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# A Determination of the Elastic Constants of Beta-Quartz

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A new technique is described for quickly locating and measuring weak resonance points of a plate of piezoelectric material. The method involves driving the resonator with a frequency modulated carrier and demodulating and amplifying a voltage related to the motion of the resonator. The output of the amplifier is placed on one set of plates of an oscilloscope and the other plates are charged with the modulating voltage. The resulting pattern on the oscilloscope screen permits easy location and measurement of resonant frequencies. This arrangement was employed with a dynamical method to determine all elastic constants of beta-quartz. Edge effects were eliminated by the use of high harmonics as described by Atanasoff and Hart. Several hundred frequencies related to six modes of four cuts were measured, this number of modes being sufficient to permit the simultaneous solution of the resulting secular equations with an over determination of the five elastic constants. Table III gives the values obtained for these constants and also contains all the known results of other experimenters.

THE experimental techniques available for evaluating the elastic properties of aelotropic or isotropic solids can be divided into two general classes. The static method consists in observing the deformation of loaded bars or plates. The constants measured in this way are termed isothermal since in the process the small temperature changes caused by flexing the specimen have ample opportunity to become equalized. In the dynamic method, on the other hand, the elastic properties are inferred from the frequency of standing waves set up in a given portion of the material. From knowledge of the frequency, dimensions, density, and mode of vibration, the elastic constants can be calculated. In this case small temperature differences will exist between regions of nodes and loops. The constants will differ slightly from those computed by the static method and are termed adiabatic.

The advantages of utilizing high order harmonics in calculations of adiabatic elastic constants from vibrating plates were first pointed out by Atanasoff and Hart.[1] They have clearly demonstrated that as the number of nodal planes between two opposite surfaces of a vibrating plate are increased, the perturbing effect of the edges has a diminishing influence on the frequency $f/n$, where $f$ is the observed frequency and $n$ the order of the frequency. The limiting frequency $f/n$ then depends only on the thickness of the plate, the mode of vibration, and the elastic properties of the medium.

Beta-quartz, also known as "high" quartz, exists between 573°C and 870°C. Although the static method of determining elastic constants becomes increasingly difficult at these temperatures, an experiment in which this technique is used on beta-quartz is described by Perrier and de Mandrot.[2] They have published data on Young's modulus in directions parallel and perpendicular to the principal axis and also at an angle of 50° to the principal axis. This information is not sufficient to permit a calculation of the five independent constants for this substance.

The announcement of Osterberg and Cookson[3] that elastic vibrations of considerable vigor could be maintained in high quartz by means of its piezoelectric effect has been confirmed by a recent research[4] conducted in this laboratory. In this latter investigation, the resonant frequencies of a particularly accessible mode of vibration were examined. A measurement of these frequencies made possible a calculation of the $C_{44}$ adiabatic elastic constant for this

[1] J. V. Atanasoff and P. J. Hart, Phys. Rev. **59**, 85–96 (1941).

[2] A. Perrier and B. de Mandrot, Memoires de la Societé Vaudoise des Sciences Naturelles, No. 7 (Imprimeries Reunies S. A., Lousanne, 1923).

[3] H. Osterberg and J. W. Cookson, J. Frank. Inst. **220**, 361–371 (1935).

[4] J. V. Atanasoff and E. W. Kammer, Phys. Rev. **59**, 97–99 (1941).

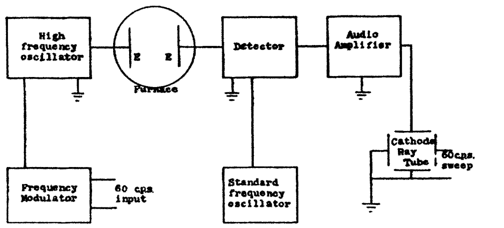


FIG. 1. Schematic diagram of experimental apparatus used in measuring crystal resonance frequencies.

