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Dynamical Determination of the Elastic Constants and Their Temperature Coefficients for Quartz

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A mathematical theory is presented giving the relations between the elastic constants and the frequencies of piezoelectric vibration for an infinite plate of homogeneous but aeolotropic material. Since no such theory is known for finite plates it is, strictly speaking, impossible to determine the elastic constants of the material from measurements on such plates. However, the viewpoint of perturbation theory indicates that certain frequencies of vibration of finite plates asymptotically approach the frequencies of vibration of infinite plates of the same material, orientation and thickness as the harmonic order increases. The experimental results confirm that this is an excellent method of eliminating edge effects and accurate data that are seemingly quite independent of mother crystal and proportions of the plate are obtained. However, in the evaluation of the elastic constants and their temperature coefficients from these data it is found that there is a small but not easily explained discrepancy between these results and the classical elastic theory for substances of the symmetry class D_3 generally accepted for quartz. Detailed observations have been made in the temperature interval from 0° to 80°C but additional results enable the calculation of the values of certain of the elastic constants at higher temperatures up to the alpha-beta transition point.

INTRODUCTION

THE mathematical relationship existing between the elastic constants of a homogeneous aeolotropic substance and the velocities of propagation of waves with different orientations of the phase planes has been known for many years.[1] Koga[2] seems to have been the first to develop an accurate theory of the frequencies of vibration of infinite plates when the phase surfaces are planes parallel to the surfaces of the plate. The harmonic frequencies of an infinite plate are exact integral multiples of the fundamental frequencies.

A rigorous solution has never been obtained for the vibrational frequencies of a plate of finite dimensions and in any study of such vibrations one must proceed by approximate methods. Strictly speaking, in order to be able to infer the elastic constants from measurements of the frequencies of vibration of a finite plate, a solution for this case would be needed, and this objection can be made to most, if not all, of the dynamical determinations of the elastic constants that have been made. In this paper, a method of procedure will be used which removes this necessity and permits the calculation of the elastic constants directly from the theory for infinite plates.

GENERAL ELASTIC THEORY

1. Thickness vibrations of an infinite anisotropic plate

If, in an anisotropic elastic substance, u is the displacement vector, ϕ is the second-rank stress tensor,[3] θ is the second-rank strain tensor,[3] c is the fourth-rank elastic tensor,[3] and F is the volume rate of force developed by the stress tensor, we have from elastic theory the fundamental equations

$$\theta_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right), \tag{1}$$

$$\phi_{ij}=c_{ij\alpha\beta}\theta_{\alpha\beta}, \tag{2}$$

$$F_j=\partial\phi_{ij}/\partial x_i. \tag{3}$$

In this paper the usual convention that repeated subscripts are to be summed is used.

The mathematical description of the free vibrations of a portion of homogeneous but anisotropic material is easily derived from these equations. By combining (1), (2) and (3) with Newton's equations of motion and making use of the symmetry[3] there results the wave equation

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[1] A. E. H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Cambridge University Press, 1934), pp. 298, 299.

[2] I. Koga, Physics **3**, 70–80 (1932).

[3] Many tensor quantities used in elastic theory possess a certain symmetry thus $\phi_{ij}=\phi_{ji}$, $\theta_{ij}=\theta_{ji}$, $c_{ijab}=c_{ijba}=c_{jiab}=c_{abij}$ and $e_{iab}=e_{iba}$. This symmetry reduces the number of independent terms in the tensor and permits the use of the common notation with fewer subscripts. For instance, $c_{2223}=c_{24}$ since $11=1$, $22=2$, $33=3$, $23=4$, $13=5$, $12=6$. From the symmetry, we also have $31=4$ etc.

for this type of material

$$\rho\ddot{u}_j = c_{ij\alpha\beta}\partial^2 u_\alpha/\partial x_i\partial x_\beta \qquad (4)$$

in which ρ is the density of the substance. The boundary condition at a free surface of the material where the unit normal is the vector ν is easily found from (1) and (2) to be

$$c_{ij\alpha\beta}\left(\frac{\partial u_\alpha}{\partial x_\beta}+\frac{\partial u_\beta}{\partial x_\alpha}\right)\nu_i = 0. \qquad (5)$$

In searching for a normal mode of vibration the substitution of

$$u_i = \psi_i e^{i\omega t} \qquad (6)$$

in (4) and (5) is permitted and there results the simpler characteristic system

$$c_{ij\alpha\beta}\frac{\partial\psi_\alpha}{\partial x_i\partial x_\beta}+\rho\omega^2\psi_j = 0, \qquad (7)$$

$$c_{ij\alpha\beta}\left(\frac{\partial\psi_\alpha}{\partial x_\beta}+\frac{\partial\psi_\beta}{\partial x_\alpha}\right)\nu_i = 0. \qquad (8)$$

The problem at hand is to obtain a solution of the system (7), (8) for an infinite plate. Let the infinite bounding surfaces be the planes $x_1 = 0$ and $x_1 = s$. Then it is easy to see that a solution of the form

$$\psi_j = A_j \cos\,(n\pi x_1/s) \qquad (9)$$

in which the A's are constants, satisfies the boundary condition (8). The condition that (9) satisfy (7) is the linear secular system

$$c_{1j\alpha 1}A_\alpha - \kappa^2 A_j = 0 \qquad (10)$$

in which

$$\kappa^2 = 4\rho s^2 f^2/n^2, \quad f = \omega/2\pi. \qquad (11)$$

This secular system determines the frequencies and modes of vibration in the usual way. The secular equation

$$\begin{vmatrix} c_{1111}-\kappa^2 & c_{1121} & c_{1131} \\ c_{1211} & c_{1221}-\kappa^2 & c_{1231} \\ c_{1311} & c_{1321} & c_{1331}-\kappa^2 \end{vmatrix} = 0 \qquad (12)$$

has three roots in κ^2 and hence there are three independent fundamental modes and, in general, three different fundamental frequencies of vibration for each orientation of the infinite plate. The harmonic frequencies of an infinite plate are exact integral multiples of the fundamental frequencies.

If one wishes to find the frequencies and modes of vibration for an infinite plate with arbitrary orientation it is convenient to introduce a transformation of coordinates which makes the new x_1 axis normal to plate. The effect of such a transformation on the c's is determined by the fact that they form a tensor of the fourth rank.

If the elastic constants are to be determined, the resonant frequencies of several plates having various orientations with respect to the natural axes of the material may be required. One must measure the frequencies of at least as many independent modes of vibration as there are constants to be evaluated.

