

that this condition prevailed except for the possibility of ions being trapped in the lattice. An additional electrometer placed in the circuit showed that the trapping probability is $<0.2\%$ in the energy range over which measurements were made (300–1200 ev).

Retarding potentials show that both ion and electron energy distributions are of the order of a few ev; hence small bias potentials are sufficient to provide satisfactory collector efficiencies without unduly disturbing the optics. The adjustment of these potentials to maximize the readings of the electrometers permitted a direct calculation of γ_i without additional corrections. (See Fig. 2.) The possibility of negative cesium ions being formed seems unlikely, since the ions apparently

come into thermal equilibrium with the lattice before being re-emitted. Using the Boltzmann factor, we obtain for the ratio of negative ions to positive ions $\sim 10^{-11}$. The ratio of ions to neutral atoms leaving the target is $\sim 10^3$.

ACKNOWLEDGMENTS

The writer wishes to acknowledge his indebtedness to Professor Leonard B. Loeb under whose direction and guidance this work was carried out, to Mr. Morley Corbett for the excellent glass blowing, and to the Office of Naval Research for their support during the progress of this work.

Theory of Plane Elastic Waves in a Piezoelectric Crystalline Medium and Determination of Elastic and Piezoelectric Constants of Quartz

ISSAC KOGA, *University of Tokyo, Tokyo, Japan*
MASANAO ARUGA, *Defense Academy, Yokosuka, Japan*

AND

YŌICHRŌ YOSHINAKA, *Meidensha Electric and Manufacturing Company, Tokyo, Japan*

(Received May 27, 1957)

Atanasoff and Hart made a series of elaborate experiments in order to determine dynamically the elastic constants of quartz. However, they reported that in the evaluation of the elastic constants from the experimental data, there was a small but not easily explained discrepancy between theory and experiment. Lawson pointed out later that the piezoelectric effect could not be neglected in the dynamic determination of elastic constants. The present writers became aware that in the case of a plane elastic wave in a piezoelectric crystalline medium, only the component of piezoelectric polarization in the direction of wave propagation produces a restoring force against mechanical strain, as far as the piezoelectric effect is concerned. Thus the writers could derive the equation of a plane wave in a piezoelectric crystalline medium in general and could further determine the elastic and piezoelectric constants, together with their temperature coefficients, from experimental data. Various experimental results reported by the foregoing authors, including Atanasoff and Hart, can now be adequately explained, even at high temperatures, so that there is no longer any discrepancy between theory and experiments.

I. INTRODUCTION

ALTHOUGH several authors have tried to determine dynamically the elastic constants of quartz from experimental data on the thickness vibration of a quartz plate, their results have not been in satisfactory agreement with each other. Atanasoff and Hart¹ found that, in the evaluation of the elastic constants from the experimental data, there was a small but not easily explained discrepancy between theory and experimental results. Lawson² pointed out that the piezoelectric effect could not be neglected in the dynamic determination of elastic constants, but he did not clarify the question that Atanasoff and Hart had raised.

Needless to say, piezoelectric polarization is produced whenever an elastic wave is transmitted through a crystalline medium; but it is important to note that, in the case of a plane wave, only the component of piezo-

electric polarization in the direction of wave transmission produces a restoring force against the strain, so far as the piezoelectric effect is concerned. Keeping this in mind, the present writers derived the equations for the plane wave in the following way.

2. GENERAL THEORY OF PLANE ELASTIC WAVE IN A PIEZOELECTRIC CRYSTALLINE MEDIUM

As the medium here is piezoelectric, the stress is composed of "electrical stress" as well as "mechanical stress." If the former be denoted by \bar{X}_x, \dots , the latter by X_x, \dots , and the displacements along the rectangular coordinate axes x, y, z by u, v, w , the equations of motion should initially be as follows:

$$\frac{\partial}{\partial x}(X_x + \bar{X}_x) + \frac{\partial}{\partial y}(X_y + \bar{X}_y) + \frac{\partial}{\partial z}(X_z + \bar{X}_z) = \rho \frac{\partial^2 u}{\partial t^2}, \quad (1)$$

etc.

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

² A. W. Lawson, *Phys. Rev.* **59**, 838 (1941).

Now, suppose that the plane wave is propagated in the direction s , so that

$$s = lx + my + nz, \tag{2}$$

then, as one of the present writers³ has already shown the mechanical restoring forces on the left-hand sides of (1) can be transformed as follows:

$$\begin{aligned} \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} - \frac{\partial^2}{\partial s^2} (Lu + Hv + Gw), \\ \frac{\partial Y_x}{\partial x} + \frac{\partial Y_y}{\partial y} + \frac{\partial Y_z}{\partial z} - \frac{\partial^2}{\partial s^2} (Hu + Mv + Fw), \\ \frac{\partial Z_x}{\partial x} + \frac{\partial Z_y}{\partial y} + \frac{\partial Z_z}{\partial z} - \frac{\partial^2}{\partial s^2} (Gu + Fv + Nw), \end{aligned} \tag{3}$$

where

$$\begin{aligned} L = PP, \quad M = QQ, \quad N = RR, \\ F = QR, \quad G = RP, \quad H = PQ, \\ P = lc_1 + mc_6 + nc_5, \\ Q = lc_6 + mc_2 + nc_4, \\ R = lc_5 + mc_4 + nc_3. \end{aligned} \tag{4}$$

Although c_1, c_2 , etc., have no physical meaning, $c_h c_k$ is supposed to stand for c_{hk} , the adiabatic elastic stiffness constant, when PP, QQ , etc., are expanded.

