$^2\Pi$ ground state. Jevons[4] and Ferguson[5] have analyzed the emission spectra of SnCl and found two systems having a common lower $^2\Pi$ state with a doublet separation of about 2360 cm^{-1}. They, however, observed the bands in emission and it is not certain that the $^2\Pi$ state is the ground state. The lowest state of the PbCl bands reported here must be the ground state since the bands were observed in absorption. If the lower state of the bands of Jevons and Ferguson corresponds to the ground state of PbCl, then the ground state of PbCl would be expected to be a $^2\Pi$ state with a doublet separation of approximately 7000 cm^{-1}. Such a separation would place the origin of the other part of a doublet system in the neighborhood of either 7000A or 3500A. No sub-system was observed in either of these regions. Such a system should have been easily observed had it been in the vicinity of 3500A since the intensity of the high frequency part of the doublet system should be greater than the intensity of the low frequency part. However, if the sub-system were in the neighborhood of 7000A it would probably not have been observed in absorption, since even at 1600°C the intensity of the high frequency part would be expected to be about 750 times that of the other.

The author wishes to express his appreciation to Professors Alpheus W. Smith, J. B. Green, and R. V. Zumstein for valuable discussions and suggestions given during the course of this investigation.

[4] W. Jevons, Proc. Roy. Soc. **A110**, 365 (1926).
[5] W. F. C. Ferguson, Phys. Rev. **32**, 607 (1926).

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The Variation of the Adiabatic Elastic Moduli of Rocksalt with Temperature Between 80°K and 270°K

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The piezoelectric method devised by Balamuth for measuring Young's modulus of a cubic crystal for any chosen direction has been extended to permit the measurement of all the elastic moduli of any solid crystal at temperatures below 0°C. Data are given which show the variation of the adiabatic and isothermal elastic moduli and elastic constants of rocksalt with temperature between 80°K and 270°K.

Introduction

In a recent issue of this journal Dr. Lewis Balamuth has described a method for measuring Young's modulus corresponding to any chosen direction in a solid crystalline substance.[1] This method utilizes the properties of a separately excited composite piezoelectric oscillator constructed by cementing an X-cut cylinder of quartz to one end of a cylinder of specimen material. The fundamental frequency of free longitudinal vibration of this system is measured by observing the variation of its electrical reactance with the frequency of the applied voltage, and Young's modulus of the specimen material for the direction of the cylinder axis is calculated from this and other readily measurable quantities. Now measurements of Young's modulus for various directions in a crystal yield some but not all its elastic constants, while the remainder can be calculated if, in addition, one or more rigidity moduli are known. The object of the present paper is to describe a method for measuring the rigidity modulus corresponding to any chosen direction in a crystal.

The success of Balamuth's method depends upon the fact that the electrically excited quartz crystal produces longitudinal vibration of sufficient purity along the whole oscillator. Now Giebe and Scheibe[2] have shown that a suitably cut cylinder of quartz can be excited to torsional

[1] L. Balamuth, Phys. Rev. **45**, 715 (1934); **46**, 933 (1934).

[2] Giebe and Scheibe, Zeits. f. Physik **46**, 607 (1928).

vibration, and the present paper deals, in the first instance, with the use of such a crystal as the driver of a composite oscillator. It appears that this *torsional* oscillator functions quite as well as the other, so that all the elastic moduli of a crystal can be evaluated with equal facility.

The Triple Oscillator

In the case of a fragile substance like rocksalt the differential thermal expansion at the cemented interface, which accompanies any change in temperature, produces longitudinal cracks in the specimen. These are without effect upon the frequency of the longitudinal mode of vibration, but materially alter that of the torsional mode. The difficulty is overcome by placing between the quartz and specimen cylinders a cylinder of stout material whose coefficient of thermal expansion is very nearly the same as that of the specimen. Accordingly the present method demands the use of a triple oscillator, a drawing of which is shown in Fig. 1.

The three cylinders are of circular cross section, about 3.5 mm in diameter, and are uniform within 0.005 mm. The factors which determine the lengths will be discussed later. The cylinder axis lies, in the quartz, parallel to an electric axis, and in the specimen, parallel to the direction for which the rigidity modulus is desired. In practice the cylinders of quartz and other hard crystals are first cut to a square cross section. The edges are ground off and the final figure obtained by grinding in a series of split, cylindrical laps. Rocksalt and other soft crystals can be turned on a bench lathe.

