}^{(n)}$ (n = 1, 2, 3) following from Eq. (4) by differentiation with respect to the temperature was made using a Burroughs Datatron 220 Computer.

The newly determined first-order temperature coefficients of the stiffnesses $Tc_{44}^{(1)}$, $Tc_{66}^{(1)}$, and $Tc_{14}^{(1)}$ are considered very accurate, as the values follow from rotated plates $(yxl)\theta$. The behavior of the AT and BT cuts, their orientation angles for the zero temperature coefficient of frequency and the change of their temperature coefficients with respect to the angle θ are very well known [17] (see Table 6). In addition, the Y cut (yx) which has a first-order temperature coefficient of frequency of $92.5 \cdot 10^{-6}/°C$ has also been used.

When the angles for the first-order zero temperature coefficient of frequency are used, $\theta_o = 35° 15'$ for the AT cut, and $-49° 13'$ for the BT cut, and for the slope of the AT cut $\frac{\partial a}{\partial \theta} = -5.15 \cdot 10^{-6}/°C/° \theta$, the values in the first column of Table 6 are obtained. By exciting a high overtone [18] or using a large electrode gap, the zero angle θ_o for the AT cut is shifted to $35°22'$ and for the BT cut to $-49°40'$ and, assuming the same slope of $\frac{\partial a}{\partial \theta} = -5.15 \cdot 10^{-6}/ °C/° \theta$ for the AT cut, values for $Tc_{44}^{(1)}$, $Tc_{66}^{(1)}$, and $Tc_{14}^{(1)}$ are obtained as shown on the right-hand side of Table 6. The difference between the two groups of values is also listed in Table 6 and this may be considered as the accuracy for determination of the temperature coefficients of the elastic stiffnesses $Tc_{44}^{(1)}$ $Tc_{66}^{(1)}$, and $Tc_{14}^{(1)}$.

$Tc_{11}^{(1)}$ follows from the X cut (xy) which has a value for the temperature coefficient of frequency of $Tf^{(1)} = -20.10^{-6}/°C$. $Tc_{33}^{(1)}$ was determined using the zero angles for the double-rotated plates $(yxwl)\phi\theta$ as listed in Table 5. Since the value for $Tc_{13}^{(1)}$ has a small influence on the temperature behavior, it therefore cannot be considered as accurate.

Table 7 lists the newly determined values for the first-order temperature coefficients of the elastic stiffnesses for alpha-quartz compared with some earlier determinations. The values listed in the columns headed "Koga et al., 1958" of Tables 7, 8, and 9 are calculated from the expressions

$$\hat{c} = \frac{c}{4\rho}, \quad \frac{\partial \hat{c}}{\partial T}, \quad \frac{1}{2}\frac{\partial^2 \hat{c}}{\partial T^2}, \text{ and } \frac{1}{6}\frac{\partial^3 \hat{c}}{\partial T^3},$$

given in their paper. It should be mentioned that the values for the temperature coefficients of the stiffnesses given by Atanasoff and Hart [20] contain an error as they assumed that for quartz $c_{56} \neq c_{14}$ and obtained the erroneous values $Tc_{14}^{(1)} = 107 \cdot 10^{-6}$ and $Tc_{56}^{(1)} = 78 \cdot 10^{-6}$. The reason for this discrepancy is that the piezoelectric effect was not taken into account. The values for the stiffnesses given by Atanasoff and Hart [20] have been corrected by Lawson [21] resulting in $c_{56} = c_{14}$ when considering the piezoelectric effect. However, he did not correct the values for the temperature coefficients of the stiffnesses. Their value for $Tc_{56}^{(1)}$ is omitted in Table 7.

The second- and third-order temperature coefficients of the elastic stiffnesses have been determined using the experimental values for the AT and BT cuts [17] and the newly observed values for the frequency dependence of the double-rotated plates. Table 8 lists the second-order temperature coefficients of the elastic stiffnesses and Table 9 the third-order temperature coefficients of the elastic stiffnesses. Both tables contain corresponding values from earlier determinations by Mason [19], [22] and Koga, et al. [24].