Next, the electrical restoring forces on the left-hand sides of (1) can be transformed as follows:

$$\begin{aligned} \frac{\partial \bar{X}_x}{\partial x} + \frac{\partial \bar{X}_y}{\partial y} + \frac{\partial \bar{X}_z}{\partial z} - \frac{\partial^2}{\partial s^2} (A_0 Au + A_0 Bv + A_0 Cw), \\ \frac{\partial \bar{Y}_x}{\partial x} + \frac{\partial \bar{Y}_y}{\partial y} + \frac{\partial \bar{Y}_z}{\partial z} - \frac{\partial^2}{\partial s^2} (B_0 Au + B_0 Bv + B_0 Cw), \\ \frac{\partial \bar{Z}_x}{\partial x} + \frac{\partial \bar{Z}_y}{\partial y} + \frac{\partial \bar{Z}_z}{\partial z} - \frac{\partial^2}{\partial s^2} (C_0 Au + C_0 Bv + C_0 Cw), \end{aligned} \tag{5}$$

where

$$\begin{aligned} \begin{vmatrix} A_0 \\ B_0 \\ C_0 \end{vmatrix} = (\epsilon_1 \gamma_1 + \epsilon_2 \gamma_2 + \epsilon_3 \gamma_3) (\gamma_1 l + \gamma_2 m + \gamma_3 n) \\ \times \begin{vmatrix} l\epsilon_1 + m\epsilon_6 + n\epsilon_5 \\ l\epsilon_6 + m\epsilon_2 + n\epsilon_4 \\ l\epsilon_5 + m\epsilon_4 + n\epsilon_3 \end{vmatrix}, \end{aligned} \tag{6}$$

and

$$\begin{vmatrix} A \\ B \\ C \end{vmatrix} = (l\epsilon_1 + m\epsilon_2 + n\epsilon_3) \begin{vmatrix} l\epsilon_1 + m\epsilon_6 + n\epsilon_5 \\ l\epsilon_6 + m\epsilon_2 + n\epsilon_4 \\ l\epsilon_5 + m\epsilon_4 + n\epsilon_3 \end{vmatrix}, \tag{7}$$

in which $\epsilon_h \epsilon_k$ is supposed to stand for ϵ_{hk} , the piezo-electric stress constant, when the right-hand sides are expanded.

³ I. Koga, Phil. Mag. 16, 275 (1933).

The proof is as follows. In general, electrical stresses (\bar{X}_x, \dots) , equivalent electric fields (E_x, \dots) , electric polarizations (Π_x, \dots) and mechanical strains (e_{xx}, \dots) are related by

$$(\bar{X}_x, \bar{Y}_y, \dots, \bar{X}_y) = (\epsilon_1 E_x + \epsilon_2 E_y + \epsilon_3 E_z) (\epsilon_1, \epsilon_2, \dots, \epsilon_6), \tag{8}$$

$$(E_x, E_y, E_z) = (\gamma_1, \gamma_2, \gamma_3) (\gamma_1 \Pi_x + \gamma_2 \Pi_y + \gamma_3 \Pi_z), \tag{9}$$

$$(\Pi_x, \Pi_y, \Pi_z) = (\epsilon_1, \epsilon_2, \epsilon_3) \times (\epsilon_1 e_{xx} + \epsilon_2 e_{yy} + \dots + \epsilon_6 e_{xy}). \tag{10}$$

Now, since, in the present case, all the displacements are functions of s only, the second factor of (10) can be transformed as follows:

$$\begin{aligned} \epsilon_1 e_{xx} + \epsilon_2 e_{yy} + \dots + \epsilon_6 e_{xy} \\ = - \frac{\partial}{\partial s} [\epsilon_1 lu + \epsilon_2 mv + \epsilon_3 nw + \epsilon_4 (mw + nv) \\ + \epsilon_5 (nu + lv) + \epsilon_6 (lv + mu)] \\ = - \frac{\partial}{\partial s} [(\epsilon_1 l + \epsilon_6 m + \epsilon_5 n) u + (\epsilon_6 l + \epsilon_2 m + \epsilon_4 n) v \\ + (\epsilon_5 l + \epsilon_4 m + \epsilon_3 n) w]. \end{aligned} \tag{11}$$

Therefore, the electric polarization produced in the direction of propagation is

$$\begin{aligned} \Pi = l\Pi_x + m\Pi_y + n\Pi_z \\ = \frac{\partial}{\partial s} (Au + Bv + Cw), \end{aligned} \tag{12}$$

where A, B, C are as shown in (7). Also, as is pointed out in the introduction, since the equivalent stresses \bar{X}_x , etc., depend only upon Γ , the component of electric polarization in the direction of wave propagation, and do not depend upon the other components, which are perpendicular to the said direction, they should be represented as follows:

Introducing, at first, (9) into (8), and replacing Π_x, Π_y , and Π_z by $l\Pi, m\Pi$, and $n\Pi$; and subsequently introducing (12), we obtain

$$(\bar{X}_x, \bar{Y}_y, \dots, \bar{X}_y) = (\epsilon_1 \gamma_1 + \epsilon_2 \gamma_2 + \epsilon_3 \gamma_3) \times (\gamma_1 l + \gamma_2 m + \gamma_3 n) (\epsilon_1, \epsilon_2, \dots, \epsilon_6) \Pi. \tag{13}$$

