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Piezoelectric Constants of Alpha- and Beta-Quartz at Various Temperatures

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The adiabatic piezoelectric constants d_{11} and d_{14} of alpha-quartz have been measured between room temperature and 571.5°C. At the latter temperature, d_{11} is about one-half of its room temperature value, whereas d_{14} has increased by a factor of almost three. At 573°C (the inversion temperature) the crystal structure changes to that of beta-quartz, and d_{11} vanishes. The constant d_{14} for beta-quartz has been measured between 584°C and 626°C. d_{14} appears to be substantially constant over this short range of temperature, and differs from d_{14} for alpha-quartz at about 570°C by only a few percent. The piezoelectric constants were deduced from measurements (with a Q-meter technique) of the equivalent circuits of long thin bars driven electrically at frequencies near resonance.

I. INTRODUCTION

A KNOWLEDGE of the variation of the piezoelectric constants of quartz with temperature near 573°C (the inversion temperature of quartz) is desirable in the design of experiments for elimination of electrical (Dauphiné) twinning. Alpha-quartz, which is the stable crystalline form at temperatures below 573°C, is susceptible to such twinning. When alpha-quartz, of symmetry D_3 (in the Schoenflies notation), is heated to 573°C, the crystal structure changes suddenly to symmetry D_6. This form, stable above 573°C, is called beta-quartz, and is not susceptible to electrical twinning.

Alpha-quartz has two piezoelectric constants, d_{11} and d_{14}. d_{11} is the electric polarization per unit normal stress on a plane perpendicular to the electric axis. d_{14} is the electric polarization per unit shearing stress on a plane perpendicular to the optic axis. More precise definitions of piezoelectric constants, and a very complete summary of the measurements of the constants d_{11} and d_{14} for alpha-quartz, for temperatures from 4°K to 568°C, are given by W. G. Cady.[1] It appears that many of the early measurements at elevated temperatures were qualitative in character. However, Fréedericksz and Michailow[2] made quantitative measurements of d_{11} up to a temperature of 568°C. No measurements of d_{14} for alpha-quartz at elevated temperatures have been found in the literature.

For beta-quartz, the symmetry D_6 requires that $d_{11}=0$. However, d_{14} is not zero. No quantitative measurements have been found in the literature on the piezoelectric constant d_{14} for beta-quartz.

In view of the foregoing we have measured d_{11} up to a temperature of 571.5°C, and d_{14} up to a temperature of 626°C. Although some consideration was given to the idea of measuring the electric charges produced by transient loads, the technique finally adopted was a determination of the equivalent circuits of long thin bars driven electrically at frequencies near resonance. This method seemed to have the advantages of high precision, freedom from systematic errors due to the appreciable electrical conductivity of quartz at high temperatures, and ease of measurement with readily available electronic equipment.

The connection between the piezoelectric constants and the equivalent circuit of a bar is well known, and is summarized briefly in the following section.

II. EQUIVALENT CIRCUITS OF QUARTZ BARS

In the neighborhood of a resonant frequency, the equivalent circuit of a quartz bar can be represented very accurately by the circuit shown in Fig. 1. If ω_0 is the pulsatance (circular frequency) of the bar at resonance, $\omega_0^2 L_1 C_1 = 1$, where L_1 and C_1 are the series-chain inductance and capacitance, respectively. These depend on the piezoelectric constants and other physical constants of quartz, and are independent of frequency.

Consider a long thin quartz bar (Fig. 2) vibrating in its fundamental longitudinal mode. Its broad flat faces, perpendicular to the x-axis, are plated so as to be conducting. The capacitance C_1 is given by

$$C_1 = 8|d_{12}'|^2 l_w l/(\pi^2 l_t s_{22}'), \tag{1}$$

where $1/s_{22}'$ = Young's modulus of the bar in zero electric field (platings short-circuited), and the equivalent piezoelectric constant is

$$|d_{12}'| = (1/2)|(1+\cos 2\alpha)d_{11} - d_{14}\sin 2\alpha|. \tag{2}$$

Although the Young's moduli of the various bars used in the experiments could have been computed from values of the known zero-field compliances s_{ij}, it was found more convenient to determine the moduli from the measured resonant frequencies and bar lengths. If ρ is the density of quartz, then

$$s_{22}' = \pi^2/(\rho l^2 \omega_0^2). \tag{3}$$

Also, it was found to be easier to compute the bar thickness than to measure it directly. In terms of the mass m, the bar thickness is

$$l_t = m/(\rho l_w l). \tag{4}$$

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[1] W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Company, Inc., New York, 1946).

