A Determination of the c_{44} Elastic Constant for Beta-Quartz

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A careful determination of the elastic constant c_{44} of beta-quartz has been made using the method of Atanasoff and Hart. The results obtained, $c_{44}=35.75\times 10^{10}$ dynes/cm², differs by a factor of nearly two from the only other published value. A study of the behavior of this constant in the range 0° to 650°C, the consistency in the value obtained from different cuts from different crystals and other facts seem to justify the value of the constant here determined.

THE work described here is an outgrowth of several researches which have been performed at this laboratory in the past few years. Wilson[1] has investigated the piezoelectric oscillations of quartz plates. Atanasoff and Hart[2] later calculated the elastic constants of quartz from measurements of the frequencies of the piezoelectric vibrations of plates cut from the crystal at specific orientations. This work has demonstrated the advantage of using high order harmonics in measuring the wave velocity to avoid edge effects. Since these researches had been confined to alpha-quartz, it was proposed to apply this technique to the determinations of the elastic properties of beta-quartz. The only measurements of the elastic properties of beta-quartz are those of Osterberg and Cookson[3] who used an interference method with monochromatic light to determine whether the crystal was oscillating and, if so, the mode of oscillation.

A detailed derivation of the mathematical expressions applicable to alpha-quartz plates of any orientation with regard to the crystallographic axes is given in the work of Atanasoff and Hart.[2] However, we are interested in a different crystal structure, that of beta-quartz, and these expressions need some modification. Since the work of Bragg and Gibbs[4] and also that of Wyckoff[5] has established the symmetry class of beta-quartz to be C_6 rather than D_3 as in alpha-quartz, the matrix of the elastic constants, using Voigt's[6] notation, becomes:

$$\begin{matrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{11} & c_{13} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & \tfrac{1}{2}(c_{11}-c_{12}). \end{matrix}$$

The c_{14} constant which is present in the matrix for alpha-quartz is zero here. An expansion of the secular equation (see Eqs. (I) and (III) of reference 2) for an infinite X cut plate will now be:

$$(c_{11}-\kappa^2)(c_{11}/2-c_{12}/2-\kappa^2)(c_{44}-\kappa^2)=0, \quad (1)$$

where κ^2 has the value, $4\rho s^2 f^2/n^2$, ρ being the density, s the thickness of the plate, and f is the frequency of the nth harmonic. An expansion of the secular equation for a Y cut plate (see Eqs. (II) and (IV) of reference 2) takes the following form:

$$(c_{11}/2-c_{12}/2-\kappa^2)(c_{22}-\kappa^2)(c_{44}-\kappa^2)=0. \quad (2)$$

To ascertain which modes of vibration will be excited when the crystal has the symmetry of beta-quartz, an examination of the piezoelectric tensor is necessary. In Voigt's[6] notation it has the components:

$$\begin{matrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0. \end{matrix}$$

The term e_{14} implies the subscripts e_{123} or e_{132} being a term of a third-rank tensor. Hence an alternating electric field applied in the x_1 direction excites vibrations involving strain compo-

[1] R. G. Wilson, "A study of the piezoelectric oscillation of quartz plates," unpublished Thesis, Library, Iowa State College, Ames, Iowa, 1936.
[2] J. V. Atanasoff and P. J. Hart, Phys. Rev. **59**, 85 (1941), preceding paper.
[3] H. Osterberg and J. W. Cookson, J. Frank. Inst. **220**, 361–371 (1935).
[4] W. Bragg and R. E. Gibbs, Proc. Roy. Soc. London **A109**, 414 (1925).
[5] R. W. G. Wyckoff, Am. J. Sci. **11**, 112 (1926).
[6] W. Voigt, *Lehrbuch der Kristallphysik* (Teubner, Leipzig, 1928), 585–586 and 830–831.

TABLE I. *Dimensions of the plates.*

CRYSTAL 1	X	Y	Z
X cut	0.4472	1.305	2.238
Crystal 2			
Y cut	2.198	0.4445	2.180

nents θ_{23}. These excited vibrations are therefore shear modes. Hence the factor,

$$c_{44}-\kappa^2=0 \qquad (3)$$

is the part of the secular equations (1) and (2) for both X and Y cuts with which we are concerned and c_{44} the elastic constant here determined.

The quartz plates used in this investigation were chosen from those used by Atanasoff and Hart[2] in their work on elastic constants. The orientations of the plates were accurate to within three minutes of arc as checked by Clark and Gross at the University of Illinois from Laue x-ray patterns. Twinned portions were in each case eliminated after examination in polarized light. Etching of these crystals also verified the uniformity of the material. The dimensions (in centimeters) of the plates used are listed in Table I. The experimental method used was identical with that of Atanasoff and Hart.[2]

Typical data obtained near the temperature of 600°C are exhibited in Tables II and III. From the term involving c_{44} in Eqs. (1) and (2), the elastic constant for beta-quartz at 600°C is:

$$c_{44}=4\rho s^2f^2/n^2=35.75\times10^{10} \text{ dynes/cm}^2$$
from the X cut plate

$$c_{44}=4\rho s^2f^2/n^2=35.78\times10^{10} \text{ dynes/cm}^2$$
from the Y cut plate.

