HIGH TEMPERATURE ACOUSTIC LOSS
OF AT-CUT QUARTZ
CRYSTALS

By

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter I

INTRODUCTION

Alpha-quartz belongs to the trigonal crystal system with point group 32. This structure has an axis of three fold symmetry, which is called the optic- or z-axis. Quartz is optically active; both right-handed and left-handed forms exist. Since it does not have inversion symmetry quartz is piezoelectric. At 573°C α-quartz undergoes a structural phase transition to a hexagonal structure known as β-quartz. Only the trigonal phase, α-quartz, is useful for frequency control.. The density of the α-quartz is 2650 kg/m^3 and its hardness is 7 on the Mohs' scale. (1) On an atomic scale the structure consist of SiO_4 tetrahedra that share each of their corners with another tetrahedron. The four oxygen ions surrounding the silicon can be divided into two groups: those with long bonds (1.612 Angstroms) and those with short bonds (1.606 Angstroms). The Si-O-Si bond angle 143.65°. (2)

Alpha quartz is found in nature. However, for most technical applications it is grown synthetically by a hydrothermal process. This process is carried out in an autoclave usually at temperatures between 340°C to 350°C and pressure in the range of 1.0 to 1.3 x 10^8 Pa. The hydrothermal process is a process in which an alkaline solution, usually sodium hydroxide or sodium carbonate, under pressure at high temperature is used to dissolve, transport and deposit quartz. The solution dissolves small pieces of natural quartz crystal and by convection transports the material through a baffle system into an isothermal recystallizing chamber. There the supersaturated solution deposits the material upon a suspended seed in the form of a plate. (1)

Defects in Quartz

Two types of twins can occur in α-quartz. These are Brazilian (optical) and Dauphine (electrical) twins. Optically twinned quartz contains both right-handed and left-handed regions. Strong Si-O bonds are broken during a creation of optical twinning which makes it a growth defect. Electrical twins are regions with reversed piezoelectric effects. This is caused by a reversal of the x-axis. Unlike the optical twinning, electrical twinning does not requires breaking the Si-O bonds; instead it can be caused by only a slight atomic displacement. Electrical twinning occurs when a quartz goes through the α-β a transition at 573°C. It can also occur when a moderate uniaxial stress is applied.

Dislocations are also found in α-quartz. Studies have shown the dislocations mostly lie normal to the growth face of sample. (3) Networks of dislocations are the origin of etch tunnels that are formed when samples are etched.

Several types of point defects can be found in quartz. The most important is substitutional aluminum. An interstitial alkali (lithium or sodium) commonly provides the required compensation. Hydrogen bonded to an adjacent oxygen or a hole on an adjacent oxygen also occur. The Al-M+ center, (lithium or sodium) consists of an interstitial alkali ion located adjacent to a substitutional aluminum. It can give rise to one or more characteristic acoustic loss peaks because of the stress-induced motion of the alkali ion from one equilibrium position to another about the aluminum ion. Near 50K an acoustic loss peak is seen in 5-MHz, AT-cut quartz resonators. (2). This loss peak is caused by the Al-Na center. The Al-Li center does not shown any loss peaks. The Al-Li occurs during growth. Electrodiffusion can be used to replace the interstitial alkali with a selected alkali or proton. Al-OH centers are formed when an interstitial proton bonds to an oxygen adjacent to the substitutional aluminum. The resulting Al-OH center is infrared active; it has absorption bands at 3367 and 3306 cm^{-1}. No acoustic loss peaks have been attributed to the to Al-OH center. Al-hole centers $[Al\text{-}O_4]^o$ consist of a hole (missing electron) trapped in a nonbonding p-orbital of an oxygen ion located adjacent to a substitutional aluminum. The Al-hole center causes the smoky color found in irradiated quartz. Loss peaks at 27 K , 100 K and 135 K are associated with the Al-hole center.

A second type of point defect is OH-molecules formed by protons trapped on oxygens near unidentified growth-defects in the lattice. Ionizing radiation creates mobile electrons and holes in the quartz lattice which interacts with these defects. (4) Radiation frees the alkali from the Al and replaces it with either hydrogen from the OH growth-defects or with a hole.