The compliances $s_{\lambda\mu}$ and their first-, second-, and third-order temperature coefficients $Ts_{\lambda\mu}$ were calculated from the values of the stiffnesses $c_{\lambda\mu}$ and their temperature coefficients $Tc_{\lambda\mu}$ using the well-known relationships between the stiffnesses and compliances

$$\Sigma\, s_{\lambda\tau}\, c_{\mu\tau} = \delta_{\lambda\mu} = \begin{cases} 1, & \lambda = \mu \\ 0, & \lambda \neq \mu \end{cases},$$

from which the relationship

$$\sum_{\lambda=1}^{6} \sum_{p=o}^{n} c_{\lambda\mu}\, s_{\lambda\nu}\, (Tc_{\lambda\mu}{}^{(n-p)} + Ts_{\lambda\nu}{}^{(p)}) = \begin{cases} 0 & n > 0 \\ \delta_{\mu\nu} & n = 0 \end{cases}$$

follows.

The values for the compliances $s_{\lambda\mu}$ are given in Table 10. The first-, second-, and third-order temperature coefficients of the elastic compliances $Ts_{\lambda\mu}$, which have been calculated from the temperature coefficients of the stiffnesses as given in Tables 7, 8, and 9, are listed in Tables 11, 12, and 13. For comparison, some values from earlier determinations are shown in these tables. All new values for the temperature coefficients of the stiffnesses and compliances refer to 25°C. The values for the stiffnesses and compliances, as determined by Bechmann [9] and given in Tables 4 and 10, refer to 20°C. It should be mentioned that all "new" values for the temperature coefficients of the stiffnesses $Tc_{\lambda\mu}{}^{(n)}$, obtained from measurements of thickness modes, and those of the compliances calculated from the stiffnesses are values at normal constant displacement D_s. The differences between $Tc_{\lambda\mu}{}^{(n)E}$, the isagric values, and $Tc_{\lambda\mu}{}^{(n)D_s}$ are within the limits of accuracy of measurements of the temperature dependence of these plates.

APPLICATIONS TO DOUBLE-ROTATED QUARTZ PLATES

Since the temperature coefficients of the stiffnesses are known, the temperature behavior of thickness modes of any orientation can be calculated from these values. Altitude charts for the first-, second-, and third-order temperature coefficients of frequency for the C mode are given in Figs. 13, 14, and 15 respectively, and it can be seen from Fig. 13 that there is a continuous series of orientations for the thickness mode C of plates having a first-order zero temperature coefficient of frequency for all values of ϕ (0° to 30°) at both positive and negative angles of θ adjoining the AT cut at ϕ = 0° and θ = 35°. Similar charts showing the distribution of the temperature coefficient of frequency for mode B are given in Figs. 16, 17, and 18. At negative angles of θ, mode B exhibits a continuous series of first-order zero temperature coefficients in the range ϕ = 0° to 14° at two angles of θ, both on the negative side adjoining the BT cut at ϕ = 0° and θ = −49°. The curves for the first-order zero temperature coefficient of frequency for modes B and C as seen in Figs. 13 and 16 are identical with the curves shown in Figs. 19 and 20.

Fig. 19 shows the calculated locus of the first-order zero temperature coefficients of frequency for modes B and C in a rectangular coordinate system compared with some measured results. The values for the mode C are indicated by X, those for the mode B by ⊖. The agreement between the calculated and measured zero angles is better than 3 percent and, taking into account the uncertainties mentioned above, the agreement is considered very satisfactory.

Figure 20 represents the locus of the first-order zero temperature coefficients of frequency in a polar coordinate system illustrating the threefold symmetry of quartz showing that, at an angle ϕ + n 120° (n = 0, 1, 2), the elastic properties of quartz are identical with those of the angle ϕ. Mode A vibrating extensionally has a negative temperature coefficient of frequency for all orientations.

Figure 21 shows the frequency constants N of the modes B and C when $Tf^{(1)} = 0$. Figure 22 shows the second- and third-order temperature coefficients of frequency for the thickness mode C when $Tf^{(1)} = 0$ for negative angles of θ.