By means of linear interpolation, the value of the frequency at 600°C has been estimated from Tables II and III for use in the above calculation. The value for the density of quartz used is that of Day, Sosman and Hostetter,[7] namely 2.517 g/cm³ at 600°C. To calculate the value of the new thickness at the high temperature from that measured at room temperature, the change in linear dimension was estimated from the work of Le Chatelier as reproduced in Vigoreux.[8]

In Fig. 1 there is plotted the value of c_{44} throughout the range from 0°C to 650°C. The values below the transition point are those of Atanasoff and Hart.[2] The point at 562°C is not known accurately because of a lack of knowledge of the elastic constant c_{24} involved in the secular equation (IV) as given in the paper of Atanasoff and Hart.[2] However, the curve at this temperature must be above the point plotted, otherwise the values of c_{24} would be imaginary. On the other hand, the crystal class of beta-quartz requires this constant to be zero. The shape of the dotted portion of the curve is suggested by direct observations of elastic coefficients near the critical temperature.[9] For some reason, the electrical response of a crystal in the neighborhood of the critical point is very weak and this accounts for the absence of data in that region. The cause of this weak response is uncertain, but it is unlikely that the piezoelectric constant involved falls to a small value near the critical point. It may be that irreversible changes induced by the vibrations absorb their energy. This explanation is supported by the observed fact that the oscillations can be followed closer to the critical point when approaching it from the high temperature side.

The value of the elastic constant c_{44} calculated above is in sharp disagreement with the value of 19.36×10^{10} dynes/cm² given by Osterberg and Cookson[3] at the same temperature. In determining this constant for beta-quartz, Osterberg and Cookson[3] have employed a theory

TABLE II. *The frequency f/n of the Y cut beta-quartz plate. Frequencies are given in kilocycles per second and temperature in degrees centigrade.*

TEMPERATURE	OBSERVED FREQUENCY f	HARMONIC OF CRYSTAL n	f/n
587	9582.8	23	416.64
592	10422	25	416.88
594	11259	27	417.00
598	10433	25	417.32
603	10440	25	417.60
606	10446	25	417.84
592	2917.4	7	416.77
598	2921.0	7	417.28
602	2922.6	7	417.52
606	2924.7	7	417.82

[7] A. L. Day, R. B. Sosman and J. C. Hostetter, Am. J. Sci. **37**, 16 (1914).

[8] P. Vigoreux, *Quartz Resonators and Oscillators* (His Majesty's Stationery Office, London, 1931).

[9] R. B. Sosman, *The Properties of Silica* (Chemical Catalog Company, New York, 1927), p. 466.

which is closely related to one given by Mason,[10] yielding an expression of the form:

$$F_{np}=\tfrac{1}{4}(c_{44}/\rho)^{\frac{1}{2}}(n^2/y^2+p^2/z^2)^{\frac{1}{2}}$$

or

$$F_{mp}=\tfrac{1}{4}(c_{44}/\rho)^{\frac{1}{2}}(m^2/x^2+p^2/z^2)^{\frac{1}{2}},$$

where F is the observed frequency of oscillation, c_{44} is the elastic constant calculated for beta-quartz, ρ is the density, while x, y and z are the half-dimensions of the rectangular parallelepiped quartz specimen along the indicated axes. This theoretical treatment was admittedly an approximation, but some such approximation was found necessary. A more exact theory of vibration is required to permit the calculation of the elastic constants with any accuracy for the lower modes. Their theory seems to stand in the following relation to an accurate theory of finite plates for which their treatment is proposed. (A) Certain body constraints are assumed which simplify the differential equation describing the problem. (B) Certain boundary conditions are left unsatisfied by the solution chosen for this differential equation.

TABLE III. *The frequency f/n of the X cut beta-quartz plate. Frequencies are given in kilocycles per second and temperature in degrees centigrade.*

Temperature	Observed Frequency f	Harmonic of Crystal n	f/n
611	2910.0	7	415.71
598	2902.8	7	414.69
592	2899.3	7	414.19
618	8738.1	21	416.10
618	7072.5	17	416.03
618	6240.5	15	416.03
618	5409.7	13	416.13
618	3746.0	9	416.22
618	2912.0	7	416.00
618	2083.2	5	416.65

[10] W. P. Mason, Bell Sys. Tech. J. **13**, 446–448 (1934).

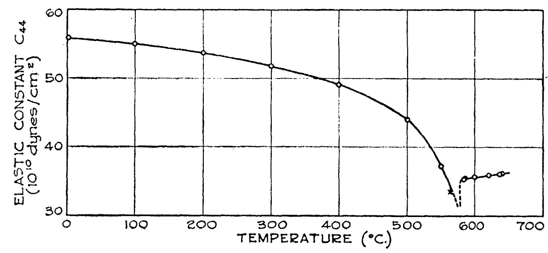

FIG. 1. Variation of the elastic constant c_{44} with temperature.

The imposition of constraints upon a vibrating system, as in A, has the effect of raising the frequency of vibration.[11] Hence, if a measured frequency of vibration is inserted into either formula above, the elastic constant c_{44} so calculated would have a value lower than it would for the case in which no constraint was supposed in the theoretical development. Leaving some boundary conditions unsatisfied, as in B, however, has the effect of removing constraints upon the vibrating system. This would cause the frequency of vibration to be decreased.[10] Thus the mathematical treatment of the problem used by Osterberg and Cookson is open to question. In fact, the elastic constant c_{44} as calculated by them has a different value for each type of vibration studied. Also the values obtained for this constant on crystals of different dimensions do not agree. This certainly indicates that the mathematical methods used in deriving these results are not adequate and it may even be that there has been an error in the identification of the modes of vibration.

It is a pleasure to thank Dr. Philip J. Hart for considerable assistance in the experimental part of this paper.

[11] R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Julius Springer, Berlin, 1931), Part II, p. 244.