Acoustic Loss

Acoustic loss which is also called internal friction is the damping of mechanical vibrations due to internal damping forces. Piezoelectric resonators such as quartz crystals are used as the oscillatory elements in electronic circuits. Significant acoustic loss will limit their performance. The quality factor, Q, is the reciprocal of the acoustic loss. In a sinousoidally driven anelastic system the stress and strain will differ by a phase angle θ where

$$\tan\theta = Q^{-1} \tag{1}$$

Defects such as the Al-Na center which have several equivalent orientation give rise to an acoustic loss given by

$$Q^{-1} = D\omega\tau/(1+\omega^2\tau^2) \quad (2)$$

where D is the relaxation strength (or coupling factor), ω is the angular frequency of the vibration and τ is the relaxation time of the defect. Often the relaxation time is given by

$$\tau = \tau_o \exp(E_b/kT) \quad (3)$$

where E_b is the energy barrier between the equivalent positions, τ_o is the period of the vibration within the potential well. (2) Acoustic loss measurement gives an insight into the effects of electrodiffusion or irradiation on the defects in the crystal. They also provide basic information for the design of oscillator circuits.

High temperature loss measurements above 300K on natural quartz samples were carried out Fraser. (3,5) The lost spectra of unswept sample were found to increase rapidly for temperatures above 450K and continued to increase up to phase transition temperature. The rapid increase of the acoustic loss is caused by the motion of thermally activated ions in the z-axis channels.

The lightly damped electromechanical oscillatory crystal can often be described as a series RCL circuit. Since the crystal is used in electronic circuits this analog description makes a convenient model for both the circuit designer and the individual studying its properties. Since practical crystals have very light damping their resonant frequency, ω_o, is given by

$$\omega_o = 1/(LC)^{1/2} \quad (4)$$

where L and C are respectively the motional inductance and capacitance. The quality factor is, Q, is

$$Q = \omega_o L/R \quad (5)$$

Since ω_o is only weakly dependent upon temperature the acoustic loss, Q^{-1}, can be found by measuring R.

Purpose of Study

The purpose of this study was to investigate the acoustic loss of AT-cut quartz crystals at high temperatures. Quartz contains interstital alkali ions which are trapped near substitutional aluminum or other defects. The alkali ions thermally escape from the traps and move along the z-axis channel at high temperature. This motion along shallow potential well causes and leads to acoustic loss. All of the resonators were AT-cut, 5^{th} overtone 5MHz blanks fabricated from cultured quartz bar. The were two groups of resonators used which were designated as PQ-ER# and X-67R#. Each group consisted of three set of resonators, where the PQ-E resonators were made up of unswept, Na-swept and D_2-swept resonators and the X-67 had H-swept, Na-swept and unswept resonators. The measurement of acoustic loss was done using the transmission technique.

CHAPTER II

EXPERIMENTAL PROCEDURE

Measurement Methods

Two basic techniques are available for measuring the acoustic loss, Q^{-1}. These are the log-decrement and the transmission method. In the log-decrement method the crystal resonator is excited at its natural frequency , f_o, for a short time and then allowed to freely decay. (1) The decay time, τ, is measured and the Q is calculated from

$$Q = \pi f_o \tau \tag{6}$$

In the transmission method the resonator is treated as a series RLC circuit. It is connected in a resistive pi-network and driven in the steady state at its resonant frequency. At f_o the inductive and capacitive reactance cancel so the circuit can be readily solved for R. Several techniques are available for determing L (or C) which are nearly temperature independent. The simplest is to use the log-decrement technique to directly measure Q at room temperature then

$$L = Q(300K)\, R(300K) / 2\pi f_o \,. \tag{7}$$

The transmission method was chosen for the this experiment because it can be automated and R(T) data can be collected nearly "hands off". The equivalent resistance R and the series resonant frequency were measured over the 300K to 700K range.

A block diagram of the system is shown in Figure 1. The system consist of an HP personal computer, an HP3325 synthesizer, an HP 5334B counter, HP3478 digital multimeter, Keithley 182 DMM, HP8495A vector voltmeter, a temperature controller, furnace and the pi-network.