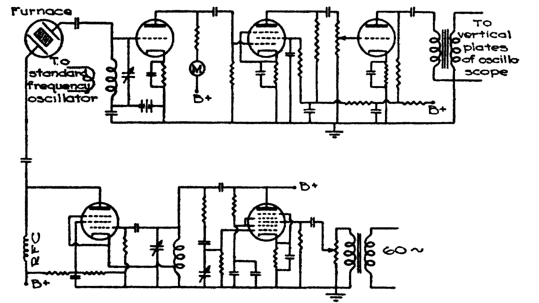


FIG. 2. Apparatus for measuring resonance frequencies.

material. The success of this measurement suggested the feasibility of determining the remaining four constants with this experimental technique.

The theoretical treatment of the present subject is the same as that used by Atanasoff and Hart in their work on alpha-quartz. Proper modifications must be made, however, for the different symmetry conditions encountered in beta-quartz which is classified as $D_6$ while alpha-quartz is $D_3$.

The method of detecting and comparing the frequency of crystal resonances in the present experiment differs considerably from that of Atanasoff and Hart. In their technique a crystal was driven by an oscillator of adjustable frequency. The resonance points of the crystal were observed by using a vacuum-tube voltmeter and then the frequency of the oscillator was compared with a standard. The measurement of harmonic resonant frequencies of the crystal could thus be carried to a high degree of precision. However, with beta-quartz the piezoelectric effect is much weaker and the losses inherent in the crystal holder circuit components when at high temperatures made the deflections of the vacuum-tube voltmeter unreadably small. A method permitting considerable amplification of the piezoelectric reaction in the circuit was essential to the success of a dynamic method in this application. The necessary amplification, as well as certain other advantages, was obtained in the technique to be described next, but with a reduction in precision of measurement to about one part in 5000.

The experimental method used in the present investigation can, perhaps, best be explained by reference to the schematic block diagram Fig. 1 and the circuit diagram Fig. 2. The output voltage of a high frequency oscillator is applied to the electrodes $EE$ between which the specimen is placed. The oscillator is frequency modulated by a 60-c.p.s. tone, causing the carrier frequency to sweep periodically across a band of controllable deviation (of the modulated frequency from its mean). If a resonance frequency of the crystal lies within the range of maximum and minimum values of frequency attained by this modulated carrier, it will absorb some energy from the field. The exact treatment of the response of a quartz resonator to a frequency modulated input is rather complicated; however, at a low modulation frequency the following intuitive interpretation is asymptotically correct.

Since the frequency of the applied field is continually changing, it remains only for an instant at the resonance frequency of the crystal. After this impulse, the quartz, having very low damping, will continue to vibrate at its natural harmonic frequency for some little time. During this time, two radiofrequencies are present in the circuit; the first, a continually changing one of constant amplitude due to the oscillator; the second, a fixed one due to the vibrating crystal whose amplitude is decreasing because of damping. These two frequencies are applied to the detector, and the result of the mixing and demodulation is a single varying-pitch audiobeat note. This audiotone is amplified and applied to the vertical plates of a cathode-ray tube whose sweep frequency is the same as that of the tone which modulated the carrier of the oscillator, in this case 60 c.p.s.

A photograph of a typical trace obtained on the screen is reproduced in Fig. 3. The abscissa of this figure represents frequency increasing from left to right, the resonant frequency of the crystal being at the center of the pattern. The fact that the frequency deviation of the modulated signal can be controlled at will is a great convenience. A compressed pattern (large frequency deviation) for resonant points permits a rapid survey. A more precise examination of a single resonance point is achieved by means of an expanded pattern.

A parallel *LC* circuit is used between the crystal holder and detector. The circuit details are shown in Fig. 2. This unit is adjusted to resonate at the center of the frequency band covered by the modulated carrier. The same network provides a convenient method for introducing a standard comparison frequency into the channel, and it also suppresses undesired harmonics in the standard oscillator output. To compare the frequency of the crystal resonant position on the fluorescent screen with a known standard, the signal from a standard oscillator is introduced by magnetic coupling and a pattern obtained somewhat similar to the one shown in Fig. 3. This trace is superposed on the screen with the crystal response. When the standard oscillator is tuned until the two minima of the patterns coincide, the standard oscillator is tuned to a resonant point of the crystal.