When the oscillator is to be used below 0°C the three cylinders are cemented together at room temperature, in a vacuum, under a compressive force of 500 g, with a sticky preparation of para-rubber dissolved in vaseline. Cements suitable for use at higher temperatures are discussed in a following paper by Mr. Milo Durand. Four electrodes of gold or aluminum leaf are pasted along the quartz cylinder and cross connected as shown in Fig. 2.

The oscillator is suspended vertically between rigid glass rods by means of fine silk threads attached with shellac to opposite sides of the quartz near a displacement node of vibration. The assembly is mounted in a glass tube, which is evacuated and immersed in the cryostatic bath described by Balamuth.[1]

Theory

The current which flows to the oscillator, and hence the reactance between its electrodes, contains a part which is associated with the piezoelectric charge distribution accompanying the vibrational stress in the quartz, and which is directly proportional to the average value of this stress taken along the cylinder. The object of the theory is to express the stress in the quartz in terms of the amplitude and frequency of the applied voltage and the physical constants of the oscillator. Its development, for the triple torsional oscillator, follows very closely that given by Balamuth for the two-part longitudinal oscillator. Initially all components are assumed to be isotropic, and the actual applied piezoelectric stress in the quartz is replaced by that which would result from equal normal torsional stresses applied across the end faces of the cylinder and varying harmonically with the time. The only significant difference between the theory of the torsional oscillator and that of the longitudinal oscillator is the existence, in the former, of functions competent completely to satisfy the equations of motion and *all* the boundary conditions. The final formulae are obtained without approximation.

It follows from this theory, as from that for *any* piezoelectric oscillator, that the reactance of the oscillator varies critically with frequency in the neighborhood of certain "resonance fre-

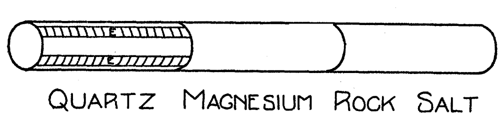

FIG. 1. The triple oscillator.

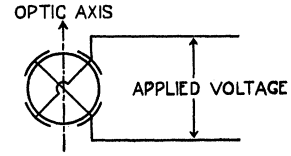

FIG. 2. The electrical connections to the quartz cylinder.

quencies" at which the amplitude of the vibrational stress passes through a maximum. In analogy with Balamuth's Eq. (14), these resonance frequencies are, for the torsional oscillator, given by the solutions for f of the equation

$$m_1 \tan y_1/y_1 + m_2 \tan y_2/y_2 + m_3 \tan y_3/y_3 - (m_1 m_2 y_3/y_1 y_2 m_3) \tan y_1 \tan y_2 \tan y_3 = 0, \quad (1)$$

where m_i = mass of a cylinder, $(i=1, 2, 3)$

$$y_i = \pi f/f_i, \quad (2)$$

f = frequency of applied voltage,

and

$$f_i = (n/2L_i)(\mu_i/\rho_i)^{\frac{1}{2}}, \quad (3)$$

where n = an integer, L_i = length of a cylinder, μ_i = modulus of rigidity for the direction of the cylinder axis, ρ_i = density, and the subscripts refer, respectively, to the specimen material, the quartz, and the intermediate material.

Eq. (1) is the fundamental working formula of the piezoelectric method for measuring *all* the elastic constants of any solid substance. For example, the resonance frequencies of a triple *longitudinal* oscillator are given by the solutions of this equation provided that, in the calculation, the symbols y_i and f_i be related to the physical constants of the materials by the formulae:

$$y_i = \pi(f/f_i)[1 - (\tfrac{1}{2})\pi^2\sigma_i^2(\theta_i/A_iL_i^2)(1 - f^2/f_i^2)],^3 \quad (4)$$

and

$$f_i = (n/2L_i)(G_i/\rho_i)^{\frac{1}{2}}(1 - \pi^2 n^2 \sigma_i^2 \theta_i/2A_iL_i^2), \quad (5)$$

where σ_i = Poisson's ratio, θ_i = moment of inertia of cross section about the cylinder axis, A_i = area of cross section, and G_i = Young's modulus for the direction of the cylinder axis.