[2] V. Fréedericksz and G. Michailow, Zeits. f. Physik **76**, 328 (1932).

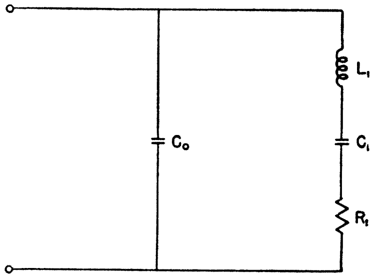

FIG. 1. Equivalent circuit of a quartz crystal bar near a natural frequency.

Combination of Eqs. (1)–(4) yields

$$|(1+\cos 2\alpha)d_{11}-d_{14}\sin 2\alpha| = \pi^2(mC_1)^{\frac{1}{2}}/(\sqrt{2}\rho l^2 l_w \omega_0). \quad (5)$$

By making measurements on two or more bars having different angles α, values of d_{11} and d_{14} can be deduced by means of Eq. (5). Only the absolute value, and not the sign, of d_{12}' can be determined from equivalent circuit measurements. This means physically that such measurements do not yield the phase angle between the mechanical vibration and the electric current.

Signs can be given to d_{11} and d_{14} on the basis of values given by Cady.[1] The signs are the same for both right and left quartz if one follows the Institute of Radio Engineers 1944 convention (described by Cady) for the choice of axes for quartz. This convention is used throughout this paper. We shall assume that the signs of d_{11} and d_{14} remain unchanged at the various temperatures used in the experiments.

Recently the I.R.E. 1944 convention was modified.[3] Under the new convention, the signs of d_{11} and d_{14} are different for right and left quartz.

III. TECHNIQUE OF MEASUREMENT OF EQUIVALENT CIRCUITS

The equivalent circuits of the quartz bars were found by means of a Q-meter circuit (Fig. 3). The basic idea is that the reactance of the bar must be determined at two known frequencies at least, both very near the resonant frequency, in order to determine C_1 and L_1 with good precision.

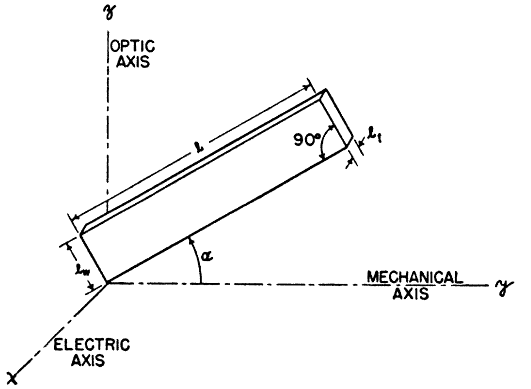

FIG. 2. Notation for quartz crystal bars.

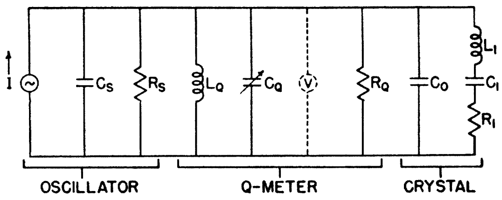

FIG. 3. Q-meter for measurement of equivalent circuits of crystal bars.

By Thévenin's theorem, the source is representable by a generator, producing current I (independent of load), in shunt with a capacitance C_s and resistance R_s. The Q-meter, consisting of a voltmeter, a high Q coil, and a variable capacitor all connected in parallel, has an equivalent circuit consisting of an inductance L_Q, capacitance C_Q, and resistance R_Q. It is clear that the parallel combination C_s, C_Q, L_Q, and C_0 (the clamped capacitance of the crystal and its leads) can be adjusted to have zero admittance at the measuring frequency. The amount ΔC, by which the variable capacitance differs from the setting for zero admittance, can be either positive or negative. Hence a simplified version of the circuit is that shown in Fig. 4.

The pulsatance at resonance is found by successive approximations. At resonance, the reactance in the crystal's series chain is zero, and hence the voltage V is a minimum with respect to frequency changes. Then $V=IRR_1/(R+R_1)\approx IR_1$, if $\Delta C=0$, and if $R\gg R_1$ (which can be achieved easily). The resonant frequency is located approximately by finding a minimum in V, then ΔC is adjusted to zero, and the resonant frequency is then located as exactly as possible at the minimum in V. The values of I and R are then determined at the resonant frequency by disconnecting the crystal and observing V for two values of ΔC. This sequence of operations therefore yields the resonant pulsatance ω_0 and the series chain resistance R_1.