Since the specimen between the electrodes *EE* must be at a temperature above 573°C if observations are to be made on beta-quartz, a special holder was devised. Nickel electrodes were used with iron rods as leads to the exterior of the furnace. A sheet of mica placed over the face of each electrode prevents contact with the specimen and reduces likelihood of breaking the plate due to non-uniform conduction of heat from the electrode. Unglazed porcelain plates and cylinders make up the balance of structural material. The holder assembly fits snugly in a resistance furnace heated by direct current to avoid induction signals being picked up by the detector. A Chromel-Alumel thermocouple was used to measure the temperature of the holder adjacent to the specimen.

With the apparatus described one may easily measure the frequencies of resonance of a given specimen which fall in any selected frequency range. The problem of classifying these raw data is somewhat similar to the technique which must be employed in atomic spectra. If the crystal is examined in the proper frequency range one can select from the observed resonances a succession of frequencies which are nearly proportional to a number of successive odd integers. Such a series of frequencies can only accurately occur under the following conditions: 1. That the crystal resonator must have parallel faces so placed that plane waves can travel between them. 2. That the frequency range must be high so as to make the odd integers large. It is natural to interpret such a series of frequencies as constituting the odd harmonics of a single mode of vibration but it is easy to see that these frequencies are not simply related to a fundamental frequency of a finite block but rather that they asymptotically approach the harmonics of a crystal plate with faces which are infinite continuations of the above-mentioned parallel pair. From these data one may easily estimate[1] the fundamental frequency of the infinite plate which yields the elastic constants according to a rather simple theory. When the parallel faces of a crystal resonator are separated by about one-half centimeter several members of each series (corresponding to these faces) occur in the octave below 10 mc. If the crystal plate has lateral dimensions of say two centimeters, it will be found that these frequencies already closely exhibit a constant difference and hence accurately determine the fundamental frequency of an infinite plate.

Some of the plates used in this experiment were selected from those prepared by Atanasoff and Hart for their work on alpha-quartz. Several additional plates were made up with orientation not found among their collection.

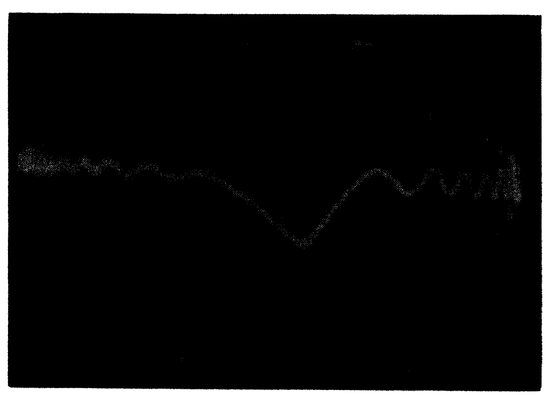

FIG. 3. Typical oscillograph of crystal response.

The material from which these new cuts were obtained was carefully examined for optical twinning by the use of polarized light. Moreover, the surfaces of the final specimens were etched with hydrofluoric acid in a further effort to detect twinning and non-uniformity of structure. The samples surviving these tests are described in Table I.

Thus far the measurements relating to linear dimensions and angles of orientations have been

TABLE I. The dimensions of the quartz plates in centimeters.

| Orientation | Thickness | Lateral dimensions in $x'_2$ | $x'_3$ |
|---|---|---|---|
| $Y$ 30° 90° | 0.4444 | 2.197 | 2.178 |
| $R$ 30°, 51° 47½′ | 0.4500 | 2.176 | 2.222 |
| 73° 30′, 59° 29′ | 0.8081 | 1.469 | 2.214 |
| 0° 45° | 0.4442 | 2.227 | 2.200 |

made on the specimen as alpha-quartz at room temperature. Since the material is to be heated to 600°C, expansion will change the dimensions of the plate as well as the orientation. Quartz expands at a different rate parallel to the optic axis as compared to that at any direction perpendicular to this axis, the latter expansion being the larger. These coefficients have been measured by LeChatelier[5] and also by Jay.[6] The values published by Jay will be used in the calculations to follow.