Thus relationship (5) is now obvious. Consequently, combining (3) and (5), the equations of motion (1) become

$$\begin{aligned} \frac{\partial^2}{\partial s^2} [(L + A_0 A)u + (H + A_0 B)v + (G + A_0 C)w] = \rho \frac{\partial^2 u}{\partial t^2}, \\ \frac{\partial^2}{\partial s^2} [(H + B_0 A)u + (M + B_0 B)v + (F + B_0 C)w] = \rho \frac{\partial^2 v}{\partial t^2}, \\ \frac{\partial^2}{\partial s^2} [(G + C_0 A)u + (F + C_0 B)v + (N + C_0 C)w] = \rho \frac{\partial^2 w}{\partial t^2}. \end{aligned} \tag{14}$$

Multiplying each equation by indeterminate coefficients λ, μ, ν , respectively, summing, and putting

$$\begin{aligned}\lambda(L+A_0A)+\mu(H+B_0A)+\nu(G+C_0A)&=\lambda c, \\ \lambda(H+A_0B)+\mu(M+B_0B)+\nu(F+C_0B)&=\mu c, \\ \lambda(G+A_0C)+\mu(F+B_0C)+\nu(N+C_0C)&=\nu c, \\ \xi &=\lambda u+\mu v+\nu w,\end{aligned}\quad (15)$$

one obtains the following equation:

$$c(\partial^2\xi/\partial s^2)=\rho(\partial^2\xi/\partial t^2).\quad (17)$$

This is the differential equation of a plane elastic wave in a piezoelectric crystalline medium. The values of the c 's in (17) can be determined as the roots of the following determinant, which is obtained by eliminating λ, μ, ν from (15):

$$\begin{vmatrix} L+A_0A-c & H+B_0A & G+C_0A \\ H+A_0B & M+B_0B-c & F+C_0B \\ G+A_0C & F+B_0C & N+C_0C-c \end{vmatrix}=0,\quad (18)$$

where $L, M, N, \dots, A_0, B_0, C_0, A, B, C$ are given by (4), (6) and (7).

As all three roots of (18) are real, it is to be noted that there are always three kinds of plane waves in any direction (l, m, n), and the propagation velocity of each wave is given by $(c/\rho)^{\frac{1}{2}}$.

In the case of quartz,⁴

$$\epsilon_{3k}=0, \quad \gamma_{hk}(h \neq k)=0, \quad \text{and} \quad \gamma_{11}=\gamma_{22}=4\pi/K,\quad (19)$$

K being the dielectric constant in the direction perpendicular to the principal axis z . Hence, upon comparing (6) and (7), it is seen that

$$(A_0, B_0, C_0) = \frac{4\pi}{K}(A, B, C).\quad (20)$$

Also, since the following relations hold in quartz,

$$-\epsilon_{12}=\epsilon_{11}, \quad -\epsilon_{25}=\epsilon_{14}, \quad -\epsilon_{26}=\epsilon_{11},\quad (21)$$

and since, furthermore, all other piezoelectric stress constants vanish, it follows from (7) that

$$\begin{aligned}A &= (l^2-m^2)\epsilon_{11}-mn\epsilon_{14}, \\ B &= -2lm\epsilon_{11}+ln\epsilon_{14}, \\ C &= 0.\end{aligned}\quad (22)$$

Concerning the elastic constants, since the following relations hold in quartz,

$$\begin{aligned}c_{22}=c_{11}, \quad c_{55}=c_{44}, \quad c_{66}=\frac{1}{2}(c_{11}-c_{12}), \\ -c_{24}=c_{56}=c_{14}, \quad c_{23}=c_{13},\end{aligned}\quad (23)$$

⁴ The z and x axes of a right-handed coordinate axes are taken respectively in the direction of the principal axis and one of the three digonal axes of right-handed quartz. Left-handed quartz, associated with the left-handed coordinate axes, is nothing but the image of the right-handed sets.

and moreover, all other elastic constants vanish, it follows from (4) that

$$\begin{aligned}L &= l^2c_{11}+m^2c_{66}+n^2c_{44}+2mnc_{14}, \\ M &= l^2c_{66}+m^2c_{11}+n^2c_{44}-2mnc_{14}, \\ N &= (l^2+m^2)c_{44}+n^2c_{33}, \\ F &= (l^2-m^2)c_{14}+mn(c_{13}+c_{44}), \\ G &= 2lmc_{14}+nl(c_{13}+c_{44}), \\ H &= 2mlc_{14}+lm(c_{11}-c_{66}).\end{aligned}\quad (24)$$

Equations (17) through (24) will prove fundamental in the subsequent discussion.

3. DETERMINATION OF THE ELASTIC AND PIEZOELECTRIC CONSTANTS OF QUARTZ

From the foregoing theory, the authors determined the elastic constants of quartz using quartz-crystal vibrators.

The resonant frequency f_q of the thickness vibration of a very high harmonic order q of a thin quartz plate with thickness a satisfies the following relation

$$\lim_{q \rightarrow \infty} \frac{f_q}{q} = \frac{1}{a} \left(\frac{c}{4\rho} \right)^{\frac{1}{2}} \quad (=f, \text{ say}),\quad (25)$$

and hence $c/4\rho$ can be determined from the values of af for specimens of various orientations.

The specimens were so finished that the orientations of the principal planes coincided (within an error of 20 seconds) with a crystal lattice plane which gave comparatively intense x-ray reflection.