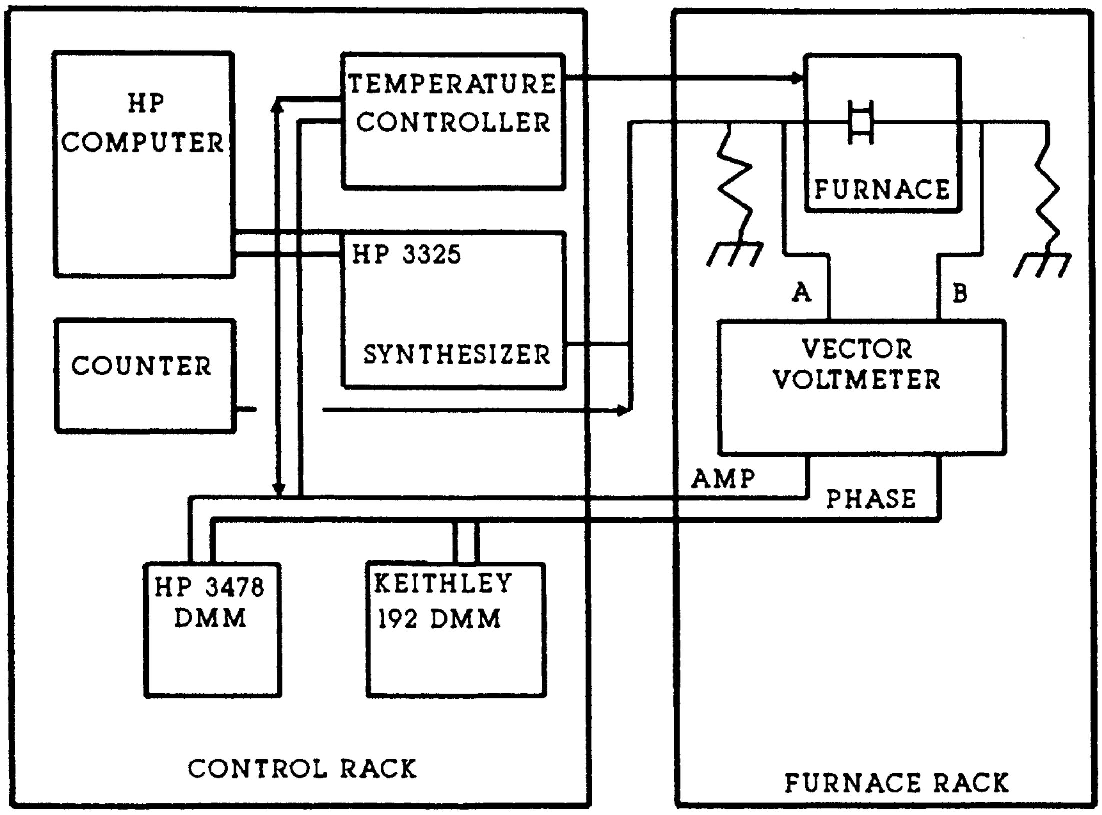

Figure 1. Block diagram for transmission technique for the measurement of acoustic loss.

The voltage at point A (V_a) of the pi-network is kept constant throughout the experimental procedure and the voltage at point B (V_b) of the pi-network and phase at B are read with respect to point A by the vector voltmeter. The DMMs send the analog amplitude and phase amplitude from the vector voltmeter to the computer. If the phase is not zero the computer then adjust the frequency that will be required to keep the phase zero. The maximum and minimum temperature is entered into the computer to define the temperature range at which the experimental data will be taken.

The system is calibrated at room temperature by reading V_a with the vector voltmeter, with the phase held at zero. The program is then paused and the vector voltmeter is switched to read V_b. Once the program is running the temperature of the sample is increased by increasing the set point on the temperature controller and the synthesizer frequency is adjusted so that the phase is held at zero. When the required temperature is reached and the phase is zero, the V_b is read by the vector voltmeter, the series resistance is calculated, the frequency measured, and the sample temperature is read. If the sample temperature is less than the maximum temperature the computer increases the set point until they are equal. In this way, the resistance and frequency are measured as a function of temperature. When the maximum temperature is reached the data is stored on a floppy disc.

When the run is completed the acoustic loss, Q^{-1}, is found from,

$$Q^{-1} = R/2\pi fL \tag{7}$$

where L was found as describe above . The Q^{-1} and f(T) data are plotted using a spreadsheet program.