To compute the thickness of the plate as beta-quartz from the thickness $d$ at room temperature, use is made of the equation:

$$d_\beta = d_\alpha(1+\gamma_z)\lambda^\beta/\lambda^\alpha.$$

The superscripts $\alpha$ and $\beta$ on the direction cosines $\lambda$ signify that they are the cosines of the angles between the normal of the plate and the optic or $z$ axis as alpha- and beta-quartz, respectively. The value $\lambda^\beta$ is not measureable and must be computed from the expansion factors. If $\mu$ is the angle between the normal to the plate and the optic axis at room temperature, then the correction in radians to be added to this angle due to the effect of increased temperature will be very nearly:

$$\epsilon = \tfrac{1}{2}(\gamma_y - \gamma_z)\sin 2\mu.$$

The quantities $\gamma_y$ and $\gamma_z$ are the changes in length per unit length over the temperature range considered for directions perpendicular or parallel to the optic axis, respectively. As a consequence of the change in angle $\mu$, the direction cosines throughout the determinantal equations must be adjusted accordingly. Table II contains the corrected values for thickness of the cuts based on Jay's results $\gamma_z = 0.00998$, $\gamma_y = 0.01733$.

The manner in which secular equations can be obtained for each plate of Table I has been explained in some detail by Atanasoff and Hart[1] in their paper on alpha-quartz. These secular equations contain the elastic constants as unknowns and for beta-quartz have the general form:

$$\begin{vmatrix} C'_{1111}-K^2, & 0, & C'_{1131} \\ 0, & C'_{1221}-K^2, & 0 \\ C'_{1311}, & 0, & C'_{1331}-K^2 \end{vmatrix} = 0. \quad (1)$$

The simultaneous solution of a set of equations of the type (1) begins with the evaluation of the characteristic value $K^2$ for the various plates.

TABLE II. Computed values of $K^2$ for the plates, with $\rho = 2.517$ g/cc; temperature 600°C.

| Orientation of plate | $\nu$ KC/sec. | Plate thickness "$d$" cm | $d(\nu)$ cm/sec. ×10³ | $K^2$ dynes/cm² ×10¹⁰ |
|---|---|---|---|---|
| 30°, 90° | 417.49 | .4521 | 188.74 | 35.85 |
| 0°, 44° 48′ | 457.63 | .4502 | 206.02 | 42.70 |
| 30°, 51° 35′ | | | | |
| Mode I | 436.60 | .4565 | 199.30 | 39.99 |
| Mode II | 723.08 | .4565 | 330.08 | 109.6 |
| 73° 30′, 59° 18′ | | | | |
| Mode I | 240.1 | .8205 | 197.0 | 39.06 |
| Mode II | 407.6 | .8205 | 334.4 | 112.5 |

To do this it is necessary to know the density of quartz as well as the thickness of the plate at the temperature in question and finally, the frequency $\nu$ of the mode of vibration being observed. The value 2.517 g/cm³ used for the density of quartz at 600°C was taken from the work of Day, Sosman, and Hostetter.[7] The thicknesses of the plates as beta-quartz after

[5] H. LeChatelier, Comptes rendus **108**, 1045–1049 (1889).
[6] A. H. Jay, Proc. Roy. Soc. London **A142**, 237–247 (1933).
[7] Day, Sosman, and Hostetter, Am. J. Sci. **37**, 16 (1914).

making correction for expansion are listed in Table II. This table also shows the magnitude of $K^2$ as computed from the relation: $K^2=4\rho d^2(\nu)^2$.

In the secular Eq. (1) which applies to the $Y$ plate, a factor appears, namely, $(C_{44}-K^2)=0$, which readily yields the constant $C_{44}$ equal to $35.85\times10^{10}$ dynes/cm$^2$. The variation from the earlier published value,[4] of $35.75\times10^{10}$ dynes/cm$^2$ is due to the use of Jay's result of 0.01733 for the $\gamma_y$ expansion coefficient for beta-quartz rather than the older value of 0.0161 estimated from the data given by LeChatelier.

