temperatures (similar to the shifts in the peaks of the thermoelectric power[5] and Hall effect[11] is undoubtedly due to the thermal excitation of electrons over a correspondingly larger gap. The Fermi level for a carbon with a given T_{ht} shifts as the ambient temperature changes, causing a change in the average curvature or effective mass of the carriers. In order to explain the existence of the plateau of susceptibility *vs* T_{ht} for all ambient temperatures, it would be necessary, then, to assume that the change in susceptibility resulting from the shift of the Fermi level with temperature is just balanced by the change in the number of carriers resulting from thermal excitation into the conduction band. While this assumption is acceptable on qualitative grounds, it seems highly improbable that such an exact cancellation of these factors could occur over the observed wide ranges of temperature and T_{ht}. The difficulties seem to be of a basic nature and probably some modifications in the general theory of diamagnetism will be required in order to explain all the experimental findings.

The problem of the simultaneous explanation of the susceptibility plateau and of the change in susceptibility of bisulfate compounds must be considered to be in an unsatisfactory state. A part of this difficulty might be due to the interpretation of the addition of bisulfate ions as affecting the number of carriers in the π band only. It may be that the band structure of the bisulfate compounds is different from that of untreated carbon of the same T_{ht} and some additional scattering effects are present.

ACKNOWLEDGMENTS

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Dislocations, Relaxations, and Anelasticity of Crystal Quartz

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By careful grinding and etching, contouring and mounting in a vacuum, very small internal friction coefficients Q^{-1} are found in *AT* shear vibrating crystals. Various tests show that the internal friction corresponds to that of the quartz itself. The internal friction at room temperature increases proportionally to the frequency up to 100 Mc/sec indicating the presence of relaxations. These have been investigated by measuring the internal friction at very low temperatures down to 1.5°K and two relaxations were found. One having a time constant of 10^{-13} second appears to be connected with a distorted lattice due to impurities while the other having a time constant of 7.7×10^{-10} second is thought to be connected with dislocation loops. Using equations developed previously for metals the indicated number of dislocations is $\bar{N}\approx10^8/\text{cm}^2$, the average loop length about 1.8×10^{-3} cm and the ratio of Peierls force to shear modulus about 5×10^{-8}. Confirmation of these values is given by the time constant 7.7×10^{-10} second and the change in frequency as a function of amplitude. A long-time aging effect is thought to be due to closer pinning of dislocations by impurity atoms. It is suggested that an improved frequency standard, free from aging, can be obtained by holding the temperature of the crystal at liquid helium temperature.

I. INTRODUCTION

During the course of development of high-Q, high-frequency crystal units for primary frequency standards,[1] it has become increasingly evident that the maximum Q obtainable for *AT*-cut crystal units at ordinary temperatures is an inverse function of frequency, ranging from 10×10^6 at 1 Mc/sec to 0.1×10^6 at 100 Mc/sec.

Techniques have been developed which virtually eliminate energy loss through the supporting structure at the edge of the quartz plate, and studies have since been carried out which show that all other sources of energy loss can be made insignificant in comparison with the energy loss caused by the anelasticity of quartz.

The resulting curve of maximum Q *vs* frequency suggests a relaxation process. To verify the existence of such a relaxation, measurements of internal friction of single crystals have been made from 1.5°K to 300°K and in the 5 to 80 Mc/sec frequency region. Two relaxations are found having activation energies and angular frequency constants equal, respectively, to

$$\begin{aligned}\gamma_1&=1.3\times10^9/\text{sec};\quad H=155\ \text{cal/mole}=6.7\times10^{-3}\ \text{ev},\\ \gamma_2&=10^{13}/\text{sec};\quad H=1300\ \text{cal/mole}=0.056\ \text{ev}.\end{aligned}\tag{1}$$

The first process can be shown to be due to dislocations in the crystal quartz, while the second process appears to be the result of impurities in the crystal.

II. EXPERIMENTAL EVIDENCE FOR Q VARYING INVERSELY PROPORTIONAL TO THE FREQUENCY AT ROOM TEMPERATURE

AT-cut quartz plates are excited electrically by centrally located electrodes and supported by wires fastened at the edge. The frequency of oscillation is a

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[1] A. W. Warner, Proc. Inst. Radio Engrs. 40, 1030–1033 (1952).

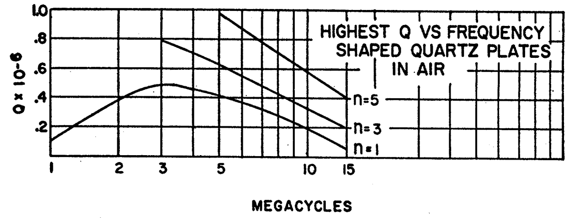

FIG. 1. Values of Q for 15 mm AT plates at atmospheric pressure.

function of plate thickness and overtone as follows —$ft=n1670$, where f is the frequency in kc/sec, t is the thickness in mm, and n is the overtone. The Q of such plates may be increased by proper shaping of the quartz blank, such as making one or both major faces convex. This has the effect of confining the mechanical motion to the center of the quartz plate, leaving the edge of the plate relatively quiescent. Energy loss at the edge and through the mounting wires is thereby minimized.