2. Excitation of vibrations

A complete treatment of piezoelectric vibrations would require the introduction of certain forces arising from the piezoelectric effect in the wave equation (4) and the solution of this modified equation with the boundary condition (5). However, the excitation of a resonance mode of vibration can be simplified by the following considerations. Because the damping forces of a vibrating quartz crystal are small, considerable amplitude is reached with a given driving force. Consequently, the elastic forces in the crystal are large compared with the piezoelectric driving forces, and the mode of vibration is not much perturbed by the driving force. If one assumes the mode of vibration as known from calculations on the free undamped case, the driving energy due to a field E can be calculated from the integral

$$\int_\tau\int E_i dP_i d\tau \qquad (13)$$

in which

$$P_i = e_{i\alpha\beta}\theta_{\alpha\beta}, \qquad (14)$$

where the e's form the third-rank piezoelectric tensor.[3] In certain special cases this integral will be zero, indicating that it is impossible to drive the given mode of vibration with the given field arrangement. Thus it is impossible to drive the even harmonics of an infinite plate with a field which is independent of position in space. In the specific case of quartz only the terms e_{11}, e_{12}, e_{14},

e_{25}, and e_{26} of the piezoelectric tensor are not zero. This indicates a further reason why the integral (13) may vanish and driving of the cut become impossible.

3. Secular equations for certain infinite plates of quartz

Since quartz belongs to the crystal class D_3 it has the following nonzero elastic constants c_{11}, c_{12}, c_{13}, c_{14}, $c_{22}=c_{11}$, $c_{23}=c_{13}$, $c_{24}=-c_{14}$, c_{33}, c_{44}, $c_{55}=c_{44}$, $c_{56}=c_{14}$, $c_{66}=\frac{1}{2}(c_{11}-c_{12})$ if it is placed in the coordinate system so that the x_3 and x_1 axes correspond to the threefold and the twofold axes of the crystal, respectively. Two angles are used to designate the orientation of the quartz plates. The first angle, the azimuth, is the angle between the projection of the normal to the plate on the x_1x_2 plane and the x_1 axis. The second angle, the altitude, is the angle between the normal to the plates and its projection on the x_1x_2 plane.

By the use of Eq. (12), the equation relating the elastic constants to the frequencies of vibration for a (0°, 0°) plate, is found to be

$$[c_{1111}-\kappa^2][(c_{1221}-\kappa^2)(c_{1331}-\kappa^2)-c_{1321}c_{1231}]=0.$$

The linear factor in the equation represents a purely longitudinal mode of vibration excited by an alternating electric field in the x_1 direction, and the quadratic factor represents two more complicated modes involving shear vibrations, and excited by a field in the x_2 direction.

Similarly, by replacing the 1's by 2's in the first and fourth subscripts of the c's in Eq. (12), the equation for the (30°, 0°) plate can be obtained:

$$[c_{2112}-\kappa^2][(c_{2222}-\kappa^2)(c_{2332}-\kappa^2)-c_{2322}c_{2232}]=0.$$

Hence, the secular equation of this plate also contains a linear factor representing a pure shear mode of vibration excited by an electric field in the x_2 direction. The other two modes of vibration can be excited by a field in the x_1 direction.

In a similar manner, the equation for the (0°, 90°) plate is found to be

$$(c_{3113}-\kappa^2)(c_{3223}-\kappa^2)(c_{3333}-\kappa^2)=0,$$

the equation being completely factorable. The first and second factors represent pure shears which should be excited by alternating electric fields in the x_2 and x_1 directions, respectively. The third factor represents a purely longitudinal mode of vibration which cannot be excited by piezoelectric methods since there is no piezoelectric constant corresponding to the θ_{33} strain.

The equation for plates of these three orientations, written in terms of the principal elastic constants, are, for a 0°, 0° plate,

$$\kappa^2-c_{11}=0, \qquad \text{(I)}$$

$$\kappa^4-(c_{44}+c_{66})\kappa^2+c_{66}c_{44}-c_{56}{}^2=0 \qquad \text{(III)}$$

for a (30°, 0°) plate

$$\kappa^2-c_{66}=0, \qquad \text{(II)}$$

$$\kappa^4-(c_{11}+c_{44})\kappa^2+c_{11}c_{44}-c_{24}{}^2=0 \qquad \text{(IV, V)}$$

and for a (0°, 90°) plate,

$$(\kappa^2-c_{33})(\kappa^2-c_{44})(\kappa^2-c_{44})=0.$$

The equation for an R plate, obtained by a transformation of the elastic constants is factorable, as are the equations for all orientations that may be expressed by (30°, x°). The mode of vibration defined by the first factor is a mode composed of the shear strains θ_{12} and θ_{13}, and thus capable of being excited by a field having a component in the x_2 direction. The second factor defines two more complicated modes of vibration involving the strains θ_{22}, θ_{33}, and θ_{23}, these vibrations being excited by a field in the x_1 direction.

The equation for a (0°, 45°) or a (0°, −45°) plate is found by similar methods to be nonfactorable. The three complicated modes of vibration for this plate involve strains such that the resulting polarization has components in both the x_1 and x_2 directions.

The equation for the R plate, written in terms of the principal elastic constants, are

$$\kappa^2-0.38260c_{44}-0.97205c_{56}-0.61740c_{66}=0, \qquad \text{V(I)}$$

$$\begin{aligned}\kappa^4-[&0.61740c_{11}+0.97205c_{24}+0.38260c_{33}\\ &+c_{44}]\kappa^2-0.23622c_{13}{}^2-0.60014c_{13}c_{24}\\ &-0.47245c_{13}c_{44}+0.23622c_{11}c_{33}\\ &+0.14638c_{33}c_{44}+0.37191c_{33}c_{24}\\ &\qquad+0.38118c_{11}c_{44}-0.38118c_{24}{}^2=0. \qquad \text{(VII)}\end{aligned}$$

The equation for the (0°, 45°) plate is

$$
\begin{aligned}
&8\kappa^6-[4c_{11}+4c_{33}+12c_{44}+4c_{66}]\kappa^4-[2c_{14}{}^2\\
&\quad+4c_{14}c_{56}+4c_{56}{}^2-4c_{11}c_{44}-2c_{11}c_{66}\\
&\quad-4c_{44}{}^2-4c_{44}c_{66}+2c_{13}{}^2+4c_{13}c_{44}-2c_{11}c_{33}\\
&\quad-2c_{33}c_{66}-4c_{33}c_{44}]\kappa^2-c_{13}(-c_{13}c_{66}-c_{13}c_{44}\\
&\quad+2c_{14}c_{56}+2c_{56}{}^2-2c_{44}c_{66}-2c_{44}{}^2)\\
&\quad-c_{33}(c_{11}c_{44}+c_{44}{}^2+c_{44}c_{66}+c_{11}c_{66}-c_{14}{}^2\\
&\quad-2c_{14}c_{56}-c_{56}{}^2)-c_{44}(c_{11}c_{44}+c_{11}c_{66}-c_{14}{}^2)\\
&\qquad\qquad\qquad+c_{11}c_{56}{}^2=0. \qquad \text{(VIII, IX, X)}
\end{aligned}
$$

In Eqs. (III) to (X), inclusive, the constant ordinarily written c_{14} is written as c_{14}, $-c_{24}$, or c_{56}, depending upon its position in the stress-strain table. The reason for splitting this constant will be explained later. The Roman numerals indicate the secular factor associated with each of the ten modes of vibration used in determining the elastic constants.