The next step is to change the frequency by a small amount (usually a few tenths of a percent), so that the new pulsatance is $\omega=\omega_0+\Delta\omega$. The crystal is connected into the circuit, and ΔC is adjusted until the voltage V is a maximum. An analysis of the circuit of Fig. 4

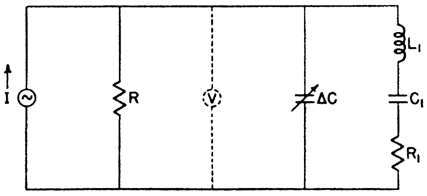

FIG. 4. Simplified version of Q-meter and equivalent circuit of crystal.

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[3] Proc. I.R.E. **37**, 1378, December (1949).

Table I. Physical constants of quartz bars (at room temperature).[a]

Bar	l, cm	l_w, cm	m, grams	l_t, cm	m', grams	α, degrees
C	6.98	0.699	1.2877	0.0997	1.2906	+18.5
D	7.02	0.698	1.2923	0.0996	1.2945	−45.0
E	5.00	0.499	0.3265	0.0495	0.3274	0.0
F	5.00	0.499	0.3263	0.0495	0.3275	+18.5

[a] The tabulated thicknesses l_t were computed on the assumption that the density of quartz at room temperature is $\rho=2.648$ g/cc. Direct measurements of l_t with a micrometer calipers yielded values which were systematically greater by about one percent. Allowance was made for the small thermal changes in density, linear dimensions, and angles of the bars, by means of the data given in *The Properties of Silica* by R. B. Sosman (Chemical Catalog Company, New York, 1927).

shows that when this occurs, then

$$\omega\Delta C=\frac{\omega L_1-1/\omega C_1}{R_1^2+(\omega L_1-1/\omega C_1)^2}, \tag{6}$$

and the combination of the capacitance ΔC and the series chain has an impedance (entirely real)

$$Z=[R_1^2+(\omega L_1-1/\omega C_1)^2]/R_1. \tag{7}$$

From Eq. (6) combined with $\omega_0^2 L_1 C_1=1$, we find

$$C_1=(2\Delta\omega/\omega_0)\Delta C[1+\Delta\omega/2\omega_0][1+(\omega R_1\Delta C)^2+\cdots]. \tag{8}$$

It is evident that the precision of measurement of $\Delta\omega$, ω_0, and ΔC must each be approximately one percent or better if C_1 is to be obtained to within one percent. In order to improve the precision a little, several determinations of C_1 were made at several different frequencies, both above and below the resonant frequency (both positive and negative values of $\Delta\omega$).

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The piezoelectric constants were deduced from measurements of the equivalent circuits of long thin bars driven electrically at frequencies near the resonant frequency for the fundamental longitudinal mode. The bars were cut with flat faces perpendicular (to within 0.1°) to the x-axis (electric axis) (Fig. 2). The flat faces were gold-plated. The platings were used as electrodes. The long dimensions of the bars lay in the yz-plane, and made known angles with the y-axis.

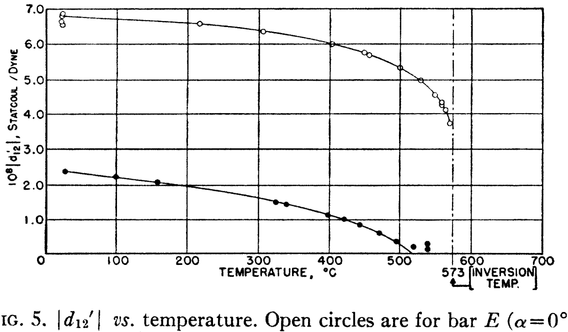

Fig. 5. $|d_{12}'|$ vs. temperature. Open circles are for bar E ($\alpha=0°$), and solid circles for bar D ($\alpha=-45°$).