Figure 1 shows Q *versus* frequency for 15-mm diameter crystal plates at atmospheric pressure. Three effects may be noticed: first for a given overtone, above the maximum value, Q follows an inverse curve with respect to frequency; second, Q is a function of overtone, or putting it another way, for a given frequency, Q is a function of plate thickness; and third, the Q falls off rapidly at lower frequencies. At 15 Mc/sec, the Q is approximately proportional to the volume to surface ratio, indicating loss of energy at the quartz plate surface. At 1 Mc/sec, the principal energy loss is at the quartz plate edge, indicating that a 15-mm diameter plate is too small for a quiescent boundary at the lower frequencies.

Figure 2 shows the Q *versus* frequency curve when the crystal plates are mounted in vacuum. The Q is increased by a factor of at least 3 over that at atmospheric pressure, and Q is no longer a function of overtone, indicating that the energy loss was due to the presence of air and not due to the condition of the quartz plate surface. For example, data at 10 Mc/sec shows the third, fifth, and ninth overtones together, a 3 to 1 difference in quartz plate thickness, and a 27 to 1 difference in the equivalent electrical inductance and resistance, all indicating the same Q. In other experiments a variation of 3 to 1 in electrode thickness at 5 Mc/sec failed to show any effect on Q. Likewise, carefully polished quartz surfaces did not show more than a 10% improvement in Q over that of carefully lapped and etched plates.

To investigate the cause of low Q at the lower frequencies, a group of nine quartz plates 30 mm in diameter were obtained, twice the diameter of normal AT plates, and their electrical characteristics measured for various degrees of convex shaping. Also, one 90-mm diameter quartz plate was measured. The effect of the larger quartz plate diameters extending the frequency to 1 Mc/sec before appreciable degradation of Q due to energy loss at the edge of the plate occurs was shown in Fig. 1 of a previous publication.[2]

A study of available high frequency AT crystal units allowed an extension of the maximum Q data to 100 Mc/sec. At frequencies above 30 Mc/sec, evacuation of the crystal units had no measurable effect. The crystal unit measured at 100 Mc/sec consisted of an extremely flat and parallel polished quartz plate, excited by air gap electrodes and considered to be quite superior to commercial crystal units at this frequency. It is significant that with the greatest care taken, a Q of only 150 000 was obtained.

III. LOW-TEMPERATURE MEASUREMENTS SHOWING TWO RELAXATIONS

An internal friction increasing proportional to the frequency, as shown previously,[2] is indicative of a relaxation since the internal friction Q^{-1} can be written in the form

$$Q^{-1}=\frac{\Delta E}{E}\frac{\omega/\omega_0}{1+(\omega/\omega_0)^2}, \tag{2}$$

where $\Delta E/E$ is a weighting factor determining the difference of the appropriate elastic constants above and below the angular relaxation frequency ω_0, and ω is 2π times the frequency of measurement. Since Q^{-1} is still increasing proportional to the frequency, it is evident that the relaxation frequency is above 100 megacycles at room temperature.

If the relaxation has an activation energy, it is necessary to lower the temperature in order to bring it down to the accessible measuring frequency range. Hence, a well-mounted crystal of 5 Mc/sec, such as discussed in Sec. II, was placed in a sealed container inside a double Dewar cryostat of conventional design.[3] The temperature was decreased to 1.5°K by pumping the liquid helium in the inner Dewar flask, and the Q of the crystal was measured as the temperature was slowly increased to room temperature. The Q was measured by determining the rectified grid current for the oscillator when the crystal was operated at resonance, then by a substitution method determining the equivalent resistance to give the same grid current for

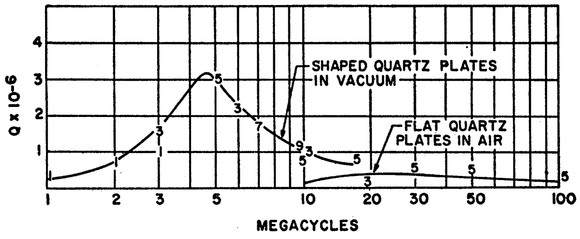

FIG. 2. Highest Q of crystals mounted in a vacuum plotted as a function of the frequency.

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[2] Bömmel, Mason, and Warner, Phys. Rev. **99**, 1894 (1955).

[3] For example, see H. J. McSkimin, J. Appl. Phys. **24**, 988–997 (1953).

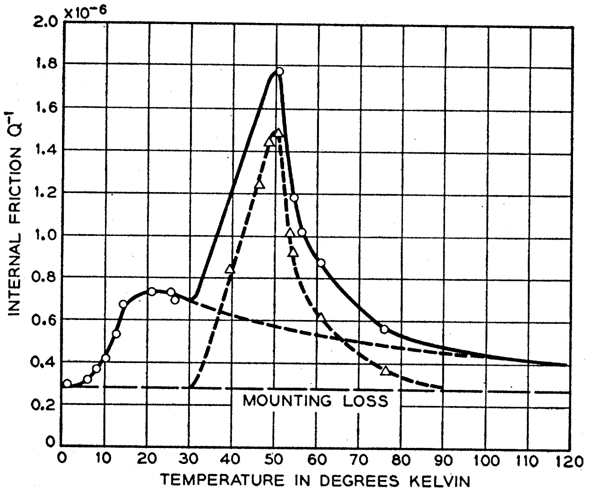

FIG. 3. A repeat of a 5-Mc/sec crystal measurement.

the oscillator at the same frequency. Knowing the separation of resonant and antiresonant frequencies of the crystal, the equivalent inductance L and hence the Q could be determined.

