least a precedent for our model, not only as a superconductor but as an admittedly crude representation of magnetic solids. We have replaced the multitudinous interactions of the electrons both with each other and the lattice, including spin, by an equivalent effective potential. It is rather pleasant and encouraging that just one model is sufficient to describe approximately a rather wide variety of properties. The parabolic potential is admirably suited to the purpose although at least one other, the Coulomb well, might serve as well.

Now this assumption of an equivalent potential to replace a complex interaction has had ample precedent in the past although the path to justification is often tortuous and long delayed. The Einstein lattice model is the one we have followed. As other examples we may cite the Lennard-Jones potential for gas molecules and Hooke (and other) forces between atoms in a solid, both of which were proposed long before there was any quantum mechanical theory of their origin. Similar examples of more recent date are the Weiss internal field and theories of the heavier nuclei, justification for which is not yet complete. These examples, we hope, give some precedent for our otherwise arbitrary assumption of parabolic wells.

PHYSICAL REVIEW VOLUME 92, NUMBER 6 DECEMBER 15, 1953

Anelasticity of Quartz

RICHARD K. COOK AND ROBERT G. BRECKENRIDGE
National Bureau of Standards, Washington, D. C.

(Received March 20, 1953)

By means of the piezoelectric effect, measurements have been made of the variation with temperature of (1) the Q of quartz bars executing free acoustical oscillations in torsion, and (2) the equivalent series electrical resistance of bars driven at their natural frequencies of longitudinal acoustical oscillations. For each of the bars studied, it was found that the internal dissipation had a maximum value at a temperature between room temperature and the quartz inversion temperature of 573°C. Measurements of resistance were made on one bar at several different frequencies. These data showed that part of the dissipation was due to a relaxation effect, whose decay time varied with temperature according to an Arrhenius equation. An activation energy of 22 kcal/mole and a relaxation-time constant of 2×10^{-14} sec were deduced from the data, which showed also that the fraction of energy lost during each sinusoidal cycle of strain was independent of the frequency of vibration. Estimates of the activation energies and relaxation-time constants were deduced for the other bars measured. In one case, the dissipation was due to the migration of gold atoms from the electrodes into the quartz lattice.

I. INTRODUCTION

When a solid material is set into free vibration in one of its normal modes, the amplitude of the vibration decays exponentially with time. This happens even in the absence of external losses through either acoustic radiation into the air or other medium in which the solid is immersed, or through transmission of vibrational energy through the supports of the solid. The conversion of the ordered vibrational motion into disordered thermal motions of the molecules has been called "internal friction" or "internal dissipation", and more recently has been named "anelasticity". A summary of measurements on anelastic effects in metals, and a discussion of the mechanisms which give rise to anelasticity, are given in Zener's book,[1] where many of the formal analogies to dielectric theory are pointed out.

To the best of our knowledge, there have been no previous reports on researches into anelastic effects in quartz or other piezoelectric materials. Such effects in quartz are technologically important wherever quartz crystals are used either for frequency control of oscillators, or for electric-circuit filters. Measurements of anelastic effects in quartz, and in other piezoelectric materials, are readily made with electrical techniques. This is because the mechanical motions of a piezoelectric material cause electrical effects through the electromechanical coupling in the material. The most important information concerning the mechanism in any particular piece of material can be obtained from a study of the variation of anelastic effects with temperature and frequency.

A convenient measure of the internal friction is the Q of a freely vibrating system. Suppose the vibration as a function of time t is representable by $\exp(-\alpha t)\sin(2\pi ft)$, where α = damping coefficient of the damped vibration and f = frequency. The Q is then given by $Q=\pi f/\alpha$.

Another convenient measure of the internal mechanical friction for a piezoelectric material, such as quartz, is the electrical resistance R_1 which appears in the equivalent circuit of the crystal (see Fig. 1) when it is driven electrically at frequencies near a mechanical resonance frequency. It can be readily seen from Fig. 1

---

[1] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948).