Samples

The cultured quartz samples used in this project were obtained from two sources. All were from pure z-growth bars. The 10-12ppm Al content samples were Sawyer Premium Q grade quartz from a bar designated PQ-E. (6) Samples from this bar have been extensively studied at Oklahoma State University. They have weak OH growth defect bands. The other samples were from a bar designated, X-67, from Rome Laboratory Hanscom AFB, MA. (7) This bar was grown from cultured quartz (III) nutrient and had an aluminum content of 0.11ppm. Cultured quartz (III) is regrown cultured quartz with the high-aluminum content x-growth region removed. The X-67 bar was also grown on a seed taken from the +X region of a cultured quartz crystal. Consequently it also has a low etch channel density.

All of the samples were Warner-design plano-convex 5MHz 5th overtone AT-cut resonator blanks. (8) Overtone operation reduces mounting losses. The PQ-E blanks had a diameter of 15mm while the X-67 blanks were 14mm in diameter. Lithium is the dominant alkali in as-grown quartz. Unswept, Na-swept and H-swept X-67 blanks were available for this study. Unswept, Na-swept and D_2-swept PQ-E blanks were also available. The low temperature properties of these resonators blanks have been investigated in several studies. (9,10) Tables I and II gives the room temperature Q as measured using the log-decrement method and the aluminum content of the PQ-E and X-67 blanks.

In order to minimize mounting losses both the log-decrement calibration and the resistance versus temperature measurements were made with the resonator blank mounted

TABLE I

PQ - E RESONATORS

SAMPLE #	TYPE	Q - VALUE	Al (ppm)
PQ - ER5	D_2 - Swept	2.46×10^6	10 - 12
PQ -ER3	Unswept	2.4×10^6	10 - 12
PQ - ER11	Na - Swept	9.09×10^5	10 - 12

TABLE II

X - 67 RESONATORS

SAMPLE #	TYPE	Q - VALUE	Al (ppm)
X67R1	Unswept	2.7×10^6	0.11
X67R2	H - Swept	2.81×10^6	0.11
X67R3	Na - Swept	2.55×10^6	0.11

in a ceramic gap-holder located at the center of the evacuated furnace. The gap-holder consisted of ceramic end cups with 5mm diameter electrodes and an AT-cut quartz ring spacer. The gap-holder supported the 14mm and 15mm diameter blanks only on the outer 1mm of their circumference. It is necessary to carefully clean the blanks prior to placing them in the gap-holder. The blanks are ultrasonically cleaned in a micro-solution, rinsed in distilled water and dried at 100°C.

CHAPTER IV

RESULTS AND DISCUSSION

Figure 2 shows the acoustic loss versus temperature data for the three PQ-E samples. These samples have 10 to 12 ppm aluminum. The acoustic loss of the unswept (Li) sample remains constant for temperatures up to 450K. Above 450K it increases rapidly with increasing temperature. The loss versus temperature curve for the Na-swept sample decreases up to about 400K and then increases rapidly at higher temperature. The decrease just above room temperature is probably due to the low temperature Al-Na loss peak. The loss in the D_2-swept sample shows a small but steady increase over the 300 to 550K range. These results suggest the possibility of a loss peak at higher temperatures that is related to the presence of hydrogen.

The rapid increase at high temperature in the unswept and Na-swept samples is probably due to motion of alkalis in the z-axis channel. Lithium is the dominant alkali in unswept cultured quartz. At high temperatures the alkali ions thermally escape from the trap near the substitutional aluminum. The resulting acoustic loss should be thermally activated. Figure 3 shows the acoustic loss of the three PQ-E samples against 1000/T(K). As shown in the log acoustic loss versus 1000/T(K) plot of both the unswept and Na-swept PQ-E crystals have an acoustic loss that increases exponentially in T^{-1}. If we assume that the loss is due to anelastic relaxation of mobile ions in the z-axis channels then it is described by equations 2 and 3. If we also assume, as did Fraser (3), that the