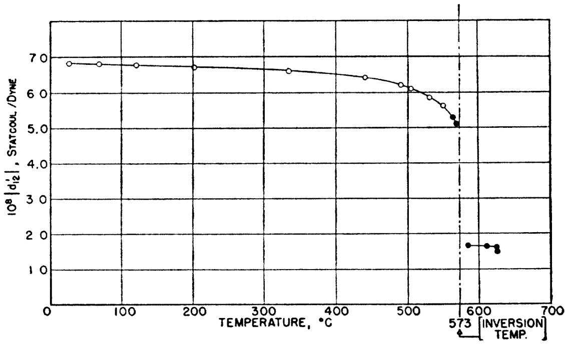

Fig. 6. $|d_{12}'|$ vs. temperature. Open circles are for bar C ($\alpha=18.5°$) and solid circles for bar F ($\alpha=18.5°$).

The physical constants of the bars at room temperature are given in Table I. m is the mass of a bar, and m' is the mass of a bar including its plated gold electrodes.

The results of determinations of $|d_{12}'|$ for the various bars are shown in Figs. 5 and 6. In general, it was not feasible, particularly at high temperatures, to determine $|d_{12}'|$ for two different bars at exactly the same temperature. Hence smooth curves were drawn through Cartesian plots of $|d_{12}'|$ against temperature. d_{11} and d_{14} were then computed from values of $|d_{12}'|$ read off at the same temperature from the curves for two differently oriented bars.

Table II. Piezoelectric constants of quarts at various temperatures.

Temperature °C	$10^8 d_{11}$ statcoulomb/dyne Bars C and D	 Bar E	$10^8 d_{14}$ statcoulomb/dyne Bars C and D
20	6.88	6.89	−2.04
50	6.84	6.86	−2.14
100	6.77	6.79	−2.33
150	6.69	6.70	−2.51
200	6.60	6.60	−2.69
250	6.50	6.49	−2.91
300	6.37	6.37	−3.15
350	6.22	6.21	−3.42
400	6.02	6.01	−3.74
450	5.74	5.74	−4.16
500	5.32	5.34	−4.72
			Bars E and C
520		5.08	−4.99
540		4.74	−5.24
550		4.53	−5.34
555		4.41	−5.40
			Bars E and F
560		4.26	−5.48
565		4.06	−5.54
570		3.81	−5.63
571.5		3.74	
573	Inversion temperature		
			Bar F
585			−5.69
612			−5.59
626			−5.47

The measurements on bar E (Fig. 5) yield d_{11} directly, and show a relatively wide spread at room temperatures. Each time d_{11} was determined at room temperature after this bar had been heated to temperatures near inversion, the value was found to be a little less than the preceding determination. We ascribe the gradual decrease to the incidence of electrical twinning caused by the heating. It was decided that the maximum value would be the best value of d_{11}.

The determinations of d_{11} and d_{14} are finally tabulated in Table II. Figure 7 is a graph of the tabulated values. The value of d_{14} at room temperature should be noted. We find it to be -2.04 (in units of 10^{-8} statcoulomb/dyne), which is in agreement with Cady's "best value" of -2.0 based mainly on static measurements. Mason,[4] however, finds a value of -2.56 by a dynamic method, which is not in agreement with Cady's and our values.

Saksena and Srivastava[5] have made quasi-empirical computations of the piezoelectric constants e_{11} and e_{14}. Their results are based on a calculation of the electric dipole moment caused by straining the covalent bonds in quartz. Our measurements of d_{11} and d_{14} can be used to get e_{11} and e_{14} by means of the equations

$$\begin{aligned} e_{11} &= (c_{11}-c_{12})d_{11}+c_{14}d_{14} \\ e_{14} &= 2c_{14}d_{11}+c_{44}d_{14}, \end{aligned} \tag{9}$$

in which the c's are the zero-electric-field elastic constants. However, the only measured elastic constants available at high temperatures are the zero-electric-charge ones determined by Atanasoff and Hart.[6] These were used to determine the experimental values shown in Fig. 8, and should not cause errors in e_{11} and e_{11} of more than a few percent. Also plotted in the same figure are the theoretical values found by Saksena and Srivastava. The agreement between the experimental and theoretical values of e_{11} is fairly good, but there are large discrepancies in the case of e_{14}.

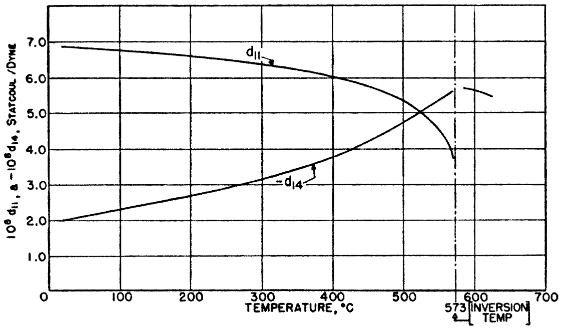

FIG. 7. Measured values of d_{11} and d_{14} for quartz as a function of temperature.