For mode C the second-order temperature coefficient of frequency is always negative and reaches a minimum value of about $-6.5 \cdot 10^{-9}/(°C)^2$ at $\phi = 15°$. The third-order temperature coefficient changes its sign as a function of the angle ϕ at negative θ angles but the zero angles for the first- and third-order temperature coefficients of frequency do not coincide.

At the angle $\phi = 15°$, $\theta = -34°30'$, mode C shows a first-order zero temperature coefficient of frequency, a second-order temperature coefficient of frequency of $-6.5 \cdot 10^{-9}/(°C)^2$, and a third-order temperature coefficient of $-2 \cdot 10^{-12}/(°C)^3$ (see Table 5). This cut has been proposed for practical applications and designated the RT cut [26]. Other double-rotated cuts may be useful for application at low temperatures. For example, the C mode of the cut $\phi = 10°$, $\theta = -33°$ shows a very small frequency change with temperature in the range $-160°$ to 0°C, as the three terms for the temperature behavior balance (Table 5). An experimental frequency-temperature curve is shown in Fig. 23. The disadvantage of the double-rotated cuts is that all three modes are excitable, modes B and C being rather close together. The separation between these modes is in the order of 7 percent for the RT cut and in the order of 10 percent for the IT cut. The B mode displays a large negative second-order temperature coefficient of frequency for all zero temperature coefficient cuts, including the BT cut, which for practical purposes makes mode B less useful than mode C.

APPLICATIONS TO AT- AND BT-CUT QUARTZ CRYSTALS IN AN EXTENDED TEMPERATURE RANGE

The frequency and temperature behavior of the plates (yxl)θ, the so-called rotated Y-plates, is shown in Figs. 24-27. Figure 24 gives values of the rotated stiffnesses $c_{66}' = c_{44} \sin^2\theta + c_{66}\cos^2\theta + 2c_{14}\cos\theta\sin\theta$, as a function of the angle θ in the range $\theta = -90°$ to $+90°$, derived from the values c_{66}, c_{44}, and c_{14} as given in Table 4 [9]. Figure 25 shows the frequency constant N in the same range. Figures 26 and 27 give the first-, second-, and third-order temperature coefficients respectively, calculated from the values given in Tables 7, 8, and 9, using Eqs.(9) through (11). The AT cut is described by the angle $\theta = 35°15'$, the BT cut by the angle $\theta = -49°13'$. The AT cut belongs to mode C while the BT cut belongs to mode B. The jump from mode B to mode C occurs because there is one orientation for which the secular Eq. (4) becomes degenerate, having two roots of the same value. It should be recognized that it results in a discontinuity in the other constants derived from the stiffnesses, e.g., the temperature coefficients.

For the family of cuts (yxl)θ ($\phi = 0°$) the secular Eq. (4) becomes

$$\begin{vmatrix} (\Gamma_{11}-c) & 0 & 0 \\ 0 & (\Gamma_{22}-c) & \Gamma_{23} \\ 0 & \Gamma_{23} & (\Gamma_{33}-c) \end{vmatrix} = 0 .$$

One root is $c = \Gamma_{11}$. This corresponds to mode C. The other roots are

$$c_{A,B} = \frac{\Gamma_{22} + \Gamma_{33}}{2} \pm \frac{1}{2}\sqrt{\Gamma_{22}^2 + \Gamma_{33}^2 + 4\Gamma_{23}^2 - 2\Gamma_{22}\Gamma_{33}} ,$$

where the minus sign corresponds to the smaller root (mode B). Modes B and C have a common eigenvalue at the value of θ for which

$$\Gamma_{11}^2 - \Gamma_{11}\Gamma_{22} - \Gamma_{11}\Gamma_{33} + \Gamma_{22}\Gamma_{33} - \Gamma_{23}^2 = 0 .$$

Substitution of the values for the $c_{\lambda\mu}$ and the direction cosines leads to a cubic equation with a single real root corresponding to an orientation of

$$\theta = -23°50' .$$

Physically, the mode of vibration designated B for the angle θ on one side of this value becomes mode C on the other side and vice versa. The difficulty arises because the modes are defined in such a way that mode A has the highest stiffness and mode C the lowest, where, for the region under consideration, modes B and C actually cross and mode B becomes, for positive angles, the lowest mode. For $\phi \neq 0°$ there is no ambiguity as the solutions of Eq. (4) are all distinct. The discontinuity is not apparent in the curves shown in Figs. 24 through 27.