This process was carried out for a 5-Mc/sec plate with the Q^{-1} values shown plotted against the absolute temperature by Fig. 2 of the previous publication.[2] As the temperature decreases, Q^{-1} increases down to 52°K where a sharp internal friction peak occurs. The internal friction first decreases, then increases to a broad peak at 21°K and then drops down to a value $Q^{-1}=2\times 10^{-7}$ at 6°K. Below this temperature the internal friction remains constant down to 1.5°K, the lowest temperature obtained.

The constant loss has been ascribed to a mounting loss at this temperature. If the loss remains independent of the temperature, the dashed line would result. The very sharp peak at 52°K is only slightly broader than a single relaxation whose value is shown by the dot dash line. In addition there is a broad relaxation which has been labeled a dislocation relaxation for reasons discussed later.

In order to see if the main characteristics were reproduced with different crystals, the characteristics of a second 5-Mc/sec crystal were measured and are shown by Fig. 3. The same features were present but the dislocation peak is only half as high while the impurity peak is about twice as high.

To study the nature of these relaxations, measurements have to be made at different frequencies in order to determine activation energies and frequency constants. Figure 4 shows a measurement of a 9-Mc/sec crystal as a function of temperature. The measurements indicate that the dislocation relaxation peak is about 5 times as high as that for a 5-Mc/sec crystal and that the impurity peak is 20 times as high. The positions of the peaks on the temperature scale fit on the lines of Fig. 5 which show the logarithms of the relaxation frequencies plotted against $1/T$. A number of other crystals up to 80 Mc/sec were also measured and their relaxation peak frequencies are shown plotted on Fig. 5.

Two curves are determined from the data of Fig. 5, and as can be seen they satisfy the equations:

$$\omega_1 = 1.3\times 10^9 e^{-155/RT}, \quad \omega_2 = 10^{13} e^{-1300/RT}.$$

It will be observed that at room temperature the first relaxation is the lower frequency one and contributes

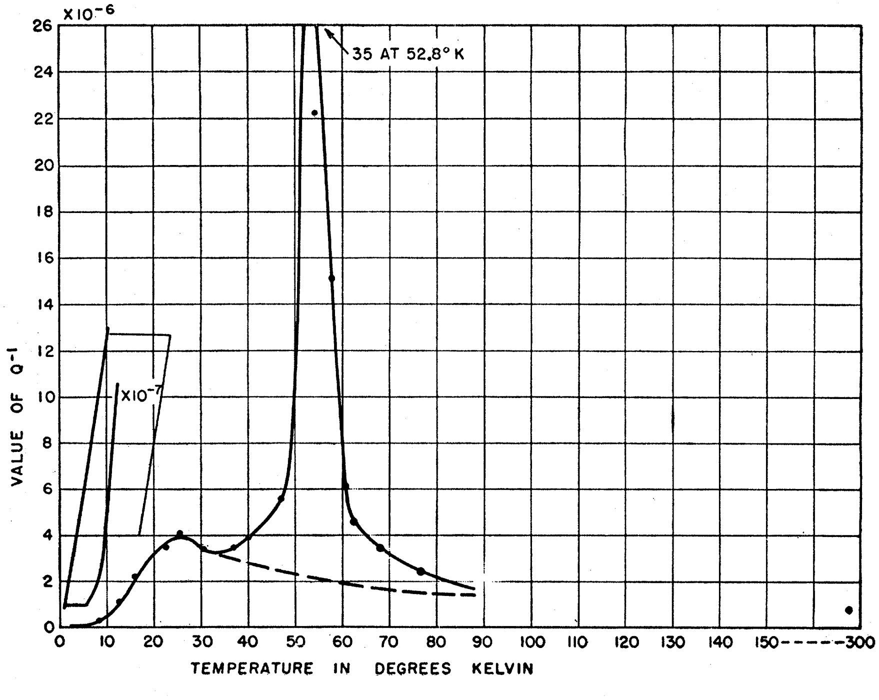

FIG. 4. Internal friction for a 9-Mc/sec crystal showing increased losses at peaks and lower mounting loss.

most of the internal friction. The indicated relaxation frequency at room temperature is slightly under 200 Mc/sec. For frequencies above this, the Q of the quartz crystals should increase again.