Again, the resonance frequencies of a *two-part* oscillator, either torsional or longitudinal, are given by the solutions of Eq. (1) with m_1 set equal to zero, that is, by the solutions of

$$m_2 \tan y_2/y_2 + m_3 \tan y_3/y_3 = 0, \quad (6)$$

in which the subscript 3 now refers to the specimen material and Eqs. (2), (3), (4) and (5) subsist.

If m_1 and m_3 are both set equal to zero Eq. (1) reduces to

$$\tan y_2 = 0, \quad (7)$$

the solutions of which yield the resonance frequencies of the quartz cylinder alone.

Lastly, the left-hand member of Eq. (1) plays exactly the same role in the description of the electrical behavior of triple oscillators as Balamuth's quantity Δ^1 plays in the description of two-part oscillators.

Experimental Method

The electric circuit arrangements for measuring the resonance frequencies are identical with those of Balamuth.[1] The experimental procedure is as follows: The fundamental resonance frequency of the quartz cylinder alone is measured. This frequency is the quantity f_2 by Eqs. (7), and (2), (3) or (4), (5). Next the intermediate cylinder is attached, the fundamental resonance frequency of the two-part oscillator is measured, and Eq. (6) is solved for f_3. If desired, the elastic modulus of this material may be calculated with the aid of Eqs. (2), (3) or (4), (5). A roughly approximate value only of Poisson's ratio is needed for an adequate evaluation of the terms in σ in Eqs. (4) and (5). Lastly, the specimen cylinder is attached, the fundamental resonance frequency of the triple oscillator is measured, Eq. (1) is solved for f_1, and Eqs. (2), (3) or (4), (5) for the elastic modulus.

In case the softness of the cement permits the removal of a cylinder without demounting the oscillator, it is desirable to obtain the resonance frequency data in the reverse of the above order; small remounting errors are thus eliminated. This procedure is adopted when the rubber-vaseline cement is used.

The lengths of the three cylinders should be adjusted so that the fundamental resonance frequencies of the single, double and triple oscillators are the same within ten percent or better. Such frequency matching minimizes the effect of inequality of areas at the interfaces, of the adhesive,[1] and of internal friction in the materials,[4] on the resonance frequency of the oscillator. It will also be noted that the term in σ in Eq. (4) vanishes when $f=f_i$. Furthermore, the specimen cylinder should be long enough to keep these frequencies below 100 kilocycles.

[3] The plus sign in this expression as printed in Balamuth's paper, reference 1, is an error.

[4] Zacharias, Phys. Rev. **44**, 118 (1933).

Above this value harmonics of low frequency modes of vibration are very likely to appear in the neighborhood of that under investigation, which vitiate the observations. Such spurious neighboring modes must always be sought and their absence established. They arise, of course, because the actual impressed piezoelectric stress in the quartz does not correspond exactly to that of any single mode of vibration, but their effect remains negligible so long as none of their resonance frequencies lies near that under observation.

The Elastic Moduli and Elastic Constants of a Cubic Crystal

Formulae which relate Young's modulus and the rigidity modulus for any direction in a cubic crystal to the elastic moduli are given by Voigt.[5] The present research is concerned with only two directions, namely (0, 0, 1) and (0, 1, 1). If the unprimed quantities refer to the former and the primed to the latter, then for the elastic moduli,

$$\begin{aligned} 1/G &= s_{11} \\ 1/G' &= s'_{11} = \tfrac{1}{2}(s_{11}+s_{12}+\tfrac{1}{2}s_{44}) \\ 1/\mu &= s_{44} \\ 1/\mu' &= \tfrac{1}{2}(s'_{44}+s'_{55}) = s_{11}-s_{12}+\tfrac{1}{2}s_{44} \end{aligned} \tag{8}$$

and for the compressibility, κ,

$$\kappa = 3(s_{11}+2s_{12}). \tag{9}$$

Furthermore,

$$\begin{aligned} c_{11} &= (s_{11}+s_{12})/(s_{11}-s_{12})(s_{11}+2s_{12}), \\ c_{12} &= -s_{12}/(s_{11}-s_{12})(s_{11}+2s_{12}), \\ c_{44} &= 1/s_{44}. \end{aligned} \tag{10}$$