4. Finite plates

Since no easy exact theory of the vibrations of a finite plate is possible, it seems best, for the present purposes, to use the following perturbation point of view.

Imagine the finite plate as being formed by moving the lateral surfaces of the plate in from infinity. One result of this change is to introduce new frequencies corresponding to the new finite lateral dimensions of the crystal. The perturbing effect of these finite boundaries on the "thickness" modes of vibration of the infinite plate (i.e., those modes of vibration with phase planes parallel to the surfaces of the plate) is twofold. The first is a shift in frequency caused by the presence of the boundaries. The second effect is the coupling which the existence of these lateral boundaries introduces between the given frequency and others which may be in the same neighborhood. One would expect theoretically, from the principle of Saint Vernant, that these perturbations of the thickness frequencies of an infinite plate of given thickness by the finite lateral boundaries in an actual physical plate of the same thickness would decrease rapidly as the wave-length becomes small compared with the lateral dimensions of the crystal. We shall see that this result is confirmed experimentally, and it is a principal precaution of the present paper that the conditions of infinite plates be closely approximated by using very high harmonics of the thickness modes of vibration and hence a wave-length very small compared with the lateral dimensions. This procedure is much better than an attempt to use plates of large lateral dimensions which attempt, of course, is limited by the size of the specimens available as well as by the size that is convenient to cut and use. The use of very thin plates is also undesirable because it is very difficult to cut such plates with a high relative accuracy and without introducing surface scratches which have a significant effect.

Experimental Methods

Two large, relatively flaw-free natural quartz crystals having well-developed, reflecting facets, were selected for use, and only those portions of the crystals distant from any twinning visible by means of polarized light were used to make the plates. The surfaces of all the plates were etched with hydrofluoric acid and were found to exhibit no traces of twinning. Plates were cut from each of the natural crystals (hereafter designated as crystals 1 and 2) having the following orientations: (0°, 0°) the so-called *x* cut; (30°, 0°) or (90°, 0°) a *y* cut; (30°, −38° 12½′), an *R* cut, and (0°, 45°). A(0°, 90°) or *z* cut was also made from crystal 1. The dimensions of all the plates were approximately 2.2×2.2×0.45 cm, all being accurate rectangular parallelepipeds in shape and having unrounded edges free from nicks.

Optical methods, making use of the reflecting facets of the crystals, were used to orient the plates. The orientations of all the plates were checked by x-ray methods which revealed no measurable error of orientation for any plate. Opposite surfaces of the plates were ground parallel to each other to within 0.0001 cm and the National Bureau of Standards determined the average thicknesses of these plates, their measurements being accurate to 0.00001 inch.

The plates were made to vibrate piezoelectrically as a filter between a variable frequency, stable oscillator and a sensitive vacuum tube voltmeter for detecting resonance frequencies of the plates. An audioamplifier was used for the approximate location of the resonance points and for obtaining beat notes between the oscillator and a frequency meter. By this method, frequencies of higher order harmonics of the plates were determined to an absolute accuracy of about one part in twenty-five thousand.

The quartz plates were mounted in a vertical position with their weight resting on a lateral face so as to leave the main surfaces as nearly as possible free of external stresses. Two sets of plane parallel electrodes were used, one for applying the alternating electric field parallel to the thickness of the plate, and the other for applying the field perpendicular to the thickness. A small air gap was left between the plate and each electrode. The electrodes and plates were contained in a constant temperature chamber, the temperature being measured to within 0.05°C by means of a thermocouple and potentiometer. The constant temperature chamber was arranged so that the air could be evacuated from it to prevent the air from damping or shifting the frequencies of the plates. However, it was found, for all harmonics except the lowest, that there was no detectable frequency change produced by the presence of the air, and so, for most of the work, the chamber was not evacuated.

Preliminary Investigation

In a preliminary study with the quartz plates previously described, the frequency "spectra" of all the plates were rather fully investigated, the temperature being maintained at 35°C. It was found that in the lower frequency region (the region up to approximately 5000 kilocycles per second for the particular plates used) there were literally many hundreds of frequencies to which a crystal plate would react, these responses, however, having a great range of amplitudes. The presence of so many frequencies of response can be explained by the fact that a finite plate in the form of a rectangular parallelepiped was used, and lateral modes of vibration and couplings between modes made possible a great multiplicity of vibrational frequencies. In general, however, the harmonics of the main modes of vibration were excited more strongly than the other frequencies and could be recognized by their greater intensity.

The measurable frequency "spectrum" became progressively simpler with higher frequencies until harmonics of only the main modes, and in some cases harmonics of certain lateral modes of vibration, were detectable, the latter much more faintly than the former. Beyond about 20,000 kilocycles per second, the harmonics of only the main modes of vibration were detectable.

The frequencies of the odd harmonics of the main modes of vibration were determined from the fundamental up to the 87th harmonic in some cases, and harmonic frequencies of certain lateral modes (those modes whose phase planes are parallel to the small lateral surfaces of the plate) were measured up to the 263rd harmonic. It was found that there was a relatively large variation in the frequency of the harmonic divided by the order of the harmonic, i.e., f/n, in the lower frequency region because of coupling between modes and because of edge effects of the plates. As the order of the harmonic was increased, coupling and edge effects decreased until variations from the mean of f/n for all harmonics above about the 31st for the main modes of vibration, with very few exceptions, amounted to less than 0.01 percent. These experimental results, therefore, confirm the basic assumption of the method employed that the higher the order of the harmonic of a finite plate, the closer the value of f/n should approach the fundamental frequency of a theoretical infinite plate of the same thickness. In general, it was also found that f/n for the lateral modes of vibration approached the theoretical value more slowly with increase in n than it did for the main modes.