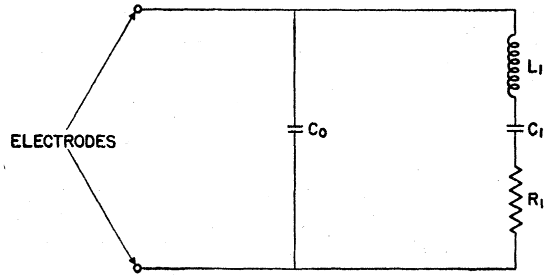

FIG. 1. Equivalent circuit of a quartz crystal bar near a natural frequency.

that the Q of a bar of quartz when it is vibrating freely with its electrodes shorted is given by $Q=2\pi fL_1/R_1$. It should be emphasized that although the quantity directly measured is an electrical resistance, R_1, the dissipation which it represents has a mechanical origin.

Measured Q's of more than 500 000 are frequently obtained for quartz bars polished and etched and vibrating in a vacuum at room temperatures. No measurements of Q, or R_1, for wide temperature ranges have been found in the literature, although Bosshard and Busch[2] found that R_1 increased linearly with temperature over a 50°C range of temperatures centered near room temperature.

II. TECHNIQUES OF MEASUREMENT AND EXPERIMENTAL RESULTS

A. Forced Vibrations of Longitudinal Bars

Measurements of the resistance R_1 were made on two quartz bars C and E described in an earlier paper,[3] which describes also the Q-meter apparatus which was used for making the measurements reported here. Briefly put, the resonant frequency of a bar was first located by the successive approximations technique, and the Q-meter was then operated at that frequency. R_1 (the series chain resistance) was deduced from the open-circuit voltage of the Q-meter, the voltage across the crystal bar when connected to the Q-meter, and the purely resistive internal impedance of the source (i.e., the Q-meter). This internal impedance, R, was adjusted both to large values, $R\gg R_1$, and to small values, $R\approx R_1$, so as to obtain checks on the measurement of R_1.

The quartz bars were placed in the holder and heated in the furnace described earlier.[3] The screening system for the crystal holder, which was devised to reduce the effects of the holder's dielectric losses on equivalent-circuit determinations at high temperatures, proved to be unnecessary when R_1 only was being determined, and was not consistently used.

The results of measurements of R_1 for bar C are plotted in Fig. 2. This bar was never heated above 555°C, and the variation of R_1 with temperature, found at the fundamental frequency of the bar, seemed to be independent of the number of heatings. R_1 was measured also at the third and fifth overtones, whose frequencies were, respectively, very near to the third and fifth harmonics of the fundamental. These results are all plotted in Fig. 2. At the fundamental frequency, the resistance R_1 had a maximum at 305°C.

The variation of the fundamental frequency with temperature is shown in Fig. 3. This latter graph shows that near the temperature (305°C) at which the dissipation is a maximum, there is no detectable anomaly in the frequency of the fundamental mode.

Figure 2 shows that the temperatures of maximum R_1 increase for the third and fifth overtones. As will be shown, these effects can be explained by a mechanical relaxation phenomenon, whose decay time is an Arrhenius function of temperature.

The assumption that a relaxation mechanism is present implies that the part of the total resistance R_1 caused by it should have its temperature variation given by

$$R_r=2R_m/(\omega\tau+1/\omega\tau)$$
$$=R_m/\cosh(\log\omega\tau_0+U/NkT), \qquad (1)$$

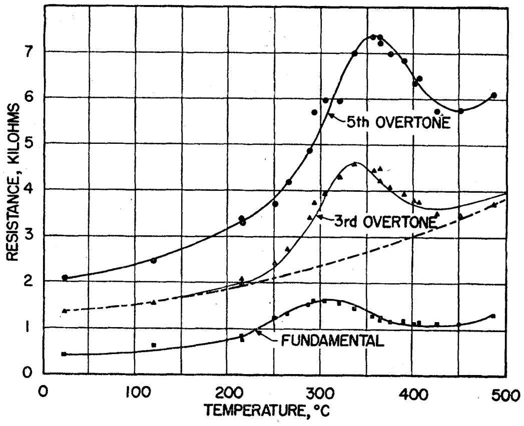

FIG. 2. R_1 *vs* temperature for bar C. For the third overtone, the solid line is computed from Eq. (1), and the open triangles are measured values.

where R_r (maximum)$=R_m$, τ is the decay time of the mechanical relaxation associated with the observed anelastic effect, and U is its activation energy.