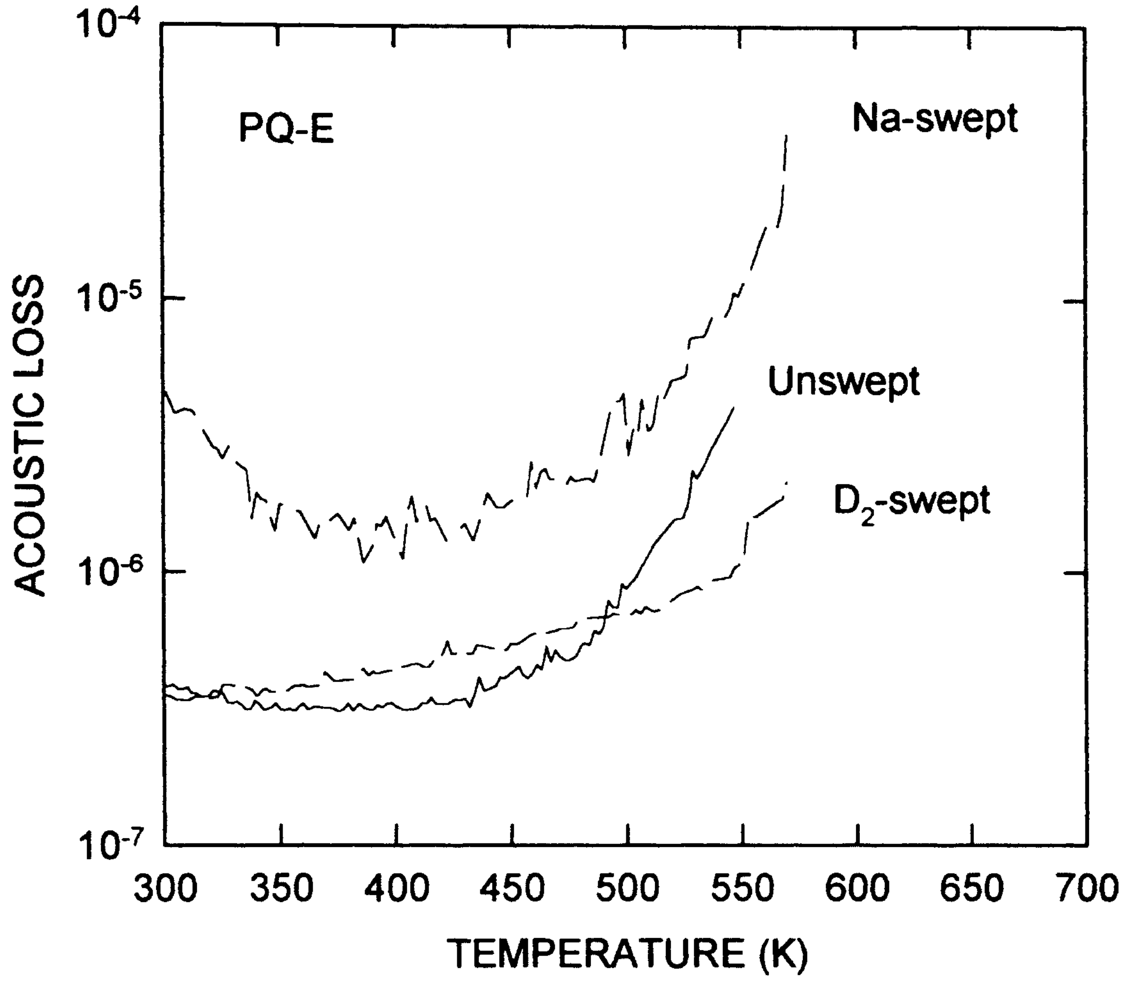

Figure 2. Acoustic Loss versus Temperature for PQ-E unswept, Na-swept and D_2-swept resonators.