IV. THEORETICAL INTERPRETATION OF RELAXATION FREQUENCIES

The relaxation mechanism with the higher activation energy has an angular frequency constant of 10^{+13} and hence involves the motion of single atoms or molecules rather than a chain of molecules. The activation energy involved—1300 calories per mole—is too low to correspond with any diffusion process. It is in fact similar to that found in previous measurements of fused silica.[4] Figure 6 shows measurements of the internal friction of fused silica at low temperatures for these frequencies and as can be seen, the relaxation frequencies parallel those of Fig. 5 for the high activation energy line. The most probable interpretation of this coincidence is that the impurities are producing a distorted structure by the strains they introduce. Figure 7 shows the most likely interpretation of the ultrasonic loss for fused silica, namely, that the loss is the result of the relaxation of the sidewise vibrations of the oxygen atoms between two equilibrium positions produced by the random network of the glass structure. The activation energies and frequency factors are consistent with this interpretation.[4] If we accept this as the cause of the results for the higher activation energy relaxation, the narrowness of the peak—which corresponds to a single relaxation—indicates that the strain due to the impurities introduces only a narrow range of bond angles rather than the very wide range found for fused silica. The amplitude of the peak which is only about 1/2000 as high as the fused silica peak in the same activation energy range also indicates that only a small fraction of the total crystal is active in the production of this relaxation. This fact and the wide variation of the height of the peak suggests again that the relaxation is the result of impurities in the lattice.

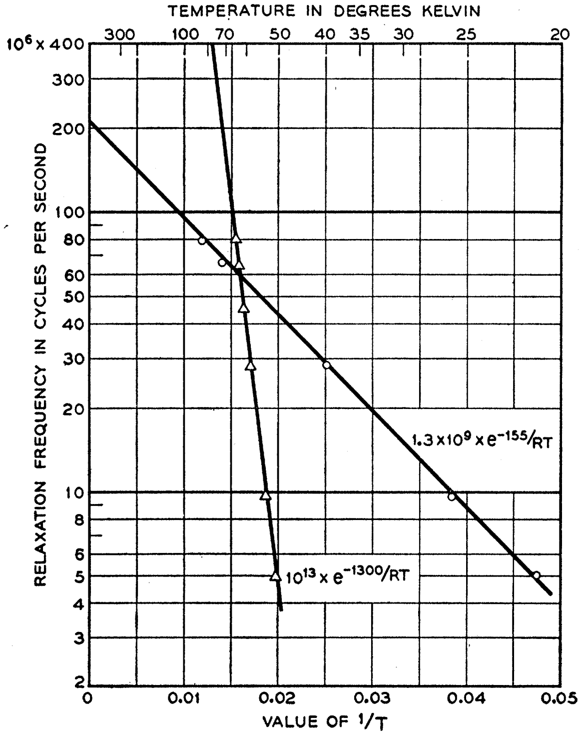

FIG. 5. Plot of two relaxation frequencies *versus* $1/T$

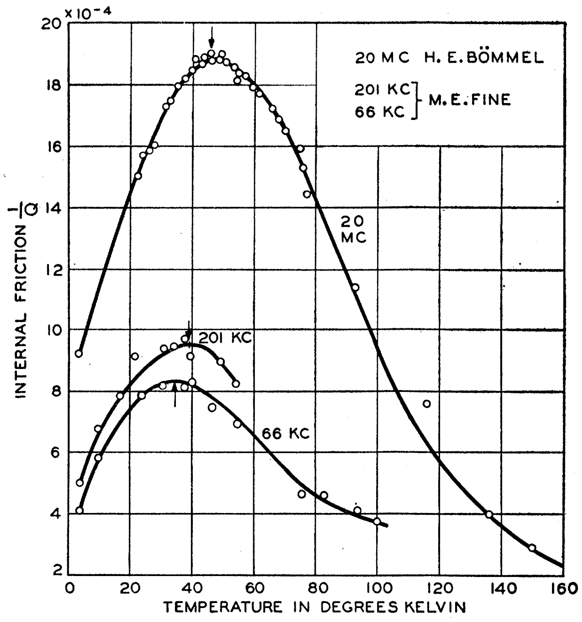

FIG. 6. Internal friction in fused silica for three frequencies (after Bömmel and Anderson).

This same relaxation has been found in the dielectric loss of crystal quartz.[5] Measurements at 32 kc/sec as a function of temperature show a large peak at 38°K which is in agreement with Eq. (1) for this frequency. The types of defects have been analyzed and by optical measurements it was shown that this peak corresponds to the replacement of an oxygen bridging atom by two aluminum atoms of valence +3. This oxygen vacancy can distort the lattice considerably and can be the cause of the ultrasonic and dielectric losses observed.

The low activation energy curve with the correspondingly low frequency factor is thought to correspond to a relaxation for dislocations. The results are similar in nature to a dislocation relaxation found in

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[4] O. L. Anderson and H. E. Bömmel, J. Am. Ceram. Soc. **38**, No. 4, 125–131 (1955).

[5] Volger, Stevels, and von Amerongen, Philips Research Repts. **10**, No. 4, 261–280 (1955). In fact, the constants found by dielectric measurements are $\omega_0 = 0.5\times10^{13}$/sec; $H = 1275$ cal/mole $= 0.055$ ev, which agrees with the ultrasonic measurements well within the experimental error.