At temperature T,

$$\tau=\tau_0e^{U/NkT}, \qquad (2)$$

where Nk is the gas constant, and τ_0 is a relaxation time constant, characteristic perhaps of a defect in the quartz lattice. The location of a temperature maximum of R_r is given by

$$2\pi f\tau=\omega\tau=1, \qquad (3)$$

where f is the frequency at which R_r is measured, and the corresponding pulsatance is $\omega=2\pi f$. Let $T_m=$ tem-

---

[2] W. Bosshard and G. Busch, Z. Physik **108**, 195 (1938).

[3] R. K. Cook and P. G. Weissler, Phys. Rev. **80**, 712 (1950).

perature of maximum R_r. Then

$$\log f = -(U/NkT_m) + \text{a constant.} \qquad (4)$$

A plot of the observed $\log f$ *versus* $1/T_m$ values is shown by the open circles in Fig. 4. The circles should lie on a straight line if Eq. (4) is valid. The solid line was drawn so as to be a best fit for the open circles. From it we find $U = 22\times 10^3$ cal/mole, and $\tau_0 \approx 2\times 10^{-14}$ sec. This value of τ_0 is to be compared with the shortest period, τ_m, of the lattice vibrations which contribute to the specific heat. From data in the literature on quartz, cristobalite, and vitreous silica, we estimate $\tau_m \approx 5\times 10^{-14}$ sec. Raman spectra and experiments with reststrahlen yield fundamental lattice periods of the same order of magnitude.

Equation (1), after addition of the "background" dissipation resistance (estimated to rise exponentially with increasing temperature, for which, however, there is no theoretical basis), is to be compared with the experimentally measured values of R_1. The agreement is exemplified by the solid curve (theoretical) for the third overtone in Fig. 2. The values of U and τ_0 given above were used, and the frequency f was that of the third harmonic. The value of R_m was adjusted so that the computed curve would fit the maximum value of R_1 found experimentally. The agreement of the computed curve with the measured resistance for the third overtone (shown by the open triangles) confirms the values of U and τ_0 found from Fig. 4. Similar agreement of the computed with the measured resistance holds for the fundamental and fifth harmonics as well.

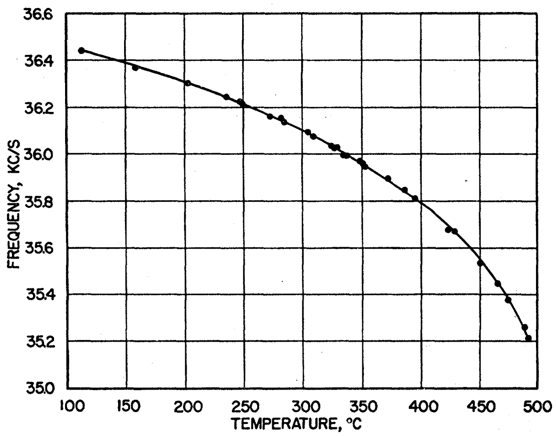

FIG. 3. Frequency *vs* temperature for the fundamental mode of bar C.

Figure 2 shows also that both R_1 at room temperature, and the maximum value of R_1 as a function of temperature, are directly proportional to the frequency. Since the inductance L_1 of a bar vibrating at a harmonic frequency is the same as the inductance at its fundamental frequency, it follows that the Q of bar C is independent of frequency. This is consistent with Mason and Fair's[4] observation that the Q (caused by internal dissipation) of a plate vibrating in thickness shear is independent of frequency.