Considering the AT and BT cuts, a maximum and minimum for the frequency-temperature curve exist as a function of the orientation angle θ following from Eqs. (8) and (8a). The behavior of the maximum and minimum can be represented by a parabola having the parabola constant b_μ (μ = max or min) for the angle considered. The calculated and observed values for T_{max} and T_{min} vs. the orientation angle θ for the AT cut in the range $\theta = 35°$ to $40°$ and for the BT cut in the range $\theta = -46°$ to $-52°$ are given in Figs. 29 and 30 respectively [17].

The inflection temperature T_i is defined by

$$\frac{\partial Tf}{\partial T} = \frac{\partial^2 f}{\partial T^2} = 0 .$$

The inflection temperature for the zero-temperature cuts depends on the angle of rotation. The inflection temperature for the AT cut is about 25°C. The inflection temperature for mode C increases when the angle ϕ on the positive side of the angle θ is increased. Figure 28* shows the inflection temperature obtained from cuts made of natural quartz when the angle ϕ is increased from 0° to 30°.

For the IT-cut ($\phi = 20°$) the inflection temperature is about 70°C. The inflection temperature T_i is given by

$$T_i - T_o = -\frac{b_o}{3\,c_o} .$$

The inflection temperatures for the AT and BT cuts, as function of the angle θ, are also shown in Figs. 29 and 30. The temperature of liquid nitrogen N is −196°C; for liquid hydrogen H is −253°C; and for liquid helium He is −269°C as indicated in these figures. The calculated values for the parabola constant b_μ as a function of the orientation angle θ, corresponding to T_{max} and T_{min} as shown in Fig. 29, are presented in Fig. 31 for the AT cut, the values corresponding to Fig. 30 are shown in Fig. 32 for the BT cut.

APPLICATIONS TO QUARTZ CUTS VIBRATING IN CONTOUR MODES

The frequencies and their temperature behavior are determined for contour modes of plates and extensional modes of bars by the elastic compliances and their temperature coefficients. Two cuts of interest exist for square plates which have one side parallel to and are rotated around the X axis at angle θ, i.e., cuts of the orientation (yxl)θ, where the first-order temperature coefficient of frequency is zero, the CT cut with an orientation angle of approximately

*Figure 28 also shows the second- and third-order temperature coefficients of frequency when $Tf^{(1)} = 0$ as a function of ϕ. At positive angles of θ, the AT cut is obtained for $\phi = 0°$, and the IT cut obtained for $\phi = 20°$.

$\theta = 38°$, and the DT cut with an angle of approximately $\theta = -51°$. There are three types of these cuts:

1. Square plates with one side parallel to the X axis, $Y_{\theta}0° \equiv (yxl)\theta$.
2. Square plates with the X axis diagonal, $Y_{\theta}45° \equiv (yxlt)\theta 45°$. Contour-extensional mode I of square plates [27].
3. Circular plates $Y_{\theta o}$.

The frequencies for these three modes are given by the equation

$$f = \frac{F}{2h}\sqrt{\frac{2}{\rho s'_{55}}}\,, \tag{12}$$

where h is the length l of square plates or the diameter ϕ of circular plates. The expressions for F for plates $Y_{\theta}0°$ and plates $Y_{\theta}45°$ where F = 1 can be found in [27], while for circular plates $Y_{\theta o}$ no solution has been derived. However, the value obtained experimentally on circular quartz plates is F = 1.0551 ± 1 percent.