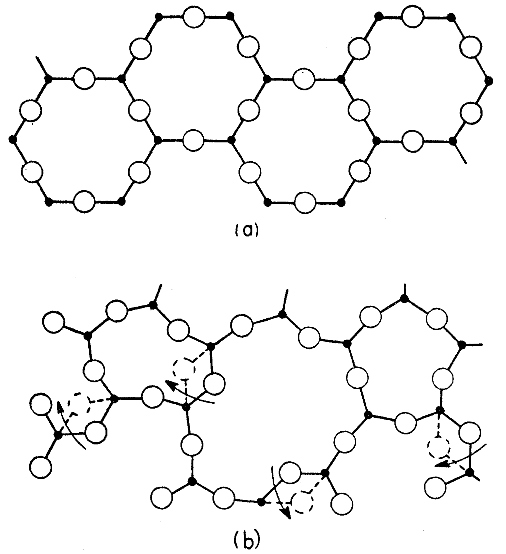

FIG. 7. Random network structure of glass compared to regular structure for perfect crystal.

face-centered metals and discussed in several papers.[6] In these papers a model for a dislocation relaxation is assumed in the form shown in Fig. 8. Edge dislocations are assumed to lie in minimum energy positions along the glide planes of the metal and to be bound at irregular lengths l by impurity atoms or dislocation nodes. At absolute zero temperatures, the dislocations remain fixed in their minimum energy positions but as the temperature increases, sufficient thermal energy is imparted to the dislocations so that a few of them can overcome the energy barrier provided by the shearing stress tending to return them to their minimum energy position.

In crystal quartz the glide planes are the y and z major and minor rhombohedral planes. The AT cut is nearly parallel to the z minor rhombohedral face which is related to the crystallographic axes as shown in Fig. 9. Since the unit cell is a primitive cell, the shortest displacement distance is along the a axis with a value of 4.9 A. Hence the Burgers vector $b=4.9$A. When the dislocation becomes displaced to its next minimum energy position, the perpendicular displacement is

$$b'=b\cos 60°=b(\tfrac{3}{4})^{\frac{1}{2}} \tag{3}$$

from the minimum position. Hence the calculations for a cubic crystal given previously[6] are slightly altered.

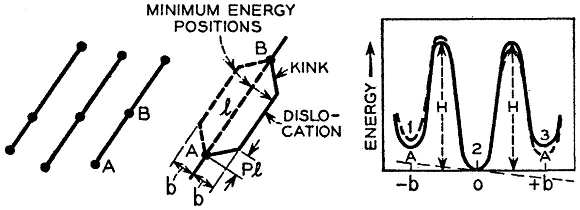

FIG. 8. Model for dislocation motions and equivalent potential well model.

The energy required to displace the dislocation with two kinks against the Peierls restoring force,

$$(T_{13})_b=(T_{13})_0 b\sin(2\pi d/b'), \tag{4}$$

is given by the equation

$$W_1=(T_{13})_0 b\int_0^y dy\int_0^{d(y)}\sin\frac{2\pi x}{b'}dx=\frac{(T_{13})_0 bb'l}{2\pi}$$
$$\times\left[1-\cos\frac{2\pi d}{b'}+2p\left[\cos\frac{2\pi d}{b'}-\frac{b'}{2\pi d}\sin\frac{2\pi d}{b'}\right]\right], \tag{5}$$

where p is the percentage of the loop covered by the two kinks, $d(y)$ is the displacement at a distance y from one end of the loop, and d is the displacement of the straight middle sections of Fig. 8. The other source of energy due to the increase in length of the dislocation is determined by the increase in length Δl:

$$\Delta l=2[(pl)^2+d^2]^{\frac{1}{2}}-pl\approx d^2/pl. \tag{6}$$

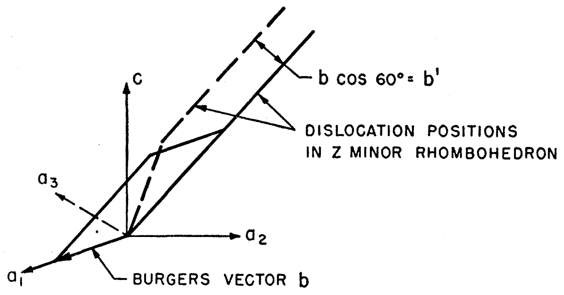

FIG. 9. Dislocation position and motion in crystal quartz.

The work is done against the tension T, which is usually taken as

$$T=\mu b^2/2, \tag{7}$$

where μ is the shearing constant in the glide plane,

$$\mu=3.12\times 10^{11}\ \text{dynes/cm}^2. \tag{8}$$

Hence

$$W_2=T\Delta l=\mu b^2 d^2/2pl. \tag{9}$$

The minimum energy A at the first atomic distance b' from the unstretched position is obtained when $d=b'$ and this case $\cos(2\pi d/b')=1$, $\sin(2\pi d/b')=0$, and

$$W_1+W_2=A=\frac{\mu b^2 b'^2}{2pl}+(T_{13})_0\left(\frac{bb'pl}{\pi}\right). \tag{10}$$

The kink length pl is determined as the length giving the minimum value for A. Differentiating A by pl and

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[6] W. P. Mason, Phys. Rev. **98**, 1136 (1955); W. P. Mason, J. Acoust. Soc. Am. **27**, 643 (1955).

setting the result equal to zero, the length pl is equal to

$$pl=[\pi\mu bb'/2(T_{13})_0]^{\frac{1}{2}}. \tag{11}$$

Hence, with this value the maximum and minimum values of W_1+W_2 are

$$H=(T_{13})_0 bb'l/\pi; \quad A=2(bb')^{\frac{3}{2}}[(T_{13})_0\mu/2\pi]^{\frac{1}{2}}. \tag{12}$$

Hence, if we define length $b_0=(bb')^{\frac{1}{2}}$, the same formulas hold for a quartz crystal as for a cubic crystal.