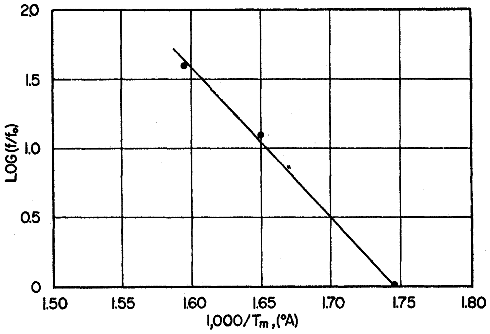

FIG. 4. Log(f/f_0) *versus* $1000/T_m$ for bar C. Open circles are observed values derived from Fig. 2 for the fundamental, third overtone and fifth overtone. f_0 = fundamental frequency of bar.

The fractional vibrational energy lost during each cycle is $2\pi/Q$ (if $Q \gg 2\pi$). Since all measurements on bar C were made in air, a part of the loss must be charged to sound radiation by the vibrating bar. It is difficult to make a quantitative estimate of this loss. However, at the temperatures where R_1 is a maximum, the relaxation effect is greatest, and sound radiation is then a negligible part of the total energy loss per cycle. From the data in Fig. 2 combined with the reactance measurements reported earlier,[3] we conclude that at room temperatures the fractional energy loss of bar C is 0.9×10^{-4} per cycle. At the temperatures where the dissipation due to the relaxation effect is greatest (Q a minimum, maximum of $R_1 = R_m$), the fractional energy loss per cycle is 2.8×10^{-4}. This is less than one-tenth of the maximum loss found for the torsional bars G and H (see part B of this section and Table I).

The results of measurements of R_1 for bar E are plotted in Fig. 5. It is evident that after repeated heatings to about 560°C, and in one case to 571.5°C, the resistance R_1 developed a maximum value at about 380°C. Furthermore, the maximum value of R_1 increased after each heating. This remarkable behavior suggested that some change was taking place in the quartz structure. The first suggestion was that electrical (Dauphiné) twinning was setting in. Bar E had been originally cut from oscillator-grade quartz, free of both optical and electrical twinning. In order to determine whether or not the heating caused electrical twinning, the gold electrodes were first dissolved (after the fourth heating and cooling) by boiling in aqua regia for ten minutes. This was sufficient to remove all gold on the surface, but the bar had a reddish-purple cast which was visible only by reflected light (the bar resting on a sheet of white paper). Most remarkable was the color distribution. It appeared to be roughly "sinusoidal," that is, there was a broad flat maximum

---

[4] W. P. Mason and I. E. Fair, Proc. Inst. Radio Engrs. **30**, 464 (1942).

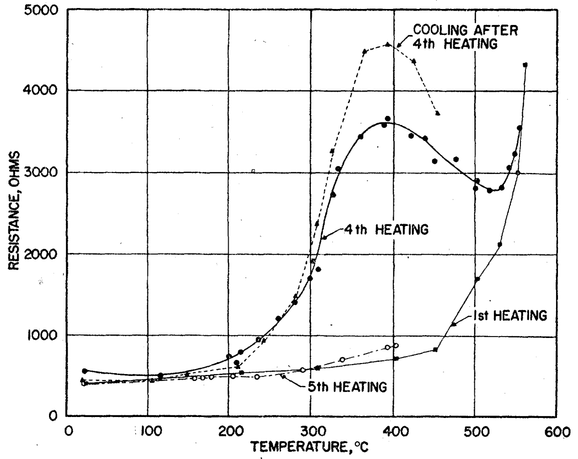

Fig. 5. R_1 *vs* temperature for bar *E*. Increase in R_1 between 1st and 4th heating is due to the migration into quartz lattice of gold atoms, which were removed by etching prior to the 5th heating (open circles).

at the middle of the bar, which shaded off to no color at the ends. We believe the coloration is due to colloidal gold, or gold atoms, which moved into the quartz lattice in the regions of greatest stress which were present during vibration of the bar at high temperatures (above 560°C). The bar was etched in order to determine whether or not twinning had occurred. Etching removed the coloration, and showed no evidence of twinning. Gold electrodes were re-applied by an evaporation technique to the bar, so as to avoid heating it. R_1 was then re-determined for the bar, and the results up to 400°C, the highest temperature used during the fifth heating, were found to be substantially the same as those shown for the first heating (see Fig. 5). The explanation of the increasing resistance R_1, therefore, is the migration of gold atoms into the quartz lattice.