The axial ratio of quartz was taken as 1:1.10000 at 20°C by referring to various authors' results.⁵⁻⁷ Thus, the direction cosines (l, m, n) are given by the indices of the lattice plane ($pq \cdot s$) as follows:

$$\begin{aligned}l &= pD, \quad m = \frac{p+2q}{\sqrt{3}}D, \quad n = \left(\frac{s}{1.1} \right) D, \\ \frac{1}{D^2} &= \frac{4}{3}(p^2+pq+q^2) + \left(\frac{s}{1.1} \right)^2.\end{aligned}\quad (26)$$

The specimens used were all rectangular plates with side lengths from about 28 to 40 mm.

The thickness, that is, the distance between the two principal planes, was from about 2.9 to 4.9 mm, and was measured by means of an optical interference comparator based on the six wavelengths (in microns) of helium light,

$$\begin{aligned}0.447 \dots, \quad 0.471 \dots, \quad 0.492 \dots, \\ 0.501 \dots, \quad 0.587 \dots, \quad 0.667 \dots.\end{aligned}\quad (27)$$

⁵ A. J. Bradley and A. H. Jay, Proc. Phys. Soc. (London) 45, 507 (1933).

⁶ P. H. Miller and J. W. M. DuMond, Phys. Rev. 57, 198 (1940).

⁷ R. W. G. Wyckoff, *The Structure of Crystals* (The Chemical Catalog Company, Inc., New York, 1931), p. 239.

TABLE I. Example of the relation of thickness *versus* frequency of a plate. The last column shows the residuals, in units of 10^{-6} , for relation (28).

a_m (mm)	f (Mc/sec)	Res.
5.0052	0.33374	1.5
4.4961	0.37154	1.4
4.0023	0.41738	-3.6
3.6117	0.46253	-4.5
2.9980	0.55729	9.3
2.5066	0.66658	6.4
2.4857	0.67213	-8.2
2.0040	0.83383	3.3
2.0017	0.83474	-6.8
1.5090	1.10752	-1.4
1.5042	1.11109	3.2

The order of harmonic, g , was generally at least 30, and the resonant frequency was determined by a precision frequency meter with the help of a crystal clock.

The surfaces of the principal planes were finished to a milky white luster, but since the writers felt that there was a question as to whether or not the measured thickness could be taken as an effective thickness, they assumed tentatively that the latter a is a certain amount α less than the former a_m and checked to see if the constancy of af could be further improved. Table I shows an example of the measured thickness a_m *versus* frequency f for a plate in the neighborhood of $r'(01 \cdot 1)$. If it is assumed that the following relation holds:

$$(a_m - \alpha)f = k, \quad \text{a constant}, \quad (28)$$

the values of constants α and k are determined, by the least-squares method, as

$$\alpha = 0.00108 \text{ mm}, \quad k = 1.670063 \text{ mm Mc/sec}. \quad (29)$$

The last column of Table I shows the residuals obtained from (28). This result shows that it is reasonable to take the effective thickness of the specimen to be 0.0011 mm less than the measured thickness. The thickness a shown hereafter is this effective thickness.

In order to separate the individual values of c_{hk} and ϵ_{hk} , the following four relations were used. As c , c_{hk} are always associated with 4ρ , the writers gave prime importance to $c/4\rho$, $c_{hk}/4\rho$, etc., instead of c , c_{hk} , etc., themselves. Thus, the following nomenclature will be used occasionally hereafter.

$$\tilde{c} = c/(4\rho), \quad \tilde{c}_{hk} = c_{hk}/(4\rho), \quad \tilde{\epsilon}_{hk} = (4\pi/K)^{1/2} \epsilon_{hk}/(4\rho)^{1/2}. \quad (30)$$

(1) For those plates parallel to the electrical (diagonal) axis of the quartz, $l=0$, so that from (18) a root c corresponding to the vibration,⁸ which can be excited piezoelectrically, is

$$c = L + (4\pi/K)A^2 \\ = m^2 c_{66} + n^2 c_{44} + 2mn c_{14} + (4\pi/K)m^2(m\epsilon_{11} + n\epsilon_{14})^2,$$

⁸ The other two vibrations cannot be excited electrically, because the corresponding c 's are independent of ϵ , that is, inactive piezoelectrically.

or

$$\tilde{c} = m^2(\tilde{c}_{66} + \tilde{\epsilon}_{11}^2) + n^2\tilde{c}_{44} + 2mn\tilde{c}_{14} \\ - m^2n^2(\tilde{\epsilon}_{11}^2 - \tilde{\epsilon}_{14}^2) + 2m^3n\tilde{\epsilon}_{11}\tilde{\epsilon}_{14}. \quad (31)$$

(2) For an X-cut plate, $l=1$, $m=n=0$, so that⁸

$$c = L + (4\pi/K)A^2 = c_{11} + (4\pi/K)\epsilon_{11}^2,$$

or

$$\tilde{c} = \tilde{c}_{11} + \tilde{\epsilon}_{11}^2. \quad (32)$$

(3) For those plates parallel to the y axis, $m=0$, so that the sum of three values of c (say c_S , c_M and c_L to indicate smallest, medium and largest values, respectively) for any direction (l, m, n) is

$$c_S + c_M + c_L = L + M + N + (4\pi/K)(A^2 + B^2) \\ = l^2(c_{11} + c_{66} + c_{44}) + n^2(2c_{44} + c_{33}) \\ + (4\pi/K)[(l^2\epsilon_{11}^2) + (lm\epsilon_{14})^2],$$

or

$$\tilde{c}_S + \tilde{c}_M + \tilde{c}_L = l^2(\tilde{c}_{11} + \tilde{c}_{66} + \tilde{c}_{44} + \tilde{\epsilon}_{11}^2) \\ + n^2(2\tilde{c}_{44} + \tilde{c}_{33}) - l^2n^2(\tilde{\epsilon}_{11}^2 - \tilde{\epsilon}_{14}^2). \quad (33)$$