For the 0°, 44° 48′ plate, the constant $C'_{1221}$ which occurs in the linear term of Eq. (1) is set equal to $42.70\times10^{10}$ dynes/cm$^2$. Thus:

$$(0.70453)^2C_{66}+(0.70967)^2C_{44}=42.70\times10^{10}. \quad (2)$$

When the above value for $C_{44}$ is substituted, the elastic constant $C_{66}$ becomes:

$$C_{66}=(\tfrac{1}{2})(C_{11}-C_{12})=49.7\times10^{10}\ \text{dynes/cm}^2. \quad (3)$$

In order to make certain that the value for $K^2$ used to find $C_{66}$ is the proper one, an examination of the constant $C_{44}$ is necessary and also the direction of the exciting electric field must be noted. For the 0°, 44° 48′ plate, the $C_{44}$ constant which appears in $C'_{1221}$ will be $C_{3223}$. The piezoelectric constant $e_{14}$ for beta-quartz is the only one with strain subscripts "23." Hence, the mode belonging to the linear term for this cut can only be excited by an alternating electric field with a component in the direction of the electric axis. Furthermore, the constants $C_{44}$ which appear in the quadratic portion of Eq. (1) when applied to the 0°, 44° 48′ plate are of the form $C_{3113}$. Since $e_{25}$ is the only piezoelectric constant with the strain subscripts "13" the modes belonging to the quadratic term require an alternating electric field with a component in the direction of the mechanical axis for excitation.

Both modes predicted for the quadratic portion of the $R$ secular equation were observed. Substitution for $K^2$ and the direction cosines together with the known value for $C_{44}$ yields the equations:

$$(0.23700)C_{11}C_{33}-(53.825)C_{11}-(37.008)C_{33} \\ -(16.993)C_{13}-(23700)C^2{}_{13}+8099=0; \quad (4)$$
$$(0.23700)C_{11}C_{33}-(11.039)C_{11}-(10.097)C_{33} \\ -(16.993)C_{13}-(0.23700)C^2{}_{13}+165.6=0. \quad (5)$$

When the plate is taken from the crystal in a manner which prevents the normal from being perpendicular to any of the crystallographic axes, as is the case for the 73° 30′, 59° 18′ cut, it is not obvious which modes belong to the quadratic factor. In the determinantal equation both $C_{3113}$ and $C_{3223}$ are present in each factor so that all three modes could appear with the electric field applied along a lateral dimension. However, only two modes were observed in this instance. If we know what $C_{66}$ should be from Eq. (3), a substitution for each $K^2$ in the linear portion of Eq. (1) involving $C'_{1221}$ verifies that both observed modes belong to the quadratic factor. This yields two more equations relating $C_{11}$, $C_{13}$, and $C_{33}$, namely:

TABLE III. The adiabatic elastic constants and moduli for beta-quartz at a temperature 600°C.

| Elastic constants $\times10^{10}$ dynes/cm$^2$ | Elastic moduli $\times10^{-12}$ cm$^2$/dyne | Lawson (adiabatic) $\times10^{-12}$ cm$^2$/dyne | Perrier and de Mandrot (isothermal) $\times10^{-12}$ cm$^2$/dyne |
|---|---|---|---|
| $C_{11}=118.4$ | $S_{11}=0.9257$ | | $S_{11}=0.9345$ |
| $C_{12}=19.0$ | $S_{12}=-0.0802$ | | |
| $C_{13}=32.0$ | $S_{13}=-0.252$ | $S_{13}=-0.226$ | |
| $C_{33}=107.0$ | $S_{33}=1.085$ | | $S_{33}=1.050$ |
| $C_{44}=35.85$* | $S_{44}=2.789$ | | |
| | $S(45°)=1.073$ | $S(45°)=1.067$ | |
| | $S(50°)=1.057$ | | $S(50°)=1.075$ |

* A value of $19.36\times10^{10}$ dynes/cm$^2$ has been given for this constant by Osterberg and Cookson (reference 3). We regard this value as untenable and a similar opinion is held by Lawson (reference 8).

$$(0.19267)C_{11}C_{33}-(63.621)C_{11}-(26.902)C_{33} \\ -(13.814)C_{13}-(0.19267)C^2{}_{13}+8634=0; \quad (6)$$
$$(0.19267)C_{11}C_{33}-(9.2840)C_{11}-(7.7460)C_{33} \\ -(13.814)C_{13}-(0.19267)C^2{}_{13}+125.5=0. \quad (7)$$

Equations (4), (5), (6), and (7) are more than enough to determine the three unknown constants they contain. The solution was achieved by a trial and error process of successive approximations. The values for the elastic constants shown in Table III satisfy the four equations within 1 percent.