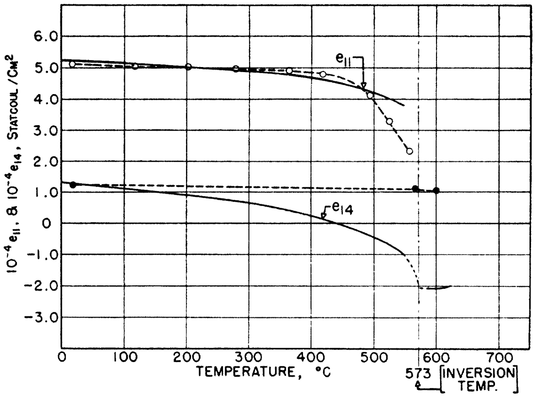

FIG. 8. e_{11} and e_{14} for quartz as a function of temperature. The solid lines are based on the experimental measurements. The open circles represent values of e_{11} computed by Saksena and Srivastava. The solid circles represent values of e_{14} computed by the same authors.

We estimate that the probable error in our measurement of d_{11} does not exceed one percent, and the probable error of d_{14} does not exceed two percent, at most temperatures. The errors are greater near the inversion temperature. The source of largest random error is probably the measurement of C_1. Figure 9 presents graphs of C_1, which should be practically independent of $\Delta\omega/\omega_0$, as a function of $\Delta\omega/\omega_0$. These graphs serve as an indication of the random errors to be expected.

Systematic errors might arise because bars of finite dimensions were used. For example, Eq. (1) is based on a calculation which assumes uniform polarization across the width of the bar when it vibrates, but actually the polarization in the middle is not quite the same as it is at the longitudinal edges. Bars of different sizes were used in order to find out whether systematic errors of significant amount were present. A study of the tabulated results (see Table II) seems to show no appreciable errors due to the finite size of the bars.

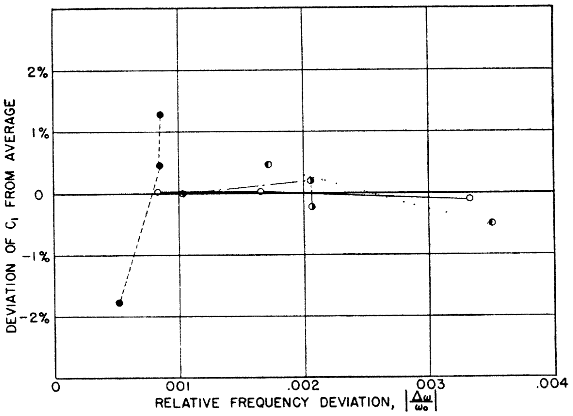

FIG. 9. Variations in C_1 as a function of $|\Delta\omega/\omega_0|$. Open circles are for bar D at 26°C. Solid circles for bar F at 626°C. Circles shaded on the left are for bar C at 492°C. Circles shaded on the right for bar E at 529°C.

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[4] W. P. Mason, Bell Sys. Tech. J. **22**, 178 (1943).

[5] B. D. Saksena and K. G. Srivastava, Proc. Ind. Acad. Sci. **28A**, 423, 437 (1948). Also see Nature **161**, 283 (1948).

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

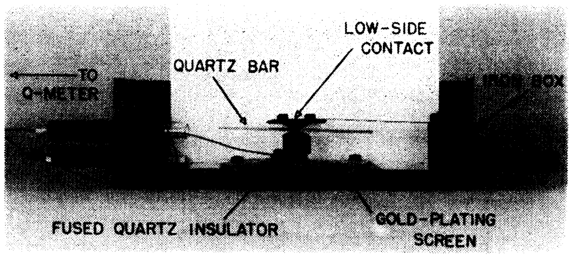

FIG. 10. Quartz crystal bar in its holder.

This indicates that bars which are ten times longer than their widths, and seventy to a hundred times longer than their thicknesses, can yield piezoelectric constants having systematic errors of less than about one percent.

The resistances R_1 and elastic compliances s_{22}' were obtained as by-products of the experiments. We hope to publish at a later date a detailed analysis of the variations of R_1 and s_{22}' with temperature.