As an example of the sort of data obtained for each of the quartz plates, there is presented in Fig. 1 the values of f/n for four modes of vibration of one of the (30°, 0°) plates. Mode III in the figure is a lateral mode of vibration. Here, the general asymptotic approach of f/n to its final value may be attributed to edge effects of the plate, and individual often stronger variations of f/n to coupling between modes. The vertical lines connecting resonance points of approximately the same frequency indicate possible coupling between modes, but it must be remembered, of course, that there are many natural modes of vibration of this plate whose frequencies were not

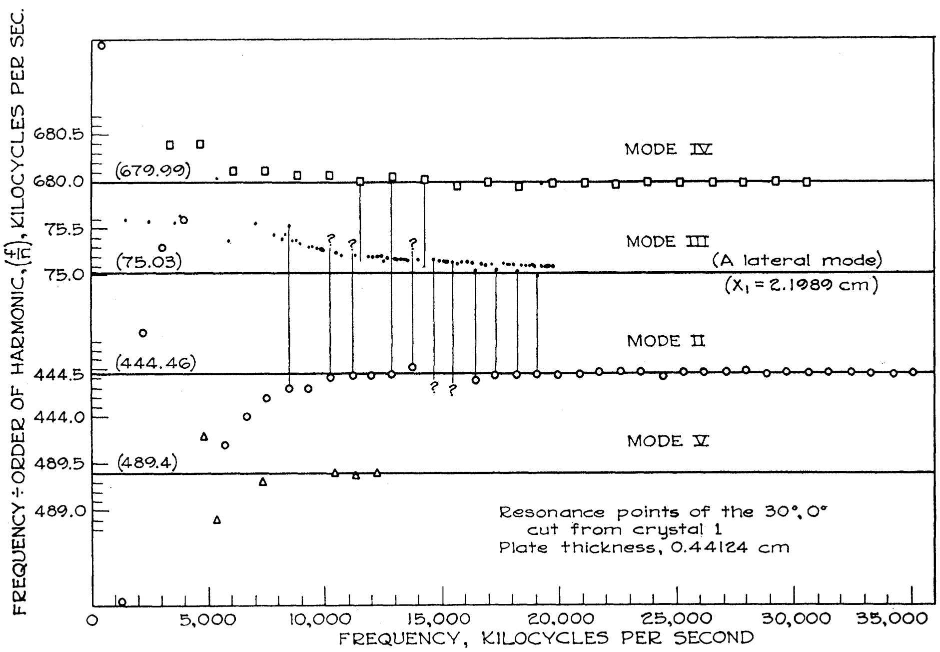

FIG. 1. Values of f/n as a function of frequency for several modes of vibration.

measured, which could be responsible for coupling.

In the experimental investigation, most of the modes of vibration defined by Eqs. (I) to (X) were excited by the appropriate alternating electric field. Only one of the two modes of vibration defined by Eq. (III) for the (0°, 0°) plates, however, was observed, the other mode probably being too weak to detect. However, both modes defined by Eq. (IV, V) for the (30°, 0°) plates were obtained, the mode designated as (V) being much the weaker of the two. Only one of the R modes defined by Eq. (VII) was observed. The modes of vibration for the (0°, 90°) plate were not excited strongly above the very lowest frequencies, possibly because of the close coupling and damping occurring between the two essentially equal modes of vibration. The three modes of vibration, (VIII), (IX), and (X) for the (0°, 45°) plates were obtained with approximately equal intensity by an electric field in the direction of the thickness of the plate. A field in the x_2 direction also excited all three of these modes of vibration, the frequencies for the higher order harmonics for the x_2 field being the same within the experimental error as the frequencies for the field in the (0°, 45°) direction, thus providing experimental evidence that the air gap width is not of consequence for high frequencies.

The values of κ^2 calculated by Eq. (7) for corresponding modes of vibration of the plates made from the natural quartz crystals 1 and 2, proved to be identical within the limits of error allowed by the thickness measurements of the plates for all the different modes of vibration. This fact is an indication of the uniformity of all flaw-free quartz.

DATA FOR ELASTIC CONSTANTS AND THEIR TEMPERATURE COEFFICIENTS

In order to be able to determine both the elastic constants and their temperature coefficients frequency measurements of the various modes of vibration were made between the approximate temperatures of 0° and 80°C. Frequencies of five consecutive harmonics were determined in the frequency region between 22,000 and 30,000 kilocycles per second for each mode of vibration, the variation of f/n from the mean value of the five f/n's seldom being greater than 0.005 percent. An average value of f/n was found for each mode of vibration at each temperature for which temperature measurements were made, for the plates from both crystals 1 and 2, these data being presented in Figs. 2 to 10. In the figures, the curves for the plates from crystals 1 and 2 are plotted close together so that the slopes may be compared. The change of frequency with temperature of mode of vibration (V) (this mode being very weak) was not measured. However, the value of f/n at 35°C for this mode was evaluated, but less precisely, by harmonics up to the 25th (see Fig. 1), this value being 489.4 kc/sec.

Since the curves of change of frequency with temperature show but small experimental error, it is possible to determine the value of f/n accurately for any desired temperature, the values of f/n used here in the evaluation of the elastic constants of quartz being determined in this way for the temperature of 35°C. It is also possible to determine accurately the slopes of these curves, (and in some cases, perhaps, even the second derivative of frequency with respect to temperature), the temperature coefficients of the elastic constants being here determined by the use of the slopes of these curves at 35°C.

In Table I are presented the selected values of f/n and of $d(f/n)/dT$ (T being temperature in °C) at 35°C for the plates from crystal 1. Also presented are the calculated values of Sf/n, of κ^2, and of $S\cdot d(f/n)/dT$, the latter three values being constants which do not depend on plate thickness. A Roman numeral in column 1 refers to the mode of vibration which is defined by the equation of the same number. The density of quartz was taken as 2.648 g/cc at 35°C.

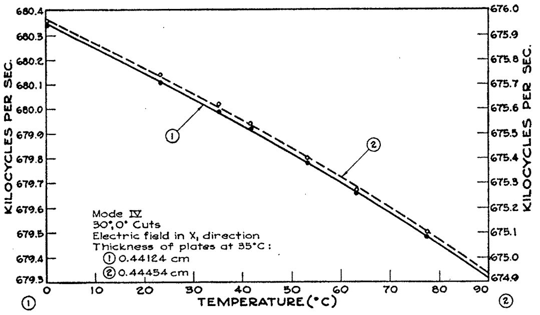

FIG. 2. Frequency of mode (I) vibration as a function of temperature.