It is of interest to compare these results with the isothermal measurements made by Perrier and de Mandrot. Their values for Young's modulus perpendicular ($E_\perp$) and parallel ($E_\parallel$) to the optic axis are expressed in kilograms per square millimeter, but in Table III these units are converted to dynes per square centimeter. After making a linear interpolation to the temperature 600°C, the reciprocals of $E_\perp$ and

$E_{11}$, namely, $S_{11}$ and $S_{33}$, become 0.934 and $1.05\times10^{-12}$ cm$^2$/dyne, respectively. The computed modulus for an angle of 50° with respect to the optic axis is $1.05\times10^{-12}$ cm$^2$/dyne. This quantity was also measured directly by Perrier and de Mandrot. Again interpolating on their table to 600°C, the estimated value for this modulus becomes $1.07\times10^{-12}$ cm$^2$/dyne. The accuracy of this latter interpolated value in particular is doubtful since the experimental points are widely separated in the region of 600°C and the curve is known to take a rather sharp bend in this same region. Considering the experimental difficulties inherent in the static method when used at these temperatures, it is felt that the agreement between isothermal and adiabatic moduli is satisfactory, the discrepancies being of the order of a few percent.

Lawson[8] has made a dynamic measurement of the modulus in a direction of 45° to the optic axis. This was accomplished by setting up longitudinal vibrations in a quartz bar and computing Young's modulus from the frequency of vibration, density, and length of the bar. Corrections were calculated for the perturbing effect of the finite dimensions of the practical bar on the theoretical frequency of a thin bar having the same length. In this manner Lawson arrives at the value $1.067\times10^{-12}$ cm$^2$/dyne for the 45° modulus while the data in Table III yield $1.073\times10^{-12}$ cm$^2$/dyne. This agreement between these two adiabatic measurements taken in such different ways is gratifying. Using Perrier and de Mandrot's measurements of $S_{33}$ and $S_{11}$ together with the recently published[4] value for $S_{44}$, Lawson proceeds further to estimate the modulus $S_{13}$ obtaining $-0.225\times10^{-12}$ cm$^2$/dyne. A greater discrepancy appears here with the value listed in Table III. Since Lawson's measurement of the 45° modulus agrees so well with the present set of constants the dependence of his result for $S_{13}$ on the work of Perrier and de Mandrot seems to be the principal source of error. On the other hand it should be noted that Lawson has made a slight error in his reduction of the results of Perrier and de Mandrot to c.g.s. units.

Each determination of elastic constants by a dynamical method requires a knowledge of the mode of vibration. This knowledge can be obtained by an experimental examination of the vibrations[3] or it can be inferred from theoretical considerations.[8] The method of Atanasoff and Hart throws a greater burden on the frequency spectrum by making the identification of modes depend on it. Since the frequency spectrum can be determined with high accuracy and since theory enters only in a simple limiting way this method seems to possess some real advantages. We feel that the principal source of error in the present investigation is the difficulty of controlling and measuring the temperature of the crystal with sufficient accuracy over the considerable period of time necessary to make readings. The slight discrepancies noted by Atanasoff and Hart and explained by Lawson[9] are less important.

[8] A. W. Lawson, Phys. Rev. **59**, 608 (1941).

[9] A. W. Lawson, Phys. Rev. **59**, 838 (1941); **62**, 71 (1942).

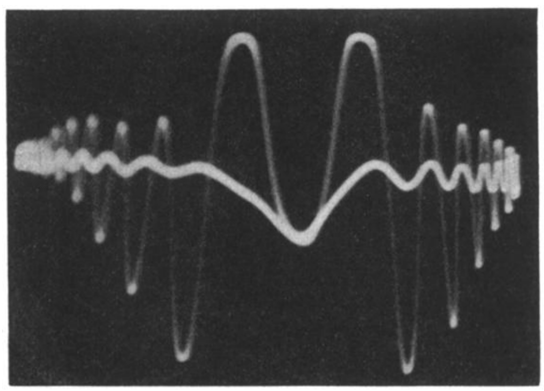

FIG. 3. Typical oscillograph of crystal response.