Equation (1) was successful in explaining the variation of R_1 with temperature for bar *C*. This suggests that the equation can be applied to the data given for bar *E* in Fig. 5, so as to obtain estimates of U and τ_0. This was done by first subtracting the resistance R_1 during the first heating from the values for the fourth heating so as to yield the resistance R_g due to the gold atoms in the quartz. Next U and R_m in Eq. (1) were adjusted so as to yield a curve having a good fit to the measured values of R_g. Values of $U = 13$ kcal/mole and $R_m = 2900$ ohms were sufficient to do this. τ_0 was then computed from

$$\log 2\pi f\tau_0 + U/NkT_m = 0, \tag{5}$$

where T_m = temperature of maximum R_g. We find $\tau_0 \approx 10^{-10}$ sec. This is to be contrasted with the value of 10^{-14} sec found for bar *C*.

The coloration phenomena were investigated further by means of bar *F*, which had been heated to temperatures above 600°C in the earlier experiments.[3] However, no systematic measurements of its R_1 had been made. The gold electrodes were removed with aqua regia. The bar had an even more pronounced reddish-purple coloration than did bar *E*. Even more remarkable, the distribution of the color was "complementary" to that for bar *E*. That is to say, the coloration was maximum at the ends and least in the middle of the bar. No explanation can as yet be offered for these curious phenomena. Since bar *F* had been heated above 573°C (the inversion temperature of quartz), it would undoubtedly be electrically twinned on cooling down to room temperature. Etching removed the coloration, and showed that the bar was indeed twinned. It had originally been cut from quartz free of both electrical and optical twinning.

B. Free Vibrations of Torsional Bars

The decay of free vibrations of two torsional bars, *G* and *H*, has also been investigated. These bars were of identical dimensions, 5.00×0.500×0.500 cm, cut with their length in the *Y* direction from untwinned quartz. Fired-on silver electrodes were applied to the bars in a configuration suitable for the excitation of torsional oscillations. The natural frequency of the bars was found to be 36.0 kc/sec at room temperature. For the measurement of the decay of free vibrations as a function of temperature, the bars were mounted on knife-edge supports in a vacuum chamber which was enclosed in a small oven. The temperatures were measured by means of a thermocouple in close proximity to the crystal. To measure the damping, the bar was forced into oscillation by an external generator and, when vibrating, was then cut off from the generator and the output of the freely oscillating crystal observed as a function of time. Since the output voltage decays exponentially, a measurement of the damping coefficient α requires a measurement of the output voltage at two

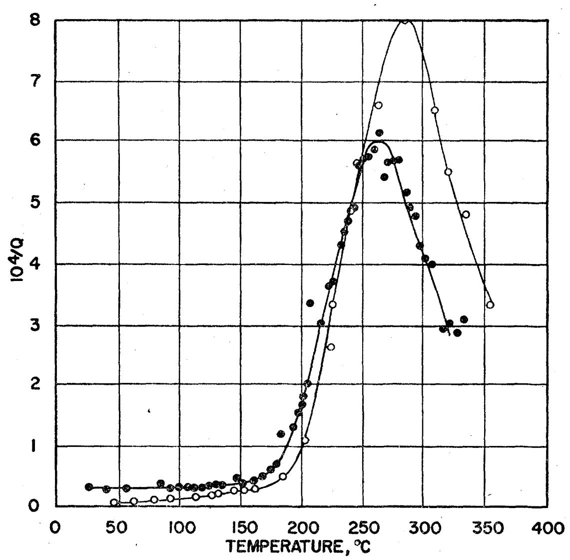

Fig. 6. $10^4/Q$ *vs* temperature for bars *G* and *H*. ● = bar *G*, ○ = bar *H*. The smooth curves are drawn through the experimental points