To determine the resonant frequency of a dislocation in its potential well, the restoring force for small displacements, obtained by differentiating the sum of W_1+W_2 by d and letting $d\rightarrow 0$ is

$$\left[\frac{2\pi(T_{13})_0 bl}{b'}+\frac{b^{\frac{3}{2}}}{b'^{\frac{1}{2}}}\left[\frac{\pi(T_{13})_0\mu}{2}\right]^{\frac{1}{2}}\left(\frac{2}{\pi}-\frac{8\pi}{3}\right)\right]. \tag{13}$$

Since the effective mass for a dislocation is $\pi\rho b^2 l$, the resonant frequency is given in the equation

$$f=\frac{1}{2\pi b_0}\left[\frac{2(T_{13})_0}{\rho}+\frac{b_0}{\rho l}\frac{(T_{13})_0\mu}{2\pi}\left(\frac{2}{\pi}-\frac{8\pi}{3}\right)\right]^{\frac{1}{2}}$$
$$\approx\frac{1}{2\pi b_0}\left[\frac{2(T_{13})_0}{\rho}\right]^{\frac{1}{2}}, \tag{14}$$

since the last part of the square root is less than 1% of the first part.

For very small stresses the dislocations cannot move out of their potential wells shown by Fig. 8(c) under the applied stress. The stress can bias the potential wells and thermal agitation will cause more dislocations to go into the low-energy wells than in the high-energy wells, thus producing a plastic deformation. The effect of this type of model is to produce a relaxation loss which has been shown to be given by the equation

$$\frac{1}{Q}=\frac{2e^{-A/kT}}{1+2e^{-A/kT}}\left[\frac{N_0 l^2(1-p)^2 b_0{}^4\mu^E}{kT}\right]\frac{\omega/\omega_0}{1+(\omega/\omega_0)^2}$$
$$=\frac{\Delta\mu}{\mu}\frac{\omega/\omega_0}{1+(\omega/\omega_0)^2}, \tag{15}$$

where $\omega_0=\gamma e^{-(H-A)/kT}$ and N_0 is the number of dislocation loops per cubic centimeter. For a distribution of loop lengths, the formula reduces to

$$Q^{-1}=\sum_{i=1}^{n}\frac{\Delta\mu_i}{\mu_0}\left(\frac{\omega/\omega_i}{1+(\omega/\omega_i)^2}\right). \tag{16}$$

Another indication of dislocations is the rising attenuation which increases exponentially with the temperature. This was shown[6] to be the result of the breakaway or repinning of dislocations by impurity atoms. The change in lengths caused by this process abstracts energy from the vibration and produces an internal friction independent of the frequency equal to

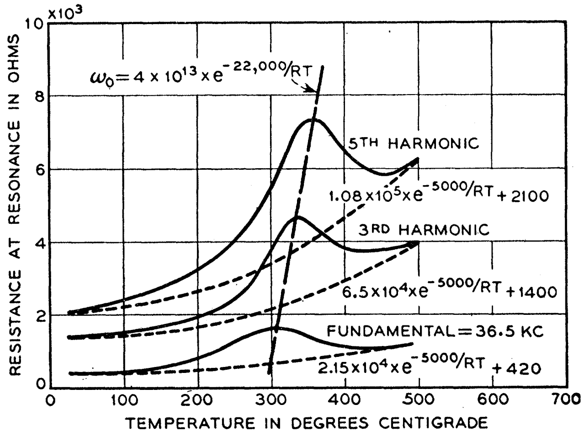

FIG. 10. Internal friction in quartz at high frequencies showing an ion relaxation and the exponentially increasing "breakaway" loss (after Cook and Breckenridge).

$$Q^{-1}=\left[\frac{2(T_{13})_0}{\mu}\right]^{\frac{1}{2}}\frac{b_0 V_s N_0 l e^{-U/kT}}{2\pi}, \tag{17}$$

where V_s is the shear velocity normal to the glide plane (3.4×10^5 cm sec for quartz), $N_0 l$ the number of dislocations per square centimeter, and U the binding energy of impurity atoms.