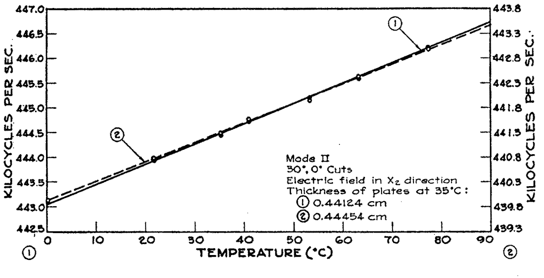

FIG. 3. Frequency of mode (II) vibration as a function of temperature.

CALCULATION OF THE ELASTIC CONSTANTS

Substitution of the values of κ^2 from Table I into Eqs. (I) and (II) gives directly, $c_{11}=87.55$ and $c_{66}=40.74$, the units being 10^{10} dynes per square centimeter. Since $c_{66}=\frac{1}{2}(c_{11}-c_{12})$, c_{12} is found to be 6.07. However, the solution of Eqs. (III) to (X) with the assumption that $c_{14}=-c_{24}=c_{56}$ (a direct consequence of the trigonal axis generally accepted for quartz), offers difficulties because of the fact that these equations are found to be inconsistent to a degree not explainable by known experimental errors. In fact, substitution of the numerical values of c_{11} and c_{66} into Eqs. (III) and (VI) and the simultaneous solution of

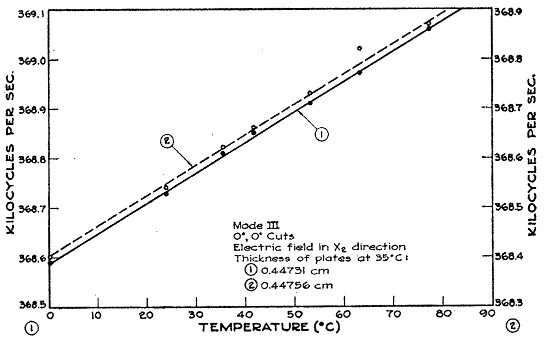

FIG. 4. Frequency of mode (III) vibration as a function of temperature.

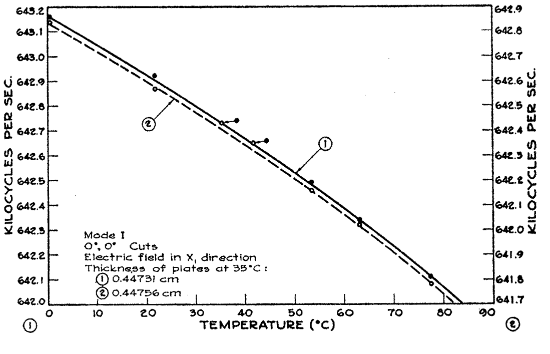

FIG. 5. Frequency of mode (IV) vibration as a function of temperature.

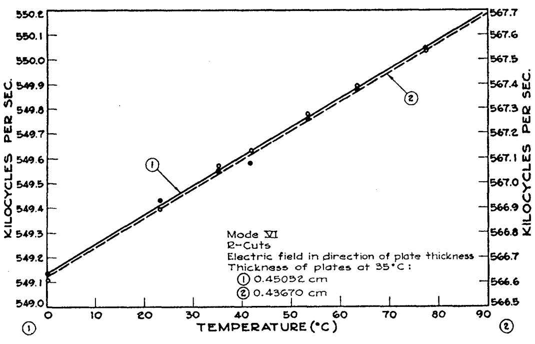

FIG. 6. Frequency of mode (VI) vibration as a function of temperature.

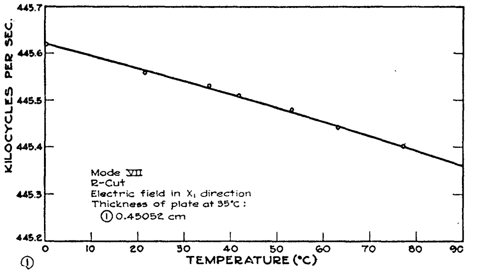

FIG. 7. Frequency of mode (VII) vibration as a function of temperature.

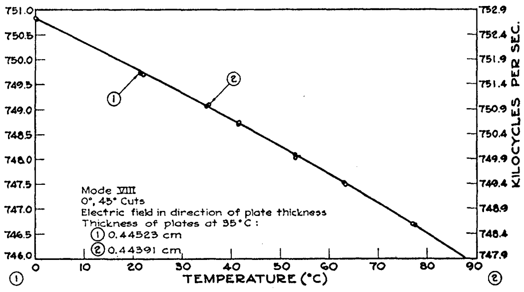

FIG. 8. Frequency of mode (VIII) vibration as a function of temperature.

these equations gives $c_{44}=57.19$ and $c_{56}=18.40$. Similarly, solution of Eqs. (IV) and (V) gives $c_{44}=\kappa_{\mathrm{IV}}^2+\kappa_{\mathrm{V}}^2-c_{11}=57.19$ and $-c_{24}=17.25$. Since the c_{44}'s in these two cases prove to be identical, and since c_{11} and c_{66} are determined directly, one has either to doubt the fact that $-c_{24}$ should be equal to c_{56} or to attempt to find some error of theory or measurement leading to this peculiar result. The data for the independent equations (VII) to (X) would be expected to present more evidence on this question.

Values of c_{11}, c_{66}, c_{44}, c_{14}, c_{24}, and c_{56} substituted into Eqs. (VII) to (X) give four equations in the two unknowns, c_{13} and c_{33}. Simultaneous solution of each possible pair of these equations should give the same set of values for c_{13} and c_{33}, provided the values of the substituted constants are correct. Average values of the four constants determined by any combinations of Eqs. (I) to (VI), inclusive, with the assumption that $-c_{24}=c_{56}$, substituted into Eqs. (VII) to (X), make the latter equations highly inconsistent. It should be mentioned that, because of the form of Eqs. (VII) to (X), the coefficients of c_{13} and c_{33} often involving differences between numbers of almost equal magnitude, the values of the known constants substituted into these equations must be very nearly correct before the equations show any great degree of consistency.

By assuming that $-c_{24}=c_{56}$, and with the values determined from Eqs. (I) to (VI), Eqs. (VII) to (X) can be solved, first, with the assumption that $c_{14}=c_{56}$, and second, with the assumption that $c_{14}=-c_{24}$. The first assumption makes the last four equations much more consistent than does the substitution of any values of the constants obtained from Eqs. (I) to (VI) by setting $-c_{24}=c_{56}$. The second assumption, however, makes the equations more consistent yet, the inconsistency in the latter case being of such small value that it can be attributed, possibly entirely, to experimental error. The experimental data, therefore, give evidence that $c_{14}=-c_{24}\neq c_{56}$.