times as indicated by the equation:

$$V_2/V_1 = e^{\alpha(t_1-t_2)} = e^{\alpha\Delta t}. \tag{6}$$

The Q of the system is then given as

$$Q = \pi f/\alpha. \tag{7}$$

The α measured directly in this fashion depends on the circuit into which the crystal discharges and must be corrected for these effects to obtain the true crystal Q.

Two methods of measuring α have been used. In the earlier work the decaying voltage was displayed on an oscilloscope with a superposed timing signal. The trace was photographed and measured using a microscope with a vernier eyepiece. This method was used to investigate the Q of bar G. In more recent studies (bar H), an electronic instrument which allows a direct measurement of Q with improved accuracy (error $\leqq 3$ percent) was employed. This device will be described in detail elsewhere:[5] The results of these measurements are given in Fig. 6 where the Q's obtained from α's corrected for the external circuit effects are presented. In both cases a pronounced relaxation loss is observed centering at 270°C. No changes in the value of the maximum loss were noted for either bar for several temperature cycles, the highest temperature reached being about 360°C.

The data on these two bars could also be described by a relaxation expression. The values of τ_0 and U chosen to give the best agreement with experiment are given in Table I in the next section.

III. SUMMARY AND CONCLUSIONS

Measurements have been made of the Q of various quartz bars, vibrating in their fundamental acoustical modes, as a function of temperature. For bars G and H, which vibrated torsionally, and for bar E, which vibrated longitudinally, the fractional energy loss per cycle (which is approximately $2\pi/Q$) has maximum values at temperatures near 300°C. For the longitudinal bar E, the maximum loss increased with repeated heatings of the bar to temperatures near 550°C. Gold atoms from the electrodes had apparently worked into the quartz lattice, and it appears that the increased dissipation is accounted for by this lattice defect.

TABLE I. Activation energies and relaxation time constants for anelastic effects in quartz.

Bar	Vibration modes	Fundamental frequency (at room temp.) kc/sec	U kcal/mole	τ_0 sec	Minimum Q
C	Longitudinal	36.5	22	2×10^{-14}	22 000
E	Longitudinal	54.3	13	10^{-10}	...
G	Torsional	36.0	16	10^{-12}	1700
H	Torsional	36.0	17	10^{-12}	1200

For bar C, measurements of acoustical dissipation were made at the third and fifth overtones of the bar, as well as at its fundamental frequency. This allowed fairly accurate determinations of an activation energy and a relaxation time constant for the observed dissipation.

Table I summarizes the activation energies U and relaxation time constants τ_0 deduced from the anelastic measurements on the various bars. The values of U and τ_0 are more accurate for bar C than for bars E, G, and H.

For bar C, we suggest that the relaxation effect is due to twinning and detwinning in the quartz lattice, over a range not much greater than the size of the unit cell in quartz. For bar E, it was established that gold atoms caused the dissipation. The relaxation time constants for bars G and H are too great to be explained by the twinning-detwinning hypothesis, hence it seems likely that the losses arise from the introduction of silver atoms or ions during the firing-on of the silver electrodes. It should be noted also that if the mechanism assigned to bar C is contributing a similar amount to the losses in bars G and H, the effect would be masked by the large losses presumably due to the presence of foreign atoms or ions. Similar large dissipation effects observed in the alkali halides have been attributed to the presence of lattice imperfection.[6] Further investigations of these anomalous effects in quartz are in progress.

We are indebted to Mr. J. Upham, Mr. J. H. Wasilik, and Mr. R. D. Laughlin for assistance in the collection and reduction of data.

---

[5] R. D. Laughlin, J. Research Natl. Bur. Standards (to be published).

[6] R. G. Breckenridge, *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952), Chap. 8.