This effect was first observed for quartz by Cook and Breckenridge[7] who measured the resistance of longitudinally vibrating crystals. The resistances for the first, third, and fifth harmonics of a 36.5-kc/sec crystal are shown by Fig. 10. Since the effective inductance of a harmonic crystal decreases in the ratio of the harmonic order, the resistance has to increase 3 and 5 times over that for the fundamental in order to preserve a constant Q. The solid line shows the actual measurements which indicate a relaxation having an activation energy of 22 kilocalories and a frequency of 5×10^{13}. This relaxation has been ascribed to the migration of vacancies[7] by Cook and Breckenridge. There is also an exponentially rising component as shown by the dashed lines which indicates an activation energy of 5000 calories per mole. Since the internal friction of the crystal, including air losses at room temperature, was found to be

$$Q^{-1}=1/70\,000=1.4\times10^{-5}, \tag{18}$$

we find that the breakaway dissipation is given by an equation

$$Q^{-1}=7\times10^{-4}e^{-5000/RT}. \tag{19}$$

Measurements have been made for AT crystals at 1070 kilocycles with closely similar results.

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[7] R. K. Cook and R. G. Breckenridge, Phys. Rev. **92**, 1419 (1953). More recent measurements of Cook's, however, indicate that this peak may be due to diffusion of metal ions. These measurements will be discussed in future publications.

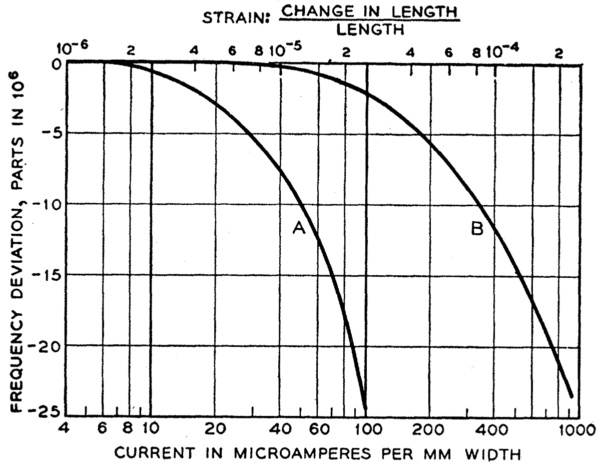

FIG. 11. Change in frequency of a *GT* cut as a function of strain amplitude.

V. EVALUATION OF PARAMETERS FOR QUARTZ CRYSTALS

Four pieces of data have been obtained which can be compared with the theoretical formulas. These are the average activation energy which has been evaluated as 155 calories per mole, the frequency constant found experimentally to be 1.3×10^9, the breakaway constant found to be 7×10^{-4} and the peak attenuation loss. The most reliable value for this is that obtained from Fig. 1 of reference 2 which indicates a value of $Q^{-1}=6\times10^{-6}$ at room temperature. The loss is still increasing proportional to the frequency with an indicated relaxation frequency from Fig. 5 of 160 Mc/sec. If this were a single relaxation, the minimum value would be 7.5×10^{-6}, and hence $\Delta\mu_0/\mu_0$ of Eq. (15) should equal 1.5×10^{-5}. Actually the width is broader than a single relaxation and hence we take the equivalent single value as

$$\frac{\Delta\mu}{\mu_0}=2\times1.5\times10^{-5}=3\times10^{-5}$$

$$=\frac{2e^{-A/RT}}{1+2e^{-A/RT}}\left[\frac{N_0l^2(1-p)^2b_0^4\mu^E}{kT}\right]. \quad (20)$$

The breaking away loss is taken as

$$7.0\times10^{-4}=\left(\frac{2(T_{13})_0}{\mu}\right)^{\frac{1}{2}}\frac{b_0V_sN_0l}{2\pi}. \quad (21)$$

The third piece of information is the activation energy

$$H-A=\left[\frac{(T_{13})_0b_0^2l}{\pi}-2b_0^3\left(\frac{(T_{13})_0\mu}{2\pi}\right)^{\frac{1}{2}}\right]$$

$$\times\frac{6.025\times10^{23}}{4.182\times10^7}=155. \quad (22)$$

These equations give enough information to solve for the three unknowns, l, N_0, and $(T_{13})_0/\mu$. Introducing the values $2e^{-A/RT}/(1+2e^{-A/RT})=\frac{2}{3}$, $b_0=4.5\times10^{-8}$, $\mu=3.12\times10^{11}$ dynes/cm², $V_s=3.42\times10^5$ cm/sec, $k=1.38\times10^{-16}$, $T=300$°K, and $p\doteq0.05$, we find the values $\bar{l}=1.8\times10^{-3}$ cm; $N_0l=\bar{N}=850$ dislocations/cm²;

$$(T_{13})_0/\mu\approx5\times10^{-8}. \quad (23)$$

One check of these values is the resonance frequency of dislocations in their potential well. Since the effect of a sudden temperature agitation will be to set the dislocation in vibration at its natural frequency, we should have $2\pi f_R=\gamma$ equal to the γ found in Fig. 5, namely, 1.3×10^9. Inserting the values of Eq. (23) in Eq. (14) we find

$$\gamma=2.4\times10^9, \quad (24)$$

which is within a factor of 2 of the measured result.

VI. FREQUENCY AGING IN QUARTZ CRYSTALS

Another indication of the presence of dislocations in crystal quartz is the existence of a nonlinear frequency change of the resonant frequency of *GT* frequency standards as a function of strain amplitude. For very low temperature coefficient *GT* crystals, Fig. 11 shows[8] the change in frequency observed plotted as a function of current per millimeter width. This is not a heating effect since we are using a *GT* crystal with a very low temperature coefficient of frequency. A large increase in internal friction also occurs when the frequency decreases nonlinearly.