(4) The sum of the squares of c_S , c_M , and c_L in the aforementioned plates is

$$(c_S)^2 + (c_M)^2 + (c_L)^2 \\ = (c_S + c_M + c_L)^2 - 2(c_S c_M + c_M c_L + c_L c_S) \\ = \left(L + \frac{4\pi}{K}A^2\right)^2 + \left(M + \frac{4\pi}{K}B^2\right)^2 + N^2 \\ + 2F^2 + 2G^2 + 2\left(H + \frac{4\pi}{K}AB\right)^2, \quad (34)$$

where G only contains $c_{13} + c_{44}$. Hence, introducing all the values of c_{hk} obtained from the foregoing relations and the measured values of \tilde{c} , $\tilde{c}_{13} + \tilde{c}_{44}$ can be determined.

Measurements were made with the specimens shown in Tables II and III, and the following values were obtained at 20°C. (Units: 10^9 cm² sec⁻², confidence coefficient: 90%.)

$$\tilde{c}_{11} = 81.957 \pm 0.014, \quad \tilde{c}_{14} = -17.0501 \pm 0.0036, \\ \tilde{c}_{33} = 99.99 \pm 0.11, \quad \tilde{\epsilon}_{11}^2 = 0.728 \pm 0.017, \\ \tilde{c}_{44} = 54.9861 \pm 0.0061, \quad \tilde{\epsilon}_{14}^2 = 0.040 \pm 0.017, \\ \tilde{c}_{66} = 37.632 \pm 0.017, \quad \tilde{\epsilon}_{11}\tilde{\epsilon}_{14} = -0.1696 \pm 0.0076, \\ \tilde{c}_{13} + \tilde{c}_{44} = 66.250 \pm 0.020, \quad (35)$$

$$(\tilde{\epsilon}_{11} = -2.698, \quad \tilde{\epsilon}_{14} = 0.628. \quad (\text{units: } 10^4 \text{ cm/sec}))$$

Table IV shows the calculated values of c or $\tilde{c}4\rho$ at 20°C based on (30), (31), (32), and (35) in order to compare with the values at 20°C given by Atanasoff and Hart¹ in their Tables I and III (their κ^2 stands for c here). As they gave the values at 35°C, the present writers reduced their values to those at 20°C by using the temperature coefficient of κ^2 given by them. The value of ρ is taken as stated in the next paragraph. It is easily seen that the calculated values by the present

writers are very close to the measured values by Atanasoff and Hart.

If the density ρ of the quartz⁹ at 20°C is taken as 2.6487 gram cm⁻³ ($4\rho=10.5948$) and the dielectric constant K as 4.50, then the adiabatic elastic stiffness constants c_{hk} , in 10¹⁰ dynes cm⁻² and piezoelectric stress constants ϵ_{hk} , in 10⁴ cgs esu at 20°C are (confidence coefficient: 90%)

$$\begin{aligned} c_{11} &= 86.832 \pm 0.015, & c_{13} + c_{44} &= 70.191 \pm 0.021, \\ c_{33} &= 105.94 \pm 0.12, & c_{14} &= -18.0642 \pm 0.0038, \\ c_{44} &= 58.2567 \pm 0.0065, & \epsilon_{11} &= -5.25, \\ c_{66} &= 39.871 \pm 0.018, & \epsilon_{14} &= 1.22. \end{aligned} \quad (36)$$

The values of ϵ_{11} and ϵ_{14} given in (36) are very close to those, -5.2 and 1.2, given by Cady,¹⁰ respectively.

The adiabatic elastic compliance constants s_{hk} in 10⁻¹³ cm² dyne⁻¹ and the piezoelectric strain constants d_{hk} in 10⁻⁸ cgs esu, both at 20°C, derived from the

TABLE II. Experimental data on plates parallel to the x axis. The first column shows the indices of principal planes, and the second column the effective thicknesses. (Y), (R), and (r') mean Y-cut, R-cut, and r'-cut plate, respectively.

Orientations	a (mm)	kc/sec
(01·0)(Y)	3.3788	579.667
(01·1)(R)	3.9590	625.048
(01·1)(r')	3.6104	462.507
(02·3)	3.6110	704.752
(02·3)	3.0418	578.731
(01·2)	4.4310	577.777
(01·2)	3.1590	588.743

values of (36) become

$$\begin{aligned} s_{11} &= 12.77_6, & s_{13} &= -1.23_5, \\ s_{33} &= 9.71_3, & s_{14} &= 4.52_4, \\ s_{44} &= 19.97_1, & d_{11} &= -7.11, \\ s_{66} &= 29.18_1, & d_{14} &= -2.31. \end{aligned} \quad (37)$$

The value of s_{33} is very close to the value 9.71 measured by Perrier and de Mandrot,¹¹ but the value of s_{11} is not so close to their value of 12.69.