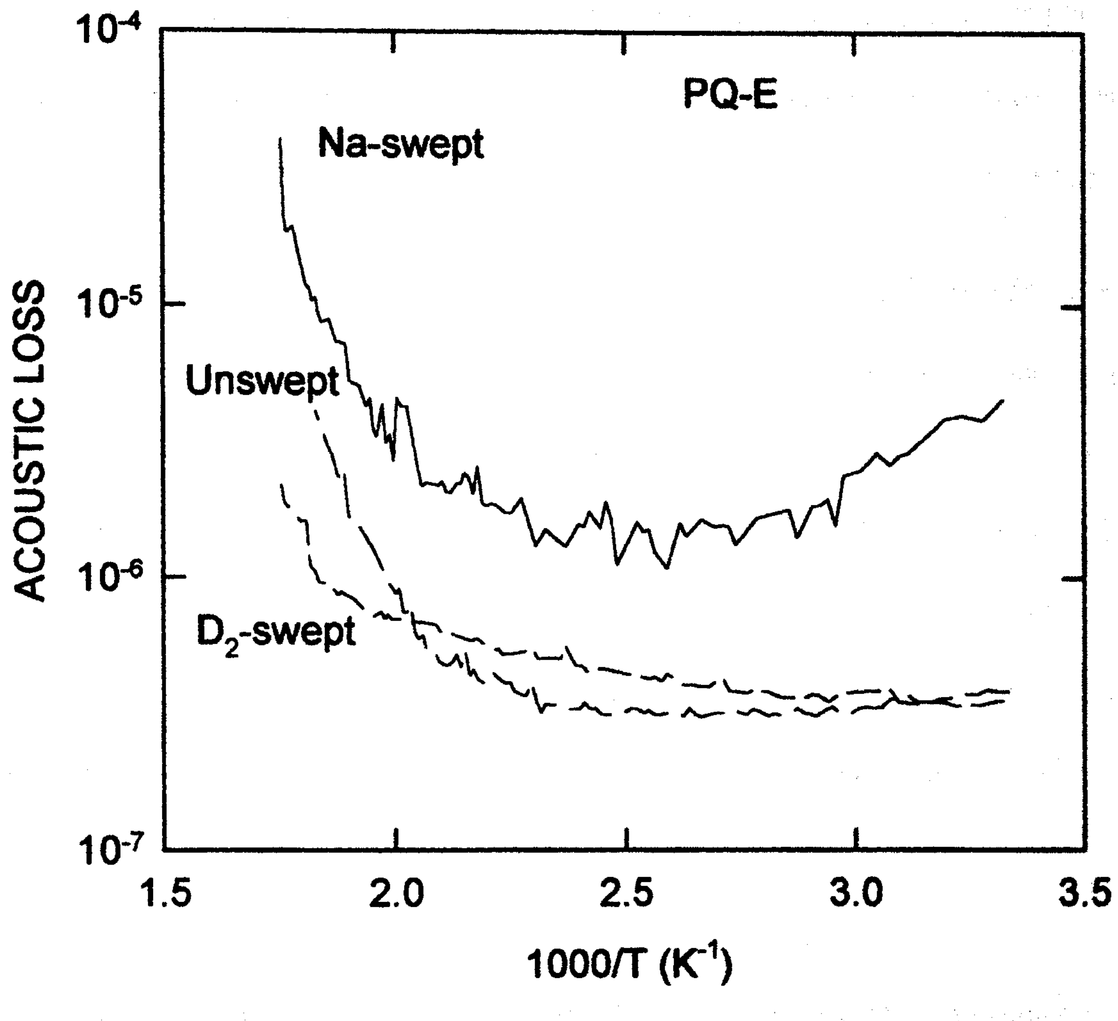

Figure 3. Acoustic Loss versus 1000/T(K) for PQ-E unswept, Na-swept and D_2-swept resonators.

temperature is well below the peak temperature where $\omega\tau = 1$ then equations 2 and 3 can be approximated as

$$Q^{-1} = (D/\omega\tau_o) \exp(-E_b/kT) \quad (8)$$

The parameters D also contains the number of relaxing center (number of ions) which is thermally activated. Therefore, the loss should increase exponentially in T^{-1} with an activation energy that contains both the barrier height and the association energy between the alkali ion and the aluminum. The slopes of the loss versus 1000/T(K) curves shown in figure 4. were used to find the activation energies of 0.78eV and 0.88eV for the unswept and Na-swept PQ-E crystals. These are in reasonably good agreement with Fraser's results of 0.72eV and 0.77eV for Li-swept and Na-swept natural quartz. (5)