From Eqs. (8),

$$s_{12} = 1/G' - \tfrac{1}{2}\mu', \tag{11}$$

or

$$= 1/G + \tfrac{1}{2}\mu - 1/\mu'. \tag{12}$$

Poisson's ratio for a (0, 0, 1)-cut cylinder is given by the formula[6] $\sigma = s_{12}/s_{11}$. When a right circular (0, 1, 1)-cut cylinder is stretched the cross section is no longer circular. The average radial displacement is readily evaluated with the aid of Voigt's analysis, and so the "average" Poisson's ratio. Thus

$$\bar{\sigma}' = (s_{11}+3s_{12}-\tfrac{1}{2}s_{44})/(2s_{11}+2s_{12}+s_{44}).$$

[5] Voigt, *Lehrbuch der Kristallphysik*, p. 739.
[6] Voigt, reference 5, p. 631.

Table I. *The elastic moduli and constants of rocksalt.*

T	Adiabatic Moduli $\times 10^{13}$(cm²/dyne)			Adiabatic Constants $\times 10^{-11}$(dyne/cm²)			Isothermal Constants $\times 10^{-11}$	
(°K)	s_{11}	$-s_{12}$	s_{44}	c_{11}	c_{12}	c_{44}	c_{11}	c_{12}
80	18.64	3.15	75.06	5.76	1.17	1.332	5.72	1.13
90	18.77	3.21	75.18	5.73	1.18	1.330	5.69	1.14
140	19.55	3.54	75.87	5.56	1.22	1.318	5.50	1.16
150	19.72	3.61	76.03	5.52	1.23	1.315	5.45	1.17
160	19.89	3.68	76.19	5.48	1.24	1.313	5.41	1.17
170	20.06	3.75	76.36	5.44	1.24	1.310	5.37	1.17
180	20.24	3.82	76.53	5.40	1.25	1.307	5.33	1.17
190	20.43	3.89	76.70	5.37	1.26	1.304	5.29	1.17
200	20.63	3.96	76.88	5.33	1.26	1.301	5.24	1.17
210	20.82	4.03	77.07	5.29	1.27	1.298	5.20	1.17
220	21.02	4.11	77.25	5.25	1.27	1.294	5.16	1.17
230	21.21	4.18	77.46	5.22	1.28	1.291	5.12	1.17
240	21.43	4.26	77.64	5.18	1.28	1.288	5.07	1.17
250	21.65	4.33	77.84	5.14	1.29	1.285	5.03	1.17
260	21.86	4.41	78.05	5.10	1.29	1.282	4.99	1.17
270	22.08	4.49	78.26	5.06	1.30	1.278	4.95	1.17

In accordance with the theory of Voigt,[7] the adiabatic and isothermal moduli and constants are related by the formulae

$$\begin{aligned} (s_{11})_{\mathrm{ad.}} - (s_{11})_{\mathrm{is.}} = (s_{12})_{\mathrm{ad.}} - (s_{12})_{\mathrm{is.}} \\ = -T\alpha^2/\rho c_p, \end{aligned} \tag{13}$$

$$\begin{aligned} (c_{11})_{\mathrm{ad.}} - (c_{11})_{\mathrm{is.}} = (c_{12})_{\mathrm{ad.}} - (c_{12})_{\mathrm{is.}} \\ = T\alpha^2/(\rho c_p)(s_{11}+2s_{12})^2, \end{aligned} \tag{14}$$

where T is the absolute temperature, α is the coefficient of linear expansion, and c_p is the specific heat at constant pressure. The adiabatic and isothermal s_{44} and c_{44} are the same.

Results

The adiabatic and isothermal moduli and constants for rocksalt over the temperature range 80°K to 270°K are given in Table I. The first column contains the adiabatic s_{11} as measured by Balamuth. The third column is the smoothed out mean of measurements of the adiabatic s_{44} taken on four different (0, 0, 1)-cut specimens. The values of s_{12} given in the second column were calculated with Eq. (12) from s_{11} and s_{44} together with the smoothed out mean of measurements of the torsion modulus on four different (0, 1, 1)-cut specimens. The specimen material was the finest grade of optical rocksalt obtainable, and was the same as that used by Balamuth. The adiabatic c's were calculated

[7] Voigt, reference 5, p. 789.