An analysis of Eqs. (I) to (VI) shows that, in

TABLE I. *Summary of results. The data are from the plates from crystal 1 at 35°C. The values of κ^2 for the plates from crystal 2 checked so closely with the values from crystal 1 that it did not seem necessary to include the data from crystal 2 in the table. Comparative examples of the results obtained from crystals 1 and 2 are, for mode of vibration I, $\kappa^2=87.55$ for crystal 1 and $\kappa^2=87.56$ for crystal 2. Similarly, for mode II, $\kappa^2=40.74$ for crystal 1 compares with $\kappa^2=40.76$ for crystal 2, and for mode III, $\kappa^2=28.82$ compares with $\kappa^2=28.83$, etc.*

MODE OF VIBRATION No.	f/n, KC/SEC.	PLATE THICKNESS, s, CM	sf/n CM·KC/SEC.	$\kappa^2=4\rho s^2(f/n)^2$ 10^{10} DYNES/CM^2	$d(f/n)/dT$ CYCLES/SEC.·°C	$s\cdot d(f/n)/dT$ CM·CYCLE/SEC.·°C
I	642.73	0.44731	287.50	87.55	−13.4	−5.99
II	444.46	0.44124	196.11	40.74	+39.3	+17.46
III	368.80	0.44731	164.97	28.82	+6.1	+2.73
IV	679.99	0.44124	300.04	95.35	−11.0	−4.89
V	489.4	0.44124	215.94	49.39		
VI	549.55	0.45052	247.58	64.92	+11.8	+5.15
VII	445.53	0.45052	200.72	42.67	−2.8	−1.26
VIII	749.06	0.44523	333.50	117.81	−53.2	−23.60
IX	489.29	0.44523	217.85	50.27	−12.5	−5.55
X	410.74	0.44523	182.87	35.42	−12.6	−5.59

order to make these equations consistent assuming $-c_{24}=c_{56}$, certain of the experimentally determined κ^2's must be raised in value and others lowered. If the absolute value of this rise or drop is assumed to be equal for each mode of vibration to be changed, the magnitude of this change can be calculated. Its value is much too large to be attributed to experimental error.

If we follow the empirical lead indicated above and assume $c_{14}=-c_{24}\neq c_{56}$, the adiabatic elastic constants of quartz are found to have the values presented in Table II.

TABLE II. *The adiabatic elastic constants of quartz at 35°C.*

$c_{11}=87.55\times10^{10}$	$c_{14}=-c_{24}=17.25\times10^{10}$ dynes/cm^2
$c_{66}=40.74$	$c_{56}=\ 18.40$
$c_{12}=\ 6.07$	$c_{13}=\ 13.3$
$c_{44}=57.19$	$c_{33}=106.8$

The authors are well aware of the grave difficulties inherent in the assumption that $c_{14}=-c_{24}\neq c_{56}$ in quartz. If confirmed, this result would force the relinquishment of the seemingly well-established trigonal axis and cause a change in its classification from D_3 to C_2 thus making quartz a monoclinic crystal. The following paragraphs indicate the rather extended effort that has been made to find another explanation of these experimental results.

The first suggestion is that quartz may not be a uniform substance even when it passes the optical and other tests previously described. One might then ascribe the results obtained to the fact that macroscopically quartz does not belong to the class D_3, being distorted by irregularities due to impurities or other causes. However, the excellent agreement between the wave velocities for similarly oriented plates cut from different mother crystals argues against this explanation. Furthermore, below, there will be described results obtained from cubes cut from the same two crystals, and these results agree, to within experimental error, with those obtained from the plates. Previous experimenters have obtained somewhat discordant results for the elastic constants of quartz but it cannot be said with certainty that these results indicate non-uniformity of tested quartz. On the contrary, it may be that difficulties of the type being outlined here have played a part in making the values of the elastic constants uncertain.

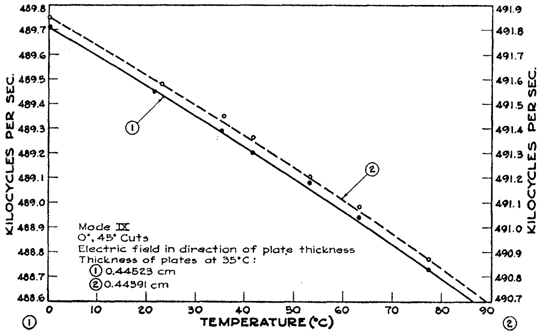

FIG. 9. Frequency of mode (IX) vibration as a function of temperature.

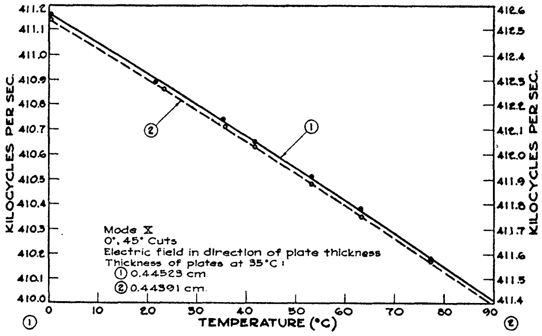

FIG. 10. Frequency of mode (X) vibration as a function of temperature.

The only likely source of error in the cutting of the plates would be in their orientation, since it is a simple matter to grind the surfaces until they are parallel and measure them. However, an examination of the modes involved will indicate that the measurement of the *X*, *Y*, and *R* cut plates is sufficient to furnish an inconsistent set of equations and these cuts are easy to orient with the crystal faces and to test with x-ray Laue photographs.

There are a variety of other possibilities. Since quartz is as good a conductor of heat as some of the metals the possibility that the wave motion is no longer adiabatic for the shortest waves used was examined. Isothermal wave motion should yield consistent secular equations for the determination of the elastic constants, but it was thought that the hybrid case might result in such inconsistencies. However, dimensional analysis, as well as more exact calculations, shows that the heat conductivity for the range of frequencies used is entirely negligible.