The adiabatic elastic stiffness constants c_{hk}^* referred to by Lawson,² containing not only thermal but also electrical parts, when divided by 4ρ (say \tilde{c}_{hk}^*) are: (unit: 10⁹ cm² sec⁻², confidence coefficient: 90%)

$$\begin{aligned} \tilde{c}_{11}^* &= \tilde{c}_{11} + \tilde{\epsilon}_{11}^2 = 82.685 \pm 0.022, \\ \tilde{c}_{33}^* &= \tilde{c}_{33} = 105.94 \pm 0.12, \\ \tilde{c}_{44}^* &= \tilde{c}_{44} + \tilde{\epsilon}_{14}^2 = 55.0256 \pm 0.0181, \\ \tilde{c}_{13}^* &= \tilde{c}_{13} = 11.264 \pm 0.024, \\ \tilde{c}_{14}^* &= \tilde{c}_{14} + \tilde{\epsilon}_{11}\tilde{\epsilon}_{14} = -17.2197 \pm 0.0084, \\ \tilde{c}_{66}^* &= \tilde{c}_{66} + \tilde{\epsilon}_{11}^2 = 38.3602 \pm 0.0024. \end{aligned} \quad (38)$$

⁹ R. B. Sosman, *The Properties of Silica* (The Chemical Catalog Company, Inc., New York, 1927), p. 295.

¹⁰ W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946), p. 219.

¹¹ A. Perrier and B. de Mandrot, *Compt. rend.* **175**, 622 (1922); reference 10, p. 137.

TABLE III. Experimental data on plates parallel to the y axis. The first column shows the indices of principal planes, and the second column the effective thicknesses. (L), (M), and (S) mean the largest, medium and the smallest value of f , respectively.

Orientations	a (mm)	kc/sec
(21·1)	2.7724	(L) 1152.575 (M) 767.881 (S) 662.310
(42·3)	3.4803	(L) 945.675 (M) 586.587 (S) 546.311
(21·2)	3.4718	(L) 959.466 (M) 616.960 (S) 530.730
(21·3)	3.6726	(L) 906.869 (M) 626.653 (S) 500.494
(21·0) X-cut	4.9395 4.9390 3.6510 3.6500	(L) 582.097 (L) 582.212 (L) 787.545 (L) 787.790

The elastic compliance constants multiplied by 4ρ (say \tilde{s}_{hk}^*) derived from the above are: (unit: 10⁻¹² cm⁻² sec²)

$$\begin{aligned} \tilde{s}_{11}^* &= \tilde{s}_{11} - \tilde{d}_{11}^2 = 13.38_9, & \tilde{s}_{13}^* &= \tilde{s}_{13} = -1.30_8, \\ \tilde{s}_{33}^* &= \tilde{s}_{33} = 10.29_6, & \tilde{s}_{14}^* &= \tilde{s}_{14} - \tilde{d}_{11}\tilde{d}_{14} = 4.74_6, \\ \tilde{s}_{44}^* &= \tilde{s}_{44} - \tilde{d}_{14}^2 = 21.14_4, & \tilde{s}_{66}^* &= \tilde{s}_{66} - \tilde{d}_{11}^2 = 30.32_9, \end{aligned} \quad (39)$$

where

$$\tilde{d}_{11}^2 = \frac{4\pi}{K} d_{11}^2 4\rho, \quad \tilde{d}_{14}^2 = \frac{4\pi}{K} d_{14}^2 4\rho.$$

The propagation velocity of the longitudinal elastic wave along a thin filament in the direction perpendicular to the principal axis of quartz should be $\sqrt{\tilde{s}_{11}^*}$ instead of $\sqrt{\tilde{s}_{11}}$, if the filament is electrically isolated. However if the filament is covered with metal along its length so that electrical stress does not appear, the propagation velocity will be equal to $\sqrt{\tilde{s}_{11}}$. As the measured

TABLE IV. Values of c 's at 20°C by Koga *et al.* compared with κ^2 at the same temperature by Atanasoff and Hart. (L), (M), and (S) mean the largest, medium and the smallest values of c , respectively. (Units: 10¹⁰ dynes cm⁻².)

Orientations		Atanasoff and Hart		κ^2 at 20°C	Koga <i>et al.</i> c at 20°C
		κ^2 at 35°C	$\frac{\partial \kappa^2}{\partial T}$ in 10 ⁻³		
(21·0)	(L)	87.55	-4.35	87.615	87.603
X-cut	(S)	28.82	0.72	28.809	28.795
(01·0)	(S)	40.74	6.93	40.636	40.642
Y-cut	(L)	95.35	-3.87	95.408	95.576
(01·1)	(M)	64.92	1.92	64.891	64.877
R-cut	(S)	42.67	1.06	42.654	42.726
$l=n$	(L)	117.81	-18.23	118.083	117.969
$=1/\sqrt{2}$	(M)	50.27	-3.24	50.319	50.441
$m=0$	(S)	35.42	-2.64	35.460	35.496

TABLE V. Linear expansion coefficients at 20°C adopted in the present paper.

a	\dot{a}/a	$\frac{1}{2}\ddot{a}/a$	$\frac{1}{6}\dddot{a}/a$
a_{11}	7.48×10^{-6}	$0.86_a \times 10^{-8}$	$< 10^{-11}$
a_1	13.74×10^{-6}	$1.20_1 \times 10^{-8}$	assumed $< 10^{-11}$

value 12.79 of s_{11} by Mason¹² is very close to the value given in (37), he must have apparently placed the electrodes very closely to the specimen in order to excite it piezoelectrically.

4. DETERMINATION OF THE TEMPERATURE COEFFICIENTS OF THE ELASTIC AND PIEZOELECTRIC CONSTANTS OF QUARTZ

The present authors determined further the temperature coefficients of the elastic and piezoelectric constants, i.e., explicitly of \tilde{c}_{hk} and \tilde{e}_{hk} .