V. APPARATUS

The Q-meter was constructed in the laboratory, largely from commercially available components. Since oscillators which could produce two frequencies differing by a few tenths of a percent, with the difference in frequency known to an accuracy of about one percent, were not readily available, a General Radio beat-frequency audio-oscillator was modified to yield such small frequency changes. These were produced by a low capacitance variable condenser connected in parallel with the main tuning condenser in the tank circuit. The oscillator covered the range from 167 to 187 kc/sec., whereas the quartz bars had resonant frequencies between 35 and 60 kc/sec. Therefore, a multivibrator was constructed and used to reduce the oscillator frequency. The multivibrator output was suitably filtered and amplified, and was then coupled to the remainder of the Q-meter by a capacitor of a few $\mu\mu$f. Frequency calibration was effected by means of standard frequencies generated by our High Frequency Standards Laboratory. It is estimated that the error in determination of the bar resonant frequencies was less than 0.05 percent, and errors in measurement of small frequency changes (from which $\Delta\omega$ was computed) were less than 2 percent.

The high Q coil was wound from Litzdraht on a glass cylinder, and had an inductance of about 22 mh. The variable air-dielectric capacitor had a least count of 0.2 $\mu\mu$f. ΔC was determined from the location, by variation of the capacitor, of a maximum in the Q-meter voltage. This was the greatest source of error in ΔC. We estimate the error, however, to be less than 2 percent. The voltages were read with a high impedance electronic voltmeter having five ranges. At 50 kc/sec., the Q-meter when tuned with the crystal disconnected had $R \approx 3.5 \times 10^6$ ohms, which is equivalent to $Q = 510$.

The crystal holder was a 15×4.5×4.5-cm iron box having 3-mm thick walls (Fig. 10). Contact was made with the bar platings, at the geometrical centers of the faces, by means of gold-alloy spherical surfaces having small fillings of pure gold at the points of contact. One contact (low side) was connected to the iron box, which served as an electrical shield, and which in turn was connected to the low side and shield of the Q-meter. The other spherical contact (high side) was mounted on a fused quartz insulating plate, and was connected to the high side of the Q-meter.

Preliminary experiments showed the fused quartz to have surprisingly large dielectric losses at temperatures above about 550°C. The losses were large enough to make precision measurements of the piezoelectric constants impossible. A screening system was devised to reduce this loss. The fused quartz insulator was plated with gold in such a way that the plating made no contact with either the iron box or the high side spherical contact, but so that the plating was geometrically between the spherical contact and the part of the box supporting the fused quartz. The gold plating (Fig. 10) was then used as a screen by connecting it to the output of a cathode follower whose input was the high side voltage. Hence the dielectric loss in that part of the fused quartz insulator which was between the screen and the high side contact was reduced because the potential difference was small. This loss is the one which was measured by the Q-meter. The loss in that part of the insulator between the screen and the iron box was large at high temperatures. However, the power to supply the loss came from the batteries of the cathode follower, and not from the Q-meter source. The screening system described above is identical in principle with the shielding system described by Daniels.[7]

The crystal holder was placed in the center of a tubular electric furnace 8 cm in diameter and 46 cm long, whose ends were plugged with asbestos fiber and blocks. The heating current was 60-cycle a.c. The temperature of the air within the iron box was measured by means of a chromel-alumel thermocouple and potentiometer. Because the resonant frequencies of the bars were strong functions of the temperature near inversion, it was found necessary to make measurements when the temperature was substantially stationary with time. In addition, this would reduce errors in temperature measurement due to systematic differences between the temperature of the air in the box and the temperature of the quartz bar. The error in determination of temperature of the bars is estimated to be less than 0.5°C.

We are particularly indebted to Messrs. M. Greenspan and R. P. DeAgro for assistance in the construction of apparatus and the collection of data.

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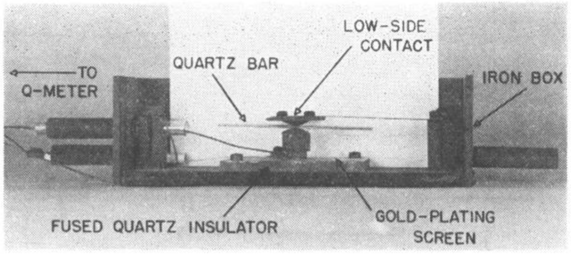
[7] H. L. Daniels, Electronics 18, 125 (February, 1945).



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