The cause of this nonlinear behavior is the production of unstable Frank-Read dislocation loops. The process for doing this is shown by Fig. 12. When the stress becomes large enough to cause a dislocation loop to bow out to semicircular form, it becomes unstable and keeps on growing until it spirals back on itself and forms a new loop between the pinning points and a free loop which can interact with the applied stress and

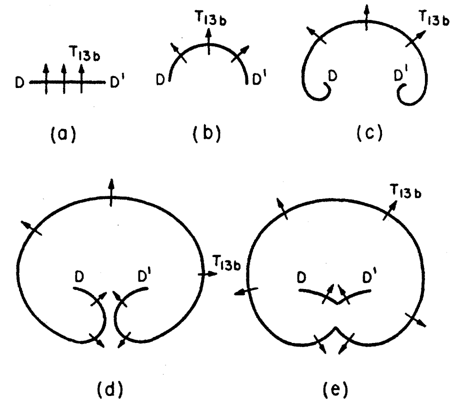

FIG. 12. Unstable Frank-Read dislocations.

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[8] A. R. D'heedene, *Quartz Crystals for Electrical Circuits* (D. Van Nostrand Company, Inc., New York, 1946), Chap. 14, p. 456.

produce more plastic strain, thus lowering the elastic constant. After a certain number has been produced they are held up by obstructions such as other dislocations, impurity atoms, etc., and react back on the Frank-Read source stopping production. Hence, a stable elastic constant results which is somewhat lower than that for quartz at low amplitudes. The initial strain for the production of unstable loops occurs when the force on the dislocation equals twice the tension. This results in the equation

$$T_{13}bl=\mu b^2, \quad \text{or} \quad l=b/T_{13}/\mu=b/(S_{13})_c. \qquad (25)$$

Hence, for strains greater than $(S_{13})_c$, unstable dislocation loops can be produced and the frequency can be lowered. The curve A which was for crystals etched less than 20 minutes begins to deviate from a straight line for strains of the order of 2×10^{-6} which correspond to dislocation lengths as long as 2.5×10^{-2} cm. The effect of more completely etching the surface is to reduce the longest loops to about 10^{-2} cm. The average dislocation loop length for maximum frequency reduction is about 10^{-3} cm in agreement with the determination from the relaxation effect.

When strains much above 10^{-4} are applied to quartz crystals, they fracture. It appears that this may be due to the unstable production of Frank-Read loops around the longer dislocation loops which may act as centers of fracture.

All frequency standards are operated at strains less than 10^{-6} and consequently the operation should not produce dislocations in the crystals. It is well known,[9] however, that they suffer a frequency aging phenomenon. For clean glass holders which minimize interchange of mass between the holder and the crystal, most of this aging represents[10] an increase in frequency with time. It appears likely that this increase in frequency is the result of the pinning down of the extra dislocations produced in the manufacturing process by the migration of impurities through the quartz. If this is the case, the change in frequency should be lower at lower temperatures. Some evidence for this is found in the work of Mitchell[10] of the British Post Office, who has observed the rates of aging of frequency standards at 50°C and -10°C. The aging at -10°C was found to be less than $\frac{1}{5}$ that of 50°C. This ratio corresponds to an activation energy of 4.6 kilocalories per mole in good agreement with the value of 5 kilocalories found from "breakaway" loss. If the temperature is reduced to liquid helium temperature or even to liquid nitrogen temperature, the aging rate should be decreased by a factor of

$$\exp\left[-\frac{4600}{2}\left(\frac{1}{77}-\frac{1}{323}\right)\right]\approx10^{-10}.$$

Hence the aging for 40 years at 77°K will be less than that for 0.1 second at 50°C and therefore this source of aging should be eliminated.

VII. CONCLUSIONS

It is evident from the foregoing data, particularly that of Sec. II, that the best frequency for the operation of quartz plates for frequency control purposes is a function of available quartz size. For a 15-mm diameter plate, which is readily available, this frequency is about 5 Mc/sec. Attempts to operate a quartz plate at a higher frequency than necessary to obtain the characteristic Q of quartz will result in diminishing returns for two reasons. One, the requirement for Q is greater due to the limitations of circuit components, and two, the available Q is lower due to the increased anelasticity of quartz at higher frequencies. Any attempt to operate the crystal at a lower frequency will result not only in a rapidly diminishing Q but in less stable operation because the mounting structure becomes part of the mechanically vibrating, frequency determining element.

The data also imply that frequency stability beyond that measured to date may be obtained by operating crystal units at liquid helium temperature (4.3°K). The Q at 5 Mc/sec is at least double that at room temperature, and frequency aging should be many times less since transfer of mass and change in elastic constants should be greatly retarded. The temperature coefficient has been found to be about 0.01 parts per million per °K for AT crystals which in combination with the excellent temperature control properties of helium might make possible stabilities in the order of one part in 100 billion.

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[9] See A. W. Warner, Proc. Inst. Radio Engrs. 43, No. 7 (1955).

[10] H. T. Mitchell, Nature 174, 41 (1954).