Differentiating the relationship $\tilde{c} = (af)^2$ with respect to temperature T we obtain

$$\frac{1}{2} \left(\frac{d\tilde{c}/dT}{\tilde{c}} \right) = (\dot{a}/a) + (\dot{f}/f), \quad (40)$$

where

$$\dot{a}/a = [n^2 \dot{a}_{11}/a_{11}] + [(1-n^2) \dot{a}_1/a_1], \quad (41)$$

because of the relation

$$a^2 = a_{11}^2 + a_1^2, \quad (42)$$

a_{11} and a_1 being the projections of a along the principal axis and its perpendicular direction, respectively.

Equation (40) shows that $d\tilde{c}/dT$ for various orientations can be determined if \dot{a}/a and \dot{f}/f are known. The

TABLE VI. Frequency temperature coefficients of quartz plates in various orientations at 20°C. For the meaning of (Y), (R), (r'), (L), (M), and (S), refer to Tables II and III.

Orientations	\dot{f}/f in 10^{-6}	$\frac{1}{2}\ddot{f}/f$ in 10^{-8}	$\frac{1}{6}\dddot{f}/f$ in 10^{-10}
(01·0) (Y)	88.60	4.78	3.37
(03̄·2)	44.72	0.25	0.54
(03·2)	36.83	3.35	1.58
(01̄·1) (R)	22.77	-1.70	-0.49
(01·1) (r')	-14.03	-1.81	-0.88
(02̄·3)	-1.09	-4.30	-1.09
(02·3)	-62.85	-7.35	-0.33
(01̄·2)	-17.12	-5.65	-1.44
(01·2)	-83.14	-9.96	-0.82
(21̄·1) (L)	-46.79	-7.08	-1.94
X-cut (M)	-10.33	-2.70	0.88
(S)	5.00	-1.79	-0.27
(21̄·2) (L)	-65.30	-9.31	-1.94
(M)	-22.88	-4.01	-0.09
(S)	-21.63	-2.24	0.07
(21̄·3) (L)	-75.89	-10.12	-1.99
(M)	-29.70	-4.97	-0.52
(S)	-55.18	-5.13	-0.99

¹² W. P. Mason, Bell System Tech. J. 22, 178 (1943).

expansion coefficients of a_{11} and a_1 have been given by many authors, but the mean value of Benoit, Fizeau, and Lindman's results were taken¹³ and reduced to the value at 20°C as shown in Table V.

Table VI shows the measured values of the temperature coefficients of the frequency of the plates at 20°C for various orientations of principal planes.

In order to determine $d\tilde{c}_{hk}/dT$, relations (31) through (34) may be used again by differentiating with respect to temperature. The results thus obtained are tabulated in the second column of Table VII.

Differentiating relation (40) with respect to temperature again, and introducing the values of $(1/\tilde{c})d\tilde{c}/dT$, \dot{a}/a and \ddot{a}/a derived from (42), one obtains $d^2\tilde{c}_{hk}/dT^2$ and $d^2\tilde{e}_{hk}/dT^2$. The quantities $d^3\tilde{c}_{hk}/dT^3$ and $d^3\tilde{e}_{hk}/dT^3$

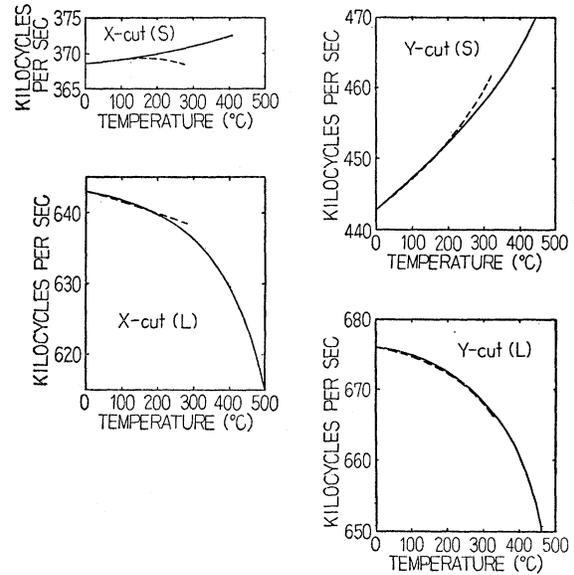


FIG. 1. Frequency-temperature relations of X-cut and Y-cut plates. The full lines are the reproductions of Atanasoff and Hart's results, while the broken lines show the computed values based upon (43), (44), and (45).

are also obtained by a similar process. These results are shown in the third and fourth columns of Table VII.

From these results the frequency temperature characteristic of a quartz plate of any orientation can be calculated from the following relation:

$$f_T = (\tilde{c}_T)^{1/2} / a_T, \quad (43)$$

where f_T , \tilde{c}_T , and a_T denote the values of f , \tilde{c} , and a at a temperature rise T above 20°C.

The value of \tilde{c}_T is a root of c in (18), where all of the values of c_{hk} and e_{hk} have been replaced by the values of \tilde{c}_{hk} and \tilde{e}_{hk} at a temperature rise T above 20°C in accordance with (30) and by means of the following relation,

$$y_T = y_{20} + \dot{y}_{20}T + \frac{1}{2}\ddot{y}_{20}T^2 + \frac{1}{6}\dddot{y}_{20}T^3, \quad (44)$$

¹³ Reference 9, p. 387, Table XX.

TABLE VII. The first, second, and third derivatives of \tilde{c}_{hk} and $\tilde{\epsilon}_{hk}$ with respect to temperature at 20°C; confidence coefficient: 90%.