TABLE II.

T (°K)	$S_{11}'\times 10^{13}$ Balamuth	Rose	$-S_{12}\times 10^{13}$ Eq. (12)	Eq. (11)
80	26.51	26.53	3.15	3.12
90	26.58	26.60	3.21	3.18
140	26.94	27.01	3.54	3.49
150	27.02	27.10	3.61	3.56
160	27.11	27.19	3.68	3.63
170	27.21	27.29	3.75	3.70
180	27.30	27.39	3.82	3.77
190	27.40	27.49	3.89	3.84
200	27.51	27.59	3.96	3.91
210	27.62	27.69	4.03	3.99
220	27.74	27.80	4.11	4.06
230	27.86	27.91	4.18	4.14
240	27.99	28.02	4.26	4.21
250	28.10	28.13	4.33	4.29
260	28.22	28.25	4.41	4.37
270	28.33	28.36	4.49	4.48

from the s's with Eqs. (10), and the isothermal c's with Eqs. (14).

The formula used in computing the density was[8]

$$\rho = 2.1680(1 - 11.2\times 10^{-5}t - 0.5\times 10^{-7}t^2).$$

Values of c_p were taken from the *International Critical Tables.*

PRECISION

Exhaustive tests, of the sort described by Balamuth, were made to demonstrate beyond doubt that the quantities calculated from the observed behavior of the triple oscillators are, in fact, the elastic moduli of the specimen material. The results of two such experimental checks are given in Table II. The first column contains the values of $1/G'$ measured by Balamuth with a two-part oscillator of square cross section. The second column contains values of the same quantity measured on a different set of specimens with a triple oscillator of circular cross section. The agreement is noteworthy. The third column contains values of s_{12} calculated *with Eq.* (*12*) from measurements of the Young's and rigidity moduli on a set of (0, 0, 1)-cut specimens and of the rigidity modulus on a set of (0, 1, 1)-cut specimens. The last column contains values of the same quantity calculated *with Eq.* (*11*) from measurements of the Young's and rigidity moduli on a set of two (0, 1, 1)-cut specimens. The agreement between the values of s_{12} obtained with these quite independent methods offers a very satisfactory overall test of the piezoelectric method, particularly as a small percentage error of measurement is very greatly magnified in the calculation of the difference quantity, s_{12}.

The accidental error in any observation on a single specimen is never greater than 0.03 percent. The source of largest systematic error is nonuniformity of cross section in the specimen cylinder. Such nonuniformity produces a shift parallel to itself of the entire modulus *vs.* temperature curve, and the curves for different specimens are invariably parallel. This is exemplified by, and accounts for, the systematic differences in Table II. Balamuth gives an observed average deviation among his specimens of 0.4 percent in s_{11}. This could have been reduced by using cylinders of circular instead of square cross section, for circular cylinders are in general more uniform. The average deviation for the torsional measurements was about 0.08 percent in s_{44}. The uncertainty in s_{12} is about 1 percent.

Steinebach[9] found the ratio of the value of s_{44} at 291°K to that at 88°K to be 1.065. This ratio, calculated from Table I, is 1.045. Voigt[10] gives $s_{4'} = 78.85\times 10^{-13}$ cm²/dynes, but does not specify the temperature. This is the value here found at 25°C. Voigt,[11] Madlung and Fuchs,[12] and Slater[13] have measured the isothermal compressibility at room temperature. They obtained, respectively, the values 41.3, 41.2, and 42.0 for $\kappa\times 10^{13}$ (cm²/dynes). The present value is 41.9 at 30°C, which was the temperature of Slater's specimens.

In conclusion, the writer desires to thank the Physics Department of Columbia University for the facilities generously placed at his disposal, and Dr. S. L. Quimby for helpful suggestions during the progress of the research.

[8] A. Henglein, Zeits. f. physik. Chemie **115**, 97 (1925).

[9] Steinebach, Zeits. f. Physik **33**, 674 (1925).
[10] Voigt, reference 5, p. 741.
[11] Voigt, reference 5, p. 742.
[12] Madlung and Fuchs, Ann. d. Physik **65**, 289 (1921).
[13] Slater, Phys. Rev. **23**, 488 (1924).