Figure 33 gives the values for the rotated compliances $s'_{55} = s'_{44} = s_{44}\cos^2\theta + s_{66}\sin^2\theta - 4s_{14}\cos\theta\sin\theta$ as a function of the angle θ in the range $\theta = -90°$ to $+90°$ as derived from the new values s_{66}, s_{44}, and s_{14} presented in Table 10. Figure 34 shows the frequency constants N in the same range mentioned for the three cases $Y_{\theta}0°$, $Y_{\theta}45°$, and $Y_{\theta o}$. Figure 35 gives the first-, second-, and third-order temperature coefficients of frequency calculated from the new values given in Tables 11, 12, and 13.

It may be mentioned that the two zero angles of the temperature coefficient of frequency, first-order, are slightly dependent (in the order of ±1%) on the configuration, the thickness of the plating, and the mounting of the plate. Table 14 gives the observed and calculated values of the frequency constants and the temperature coefficients of frequency for the CT cut. Table 15 presents the same information for the DT cut. The experimental values given in Tables 14 and 15 for the zero angles are obtained from earlier investigations where the electrodes were sprayed and baked [28]. According to Eq. (12), the values for the temperature coefficients of frequency of the three modes are equal, as F is a constant determined by boundary conditions and therefore all three modes should have identical angles for their first-order zero temperature coefficients of frequency.

The calculated maximum and minimum for the frequency-temperature curve as a function of the orientation angle θ are shown in Fig. 36 for the CT cut. In this curve the experimental values for T_{min}, assumed to be linear in [28], are also presented by dashed lines. The theoretical and experimental values are in very good agreement. The calculated values for the parabola constant b_{μ} for this cut as a function of the orientation angle θ, corresponding to Fig. 36, are exhibited in Fig. 37. Similarly, the calculated temperature of the zero temperature coefficient of frequency vs the orientation angle θ for the DT cut is shown in Fig. 38. The calculated values for the parabola constant b_{μ} for the DT cut as a function of the orientation θ, corresponding to the zero coefficient temperature curve of Fig. 38, are shown in Fig. 39.

REFERENCES

1. G. Green, Trans. Cambridge Phil. Soc., vol. 7; 1839.

2. E. B. Christoffel, "Ueber die Fortpflanzung von Stössen durch elastische feste Körper." *Ann. di Matematica Milano,* vol. 8, pp. 193-243; 1877.

3. I. Koga, "Thickness Vibrations of Piezoelectric Oscillating Crystals," *Physics,* vol. 3, pp. 70-80; August 1932.

4. R. D. Mindlin, "Thickness-Shear and Flexural Vibrations of Crystal Plates," J. Appl. Phys., vol. 22, pp. 316-323; March 1951.

5. R. Bechmann, "Über die Temperatur-Koeffizienten der Eigenschwingungen piezoelektrischer Quarzplatten und Stäbe," *Hochfrequenz. und Elektroak.,* vol. 44, pp. 145-160; November 1934.

6. J. Laval, "Élasticité des Cristaux," *Compt. rend. Acad. Sci., (Paris),* vol. 232, pp. 1947-1948; 21 May 1951.
"Sur l' élasticité du milieu cristallin, L' état solide," Congres Solvay, Stoops, Bruxelles, pp. 273-313; 1952.

7. H. Jaffe and C. S. Smith, "Elastic Constants of Ammonium Dihydrogen Phosphate and the Laval Theory of Crystal Elasticity," *Phys. Rev.,* vol. 121, pp. 1604-1607; 15 March 1961.

8. V. G. Zubov and M. M. Firsova, "On the Measurement and New Computation of the Dynamic Elastic Constants of Quartz," *Kristallografiya,* vol. 1, pp. 546-556; May 1956. (In Russian.)

9. R. Bechmann, "Elastic and Piezoelectric Constants of Alpha-Quartz," *Phys. Rev.,* vol. 110, pp. 1060-1061; 1 June 1958.

10. R. D. Mindlin, Letter-type Report, U.S. Signal Corps Contract DA36-039 SC-87414; 29 March 1961. (Unpublished.)

11. W. G. Cady, "Piezoelectricity," McGraw-Hill Book Co., New York, N.Y., London, England; 1946.
J. A. Schouten, "Tensor Analysis for Physicists," Clarendon Press, Oxford, England; 1951.
J. P. Musgrave, "The Propagation of Elastic Waves in Crystals and Other Anisotropic Media," *Repts. Progr. Phys.,* vol. 22, pp. 74-96; 1959, Physical Soc., London, England; 1959.