It was suggested that the inconsistencies might

TABLE III. *Values of differential coefficients. The units are 10^{10} dynes/cm^2/°C.*

MODE OF VIBRATION NO.	$\frac{\partial\kappa^2}{\partial f}\frac{df}{dT}$	$+\ \frac{\partial\kappa^2}{\partial s}\frac{ds}{dT}$	$+\ \frac{\partial\kappa^2}{\partial\rho}\frac{d\rho}{dT}$	$=\ \frac{d\kappa^2}{dT}$
I	−0.00365	+0.00234	−0.00304	−0.00435
II	+0.00725	+0.00109	−0.00141	+0.00693
III	+0.00095	+0.00077	−0.00100	+0.00072
IV	−0.00311	+0.00255	−0.00331	−0.00387
V		+0.00132	−0.00172	
VI	+0.00270	+0.00147	−0.00225	+0.00192
VII	−0.00054	+0.00096	−0.00148	−0.00106
VIII	−0.01666	+0.00251	−0.00408	−0.01823
IX	−0.00256	+0.00107	−0.00175	−0.00324
X	−0.00217	+0.00076	−0.00123	−0.00264

be due to surface effects or to nearly plane standing waves not parallel to the faces of the crystal. Since these effects should be sensitive to changes in the thickness and relative proportions of the crystal plates, respectively, a further investigation was made with crystal blocks approximately cubical in proportion. One such cube was cut from each of the mother crystals, with its edges parallel to the coordinate axes, and, of course, such a block could be regarded as either a (0°, 0°) or as a (30°, 0°) plate. The method of investigation was the same as that previously used except that very high harmonics (up to the 263rd) had to be used in order to eliminate the perturbing effects of the edges. Without giving details, it may be stated that calculation of κ^2 from the constant value of f/n approached by the modes of vibration (I), (II), (III), and (IV) gave values which were identical, within experimental error, with the values obtained by means of the plates previously used. It thus appears that effects of these two types cannot be responsible for the observed inconsistency existing between the equations of vibration.

There remains the interesting question of the adequacy of the theoretical treatment. The mathematical theory of elasticity which forms the basis of this treatment has not, in the main, been experimentally verified to any high degree of accuracy because the irregularities of most materials tend to cloud the results. Only the more perfect crystals, of which quartz is one, offer material of sufficient uniformity to make such a verification possible and experiments of the type discussed probably constitute one of the best experimental procedures. On the mathematical side, it must be said that the tensor-invariant point of view used in constructing mathematical elasticity leaves its structure so secure that it is not easy to imagine any simple modification that will be an improvement. There are, of course, certain restrictions in the use of the theory of elasticity, the principal one being due to the fact that Hooke's law is only valid for small values of the strains but the present method is admirably suited to work within this limit.

To summarize, there seem to be three alternatives to account for contradictory secular equations: (a) There has been some systematic error of experimentation in spite of the consistency of the data; (b) the classical theory of vibrations is inadequate; or (c) macroscopically, quartz does not possess a trigonal axis, at least the two mother crystals examined show a common deviation from the class D_3. The third choice has been adopted in calculating the elastic constants presented but this is done from a heuristic point of view. If quartz is really monoclinic, the observations made are insufficient to determine the thirteen elastic constants which it would possess and one can only say that the wave velocities obtained are in good agreement with those of a monoclinic crystal with the elastic constants which are not zero having the values indicated in the table. There may be some justification for this arbitrary assumption that certain of the constants are zero since, if quartz is not of trigonal symmetry, it must be very nearly so.

CALCULATION OF THE TEMPERATURE COEFFICIENTS

Values of the temperature coefficients of the elastic constants of quartz obtained by various investigators differ greatly in magnitude, probably because of experimental errors involved in measuring a small change in rigidity or frequency. It is also a difficult task to design a quartz plate of finite dimensions whose lower harmonics will not be distorted by coupling with other modes of vibration. The consistency obtaining in the data here presented for frequency *versus* temperature, indicates that the use of harmonics of higher order for frequency measurements provides a very successful method for eliminating the perturbations of the frequency caused by edge effects.

In the equation of vibration for the plates (Eqs. (I) to (X)), the elastic constants and the κ^2's involved are all functions of temperature. Furthermore, in Eqs. (VI) to (X), the coefficients of the c's are direction cosines of the plate orientations which are also functions of temperature. From the manner in which the κ^2's and the direction cosines vary with temperature, it is possible to differentiate Eqs. (I) to (X) with respect to temperature, and to solve the resulting equations for the dC_{ij}/dT's, T being temperature.

By Eq. (11)

$$\kappa^2 = 4\rho s^2 f^2, \quad (f = \lim f_n/n \text{ as } n \rightarrow \infty)$$

f here being the theoretical fundamental frequency of the plate. Since the density, thickness, and frequency, are all functions of temperature, then

$$\frac{d\kappa^2}{dT} = \frac{\partial\kappa^2}{\partial f}\frac{df}{dT} + \frac{\partial\kappa^2}{\partial s}\frac{ds}{dT} + \frac{\partial\kappa^2}{\partial\rho}\frac{d\rho}{dT}$$

$$= 8\rho s^2 f \frac{df}{dT} + 8\rho s f^2 \frac{ds}{dT} + 4s^2 f^2 \frac{d\rho}{dT}.$$

All the quantities on the right side of this equation are determined (see Table I) except the quantities ds/dT and $d\rho/dT$ which can be calculated from the accepted coefficients of expansion of quartz, so it is possible for $d\kappa^2/dT$ to be determined. These data are presented in Table III. It may be pointed out that the term $(\partial\kappa^2/\partial f)(df/dT)$, column 2, and not $d\kappa^2/dT$, is the term which must be zero in order for a quartz plate to have a zero temperature coefficient.

By use of the derivatives of Eq. (I) and (II), dC_{11}/dT and dC_{66}/dT are found to be equal to -0.00435 and $+0.00693$, respectively, the units being 10^{10} dynes/cm²/°C. Similarly, by use of Eqs. (III), (V), and (VI), the quantities dC_{44}/dT, dC_{24}/dT, and dC_{56}/dT can be determined, and these values substituted in the remaining equations for the determination of dC_{13}/dT and dC_{33}/dT.

TABLE IV. *The temperature coefficients of the elastic constants of quartz.*

c_{ij}	$\frac{dc_{ij}}{dT}$	$\delta c_{ij} = \frac{dc_{ij}}{dT} \Big/ c_{ij}$	δc_{ij} As Determined by Bechmann[1, 2]	δc_{ij} As Determined by Mason[3]	δc_{ij} As Determined by Koga[4]
c_{11}	-0.00435	-49.7×10^{-6}	-48×10^{-6}	-54×10^{-6}	-61.1×10^{-6}
c_{66}	$+0.00693$	$+170.1$	$+144$	$+161$	$+199$
c_{12}	-0.01821	-3000	-2115	-2350	
c_{44}	-0.00965	-169	-151	-160	-199
c_{14}	$+0.00184$	$+107$	$+82$	$+96$	$+110$
c_{56}	$+0.00143$	$+78$			
c_{13}	-0.00765	-580	-530	-687	
c_{33}	-0.0227	-213	-208	-251	

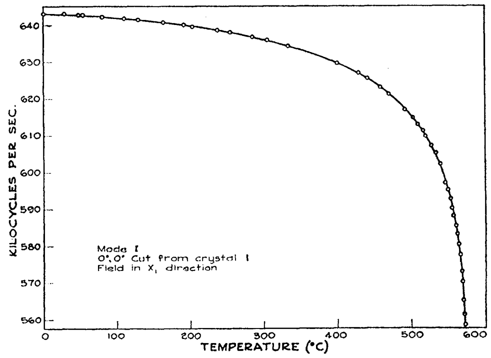

FIG. 11. Variation of the fundamental frequency of mode (I) with temperature.