	First diff. coeff. in 10 ⁶ cm ² sec ⁻² °C ⁻¹	One-half of the second diff. coeff. in 10 ⁴ cm ² sec ⁻² °C ⁻²	One-sixth of the third diff. coeff. in 10 ² cm ² sec ⁻² °C ⁻³
\tilde{c}_{11}	-0.77 ± 0.46	-3.2 ± 2.1	-0.32 ± 0.45
\tilde{c}_{33}	-15.32 ± 0.60	-14.0 ± 2.8	-0.30 ± 0.59
\tilde{c}_{44}	-7.529 ± 0.038	-1.17 ± 0.10	-0.113 ± 0.078
\tilde{c}_{66}	8.076 ± 0.096	0.85 ± 0.26	-0.29 ± 0.19
\tilde{c}_{13}	-5.15 ± 0.51	-0.67 ± 0.52	-0.63 ± 0.81
\tilde{c}_{14}	-2.273 ± 0.019	-0.015 ± 0.051	0.107 ± 0.038
$\tilde{\epsilon}_{11}^2$	-0.23 ± 0.10	-0.33 ± 0.26	0.55 ± 0.21
$\tilde{\epsilon}_{14}^2$	-0.018 ± 0.020	-0.013 ± 0.045	0.018 ± 0.035
$\tilde{\epsilon}_{11}\tilde{\epsilon}_{14}$	0.065 ± 0.041	0.07 ± 0.11	-0.103 ± 0.084

where y_T stands for each of the values of \tilde{c}_{hk} and $\tilde{\epsilon}_{hk}$ at a temperature rise T above 20°C, and y_{20} , \dot{y}_{20} , etc., for its value and its first, second, and third differential coefficient with respect to the temperature at 20°C, respectively. All the necessary data for these calculations are given in (35) and Table VII.

On the other hand, the thickness a_T is quite closely given by

$$a_T = a_{20} [1 + n^2(7.48 \times 10^{-6} \times T + 0.86_9 \times 10^{-8} \times T^2) + (1 - n^2)(13.74 \times 10^{-6} \times T + 1.20_4 \times 10^{-8} \times T^2)]. \quad (45)$$

As Atanasoff and Hart¹ reported experimental results on the frequency-temperature relations of X-cut and Y-cut plates up to very high temperatures, the present writers tentatively computed them up to temperatures above 100°C, where (44) is not necessarily valid any more, because all terms of the fourth and the higher powers of temperature T have been dropped. The full lines in Fig. 1 are the reproduction of Atanasoff and Hart's results and the broken lines show the computed values. It is rather surprising to discover that the computed values are very close to the measured results up to about 200°C in the case of X-cut plates, and even up to temperatures above 300°C in the case of Y-cut plates.

Energy Storage in ZnS and ZnCdS Phosphors*†

HARTMUT KALLMANN AND EUGENE SUCOV

Department of Physics, New York University, Washington Square, New York, New York

(Received October 4, 1957)

The deficiency area above a rise curve of fluorescence due to excitation by high-energy electrons is a measure of the total amount of energy stored in traps. In order to investigate the rate of decay of this energy, rise curves were taken for six phosphors of various luminescent properties and activation after various dark decay periods following excitation to equilibrium and after de-excitation by exposure to infrared light and heat. For all phosphors the trap concentration was found to be of the order of 10¹⁵/cc independent of the type of activator. In addition, the rates of decay of stored energy were determined and were found to be similar; from 20% to 60% of the energy remained in the phosphors after 1 week. This slow rate of decay is explained by predominant retrapping in traps of various depths.

The areas under curves of phosphorescent emission were compared to the deficiency areas above rise curves taken immediately

after the end of decay. For four of the phosphors these two areas are nearly equal to each other. One phosphor, especially activated with Ni and with practically no phosphorescence exhibited, however, a rate of energy decay similar to the phosphorescent phosphors. This means that the decay of stored electrons can take place radiatively and/or nonradiatively and that the rate for both processes is of the same order of magnitude.

The areas under curves of visible light stimulated by infrared irradiation were compared with areas above rise curves taken immediately after the end of stimulation. If all stored electrons were released radiatively, these two areas would be equal. For only one phosphor (specially Pb activated ZnS) was this the case. All others exhibited only from 0.6% to 5% radiative recombinations. Thus the light sum under a stimulation curve does not give a true picture of the trap population.

I. INTRODUCTION

ELECTRONS which are stored in traps can be removed by the addition of thermal energy or infrared irradiation. The resulting recombinations are often radiative so that a correspondence has been made between the area under a glow curve¹⁻³ or under

a stimulation curve⁴⁻⁶ and the total number of electrons which were originally in the traps. Both of these methods suffer from the fact that nonradiative transitions are induced along with the radiative ones so that determinations of trap population can be in error. Several investigators have found, for instance, that the area under a stimulation curve is many times greater than the corresponding area under a glow curve.⁴⁻⁶ Information about electrons stored for long periods of

* Part of a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree (E.S.) at New York University, New York, New York.

† This work was supported by the Signal Corps Engineering Laboratories, Evans Signal Laboratory, Belmar, New Jersey.

¹ J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 366, 390 (1945).

² G. F. J. Garlick and M. H. F. Wilkins, Nature **161**, 565 (1948).

³ R. H. Bube, Phys. Rev. **80**, 655, 764 (1950).

⁴ R. T. Ellickson, J. Opt. Soc. Am. **36**, 264 (1946).

⁵ G. F. J. Garlick and D. E. Mason, J. Electrochem. Soc. **96**, 90 (1949).

⁶ C. Bull and D. E. Mason, J. Opt. Soc. Am. **41**, 718 (1951).