12. K. Heegner, "Gekoppelte selbsterregte elektrische Kreise und Kristalloszillatoren," *Elektr. Nachrichtentech,* vol. 15, pp. 359-368; December 1938.

13. "IRE Standards on Piezoelectric Crystals, 1949," Proc. IRE, vol. 37, pp. 1378-1395; December 1949.

14. W. R. Ives, "A New Zero Temperature Coefficient Quartz Oscillator Plate," M.S. thesis, Colorado A & M College, Ft. Collins, Colorado; March 1951.

15. R. D. Mindlin and D. C. Gazis, "Strong Resonances of Rectangular AT-cut Quartz Plates," Report, U.S. Signal Corps Contract DA36-039 SC-87414; July 1961.

16. J. L. Saunders and D. L. Hammond, "Design and Development of Extended Temperature Range CR-(XA-21)/U Crystal Units," Wright Air Dev. Ctr., Wright Patterson AF Base, Ohio, Final Rept. AF 33(600)33889, 16 September 1956-26 June 1959.

17. R. Bechmann, "Frequency-Temperature-Angle Characteristics of AT- and BT-Type Quartz Oscillators in an Extended Temperature Range," Proc. IRE, vol. 48, p. 1494; August 1960.

18. R. Bechmann, "Influence of the Order of Overtone on the Temperature Coefficient of Frequency of AT-Type Quartz Resonators," Proc. IRE, vol. 43, pp. 1667-1668; November 1955.

19. W. P. Mason, "Low Temperature Coefficient Quartz Crystals," *Bell System Tech. J.*, vol. 19, pp. 74-93; January 1940.

20. J. V. Atanasoff and P. J. Hart, "Dynamical Determination of the Elastic Constants and their Temperature Coefficients for Quartz," *Phys. Rev.*, Vol. 59, pp. 85-96; 1 January 1941.

21. A. W. Lawson, "Comment on the Elastic Constants of Alpha-Quartz," *Phys. Rev.*, vol. 59, pp. 838-839; May 1941.

22. W. P. Mason, "Zero Temperature Coefficient Quartz Crystals for Very High Temperatures," *Bell System Tech. J.*, vol. 30, pp. 366-380; April 1951.

23. R. Bechmann and S. Ayers, "The Shear Elastic Constants of Quartz and their Behaviour with Temperature," Post Office Res. Sta., Engrg. Dept., London, Dollis Hill, England, Res. Rept. No. 13524; December 1951.

24. I. Koga, M. Aruga and Y. Yoshinaka, "Theory of Plane Elastic Waves in a Piezoelectric Crystalline Medium and Determination of Elastic and Piezoelectric Constants of Quartz," *Phys. Rev.*, vol. 109, pp. 1467-1473; March 1958.

25. E. Giebe and E. Blechschmidt, "Über Drillungsschwingungen von Quarzstäben und ihre Benützung für Frequenznormale," *Hochfrequenz. und Elektroak.*, vol. 56, pp. 65-87; March 1940.

26. R. Bechmann, "Thickness-Shear Mode Quartz Cut with Small Second- and Third-Order Temperature Coefficients of Frequency (RT Cut)," Proc. IRE, vol. 49, p. 1454; September 1961. USASRDL Docket No. 12831 (19 August 1960).

27. "IRE Standards on Piezoelectric Crystals: Determination of the Elastic, Piezoelectric, and Dielectric Constants -- The Electromechanical Coupling Factor, 1958," Proc. IRE, vol. 46, pp. 764-778; April 1958.

28. R. Bechmann, "Quarzoszillatoren und Resonatoren im Bereich von 50 bis 300 kHz.," *Hochfrequenz. und Elektroak.*, vol. 61, pp. 1-12; January 1943.

29. R. Bechmann, "Zur Festlegung der Orientierung von Kristallplatten und die zugehorige Koordinatentransformation," Archiv d. elektr. Übertragung, 7, 305-307; 1953.