In the differentiation of the equations, the direction cosines occurring in Eqs. (VI) and (VII) were taken as variables, the effect of the variation of these cosines with temperature being found to be small but not negligible. In Eqs. (VIII), (IX), and (X), however, because of the extreme complexity of these equations, the direction cosines were assumed to be constants. It was found, however, that the two unknowns, dC_{13}/dT and dC_{33}/dT, obtained by solving the different possible combinations of pairs of the differentials of the four equations (VII) to (X), were surprisingly consistent. Table IV contains the experimentally determined values of the rates of change of the elastic constants with respect to temperature, and also the values of the temperature coefficients of the elastic constants, δc_{ij}, the latter being the quantities dc_{ij}/dT divided by the corresponding c_{ij}'s. For purposes of comparison, the table also contains values of the temperature coefficients obtained by other investigators.

THE ELASTIC CONSTANTS AT HIGHER TEMPERATURES

In a further investigation, the resonance frequencies of certain of the (0°, 0°) and (30°, 0°) plates were investigated up to and beyond the critical point of quartz. In Figs. 11 to 14 are

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[1] R. Bechmann, Hoch: tech. u. Elek: akus. **44**, 145 (1934).

[2] A. Scheibe, *Piezoelektrizität des Quarzes* (Theodor Steinkopff, Dresden, 1938), p. 54.

[3] W. P. Mason, Bell Sys. Tech. J. 19, 85 (1940).

[4] I. Koga, Rep. Radio Research, Japan **6**, 1 (1934).

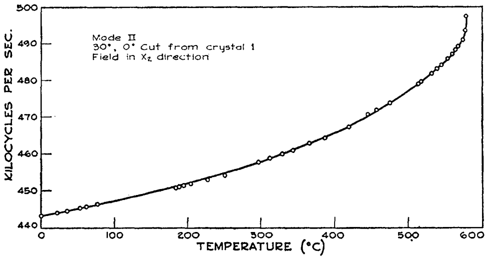

FIG. 12. Variation of the fundamental frequency of mode (II) with temperature.

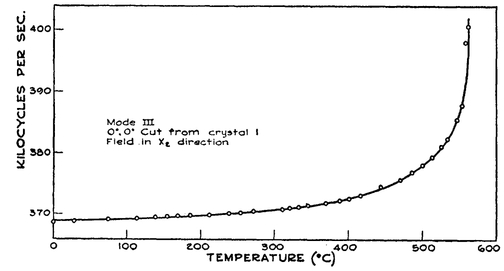

FIG. 13. Variation of the fundamental frequency of mode (III) with temperature.

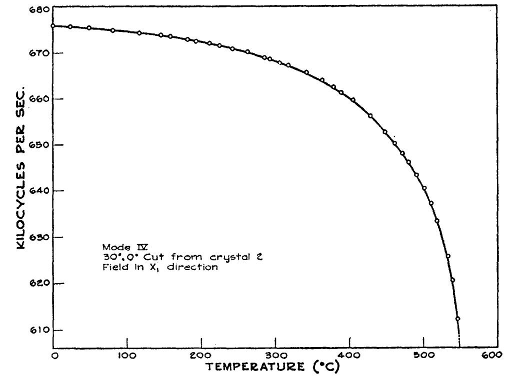

FIG. 14. Variation of the fundamental frequency of mode (IV) with temperature.

presented the fundamental frequencies of modes of vibration (I), (II), (III), and (IV), as a function of the temperature. The data for these curves were obtained by following the 17th, 27th, 27th, and 15th plate harmonics, respectively, in the above modes of vibration as the temperature was changed. The thickness of the plates at 35°C for modes (I) to (IV) were, 0.44731 cm, 0.44124 cm, 0.44731 cm, and 0.44454 cm, respectively.

If it be assumed that $-c_{24}=c_{56}=c_{14}$, it is possible to solve Eqs. (I) to (IV) simultaneously for the evaluation of four of the elastic constants at temperatures approaching the critical point. While the previous evidence given here indicates that $-c_{24}$ may not equal c_{56}, still such calculations may yield useful information on the behavior of the elastic constants at higher temperatures, although the values of c_{44} and c_{14} obtained will not agree with those obtained before because of the assumption here that $-c_{24}=c_{56}$. In Table V are presented the elastic constants obtained by Eqs. (I) to (IV) through the use of the data given in Figs. 11 to 14, the elastic constants being corrected for the change in thickness and density of the plates with temperature.

Since modes (III) and (IV) became too weak to measure as the critical point was approached, c_{44} and c_{14} cannot be evaluated at that point through these data. However, the trend of the data indicates that c_{44} approaches a minimum of about 30 at the transition point, while c_{14} seems to fall to zero, c_{14} for β-quartz being equal to zero. It will be noticed that c_{14} first exhibits a positive temperature coefficient and that this coefficient later becomes negative.

TABLE V. *Four of the elastic constants of quartz at various temperatures.*

	0°C	100°	200°	300°	400°	500°	540°	550°	562°	573°	580°
c_{11}	87.7	87.3	86.6	85.5	83.6	79.6	76.3	74.6	71.6	65.7	
c_{66}	40.5	41.2	42.0	43.1	44.5	46.7	47.8	48.2	48.7	49.3	50.6
c_{44}	55.9	55.0	53.7	51.8	49.2	44.1	38.0	37.4	<33.8		
c_{14}	17.8	17.9	18.0	17.9	17.4	15.2	12.4	10.1			

Mode of vibration (II) seems to have continued being excited for a short time after the transition point (probably indicated by the sudden change in slope in Fig. 12) was reached, thus determining the value of c_{66} for β-quartz at 580°C, although this latter point may be somewhat in doubt.

The frequencies of vibration of modes (I) to (IV) were all carefully checked at 35°C both before and after being heated beyond the critical point, and these frequencies were found to coincide exactly. Therefore, although the piezoelectric strength was observed in certain cases to have been changed by the heating, the elastic constants evidently were not altered.

In conclusion we wish to thank Professor G. L. Clark and Dr. S. T. Gross of the University of Illinois for making the Laue photographs to check the orientations of the plates and for several helpful discussions.