The frequency of an AT-cut crystal increases by only 5000 ppm over the 0 K to 600 K temperature range. Crystal oscillators are operated at the upper turnover frequency, f_u, which is a local minimum in the f(T) curve. Figure 5 shows the fractional frequency offsets from the f_u for the PQ-E samples. The fractional frequency offset was calculated from

$$\Delta f/f_u = (f(T) - f_u) / f_u \quad (9)$$

The unswept and D_2-swept samples show nearly the same temperature dependence while the frequency of the Na-swept sample increases more slowly with temperature. This result is shown more clearly in the expanded plot of figure 6. Sodium is known to drastically alter the frequency- temperature characteristics of quartz crystals. (3,5) Figure 7 shows acoustic loss versus temperature results for the three X-67 resonators. For the H-swept resonator the acoustic loss remains nearly constant over the 300K to 700K temperature

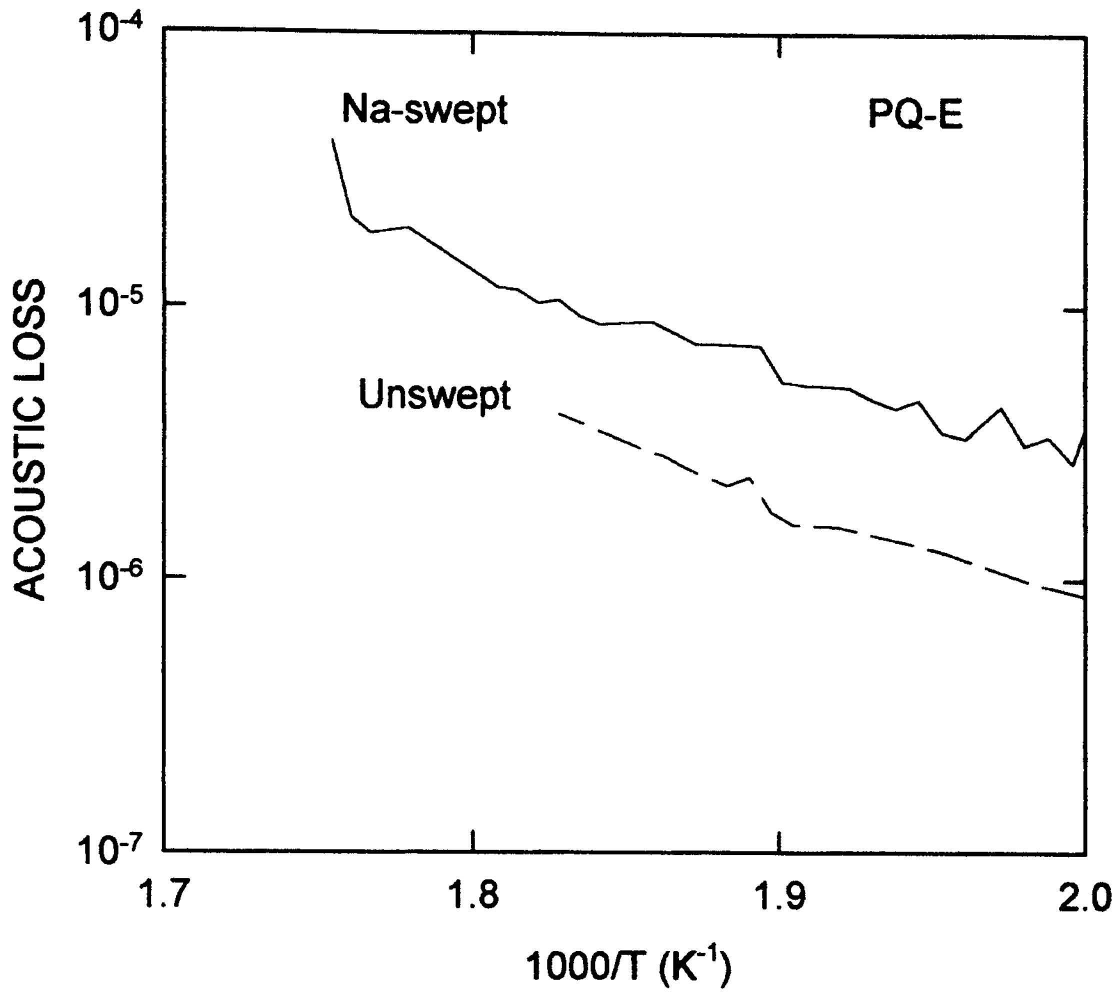

Figure 4. Acoustic Loss versus 1000/T(K) for PQ-E unswept and Na-swept resonators.

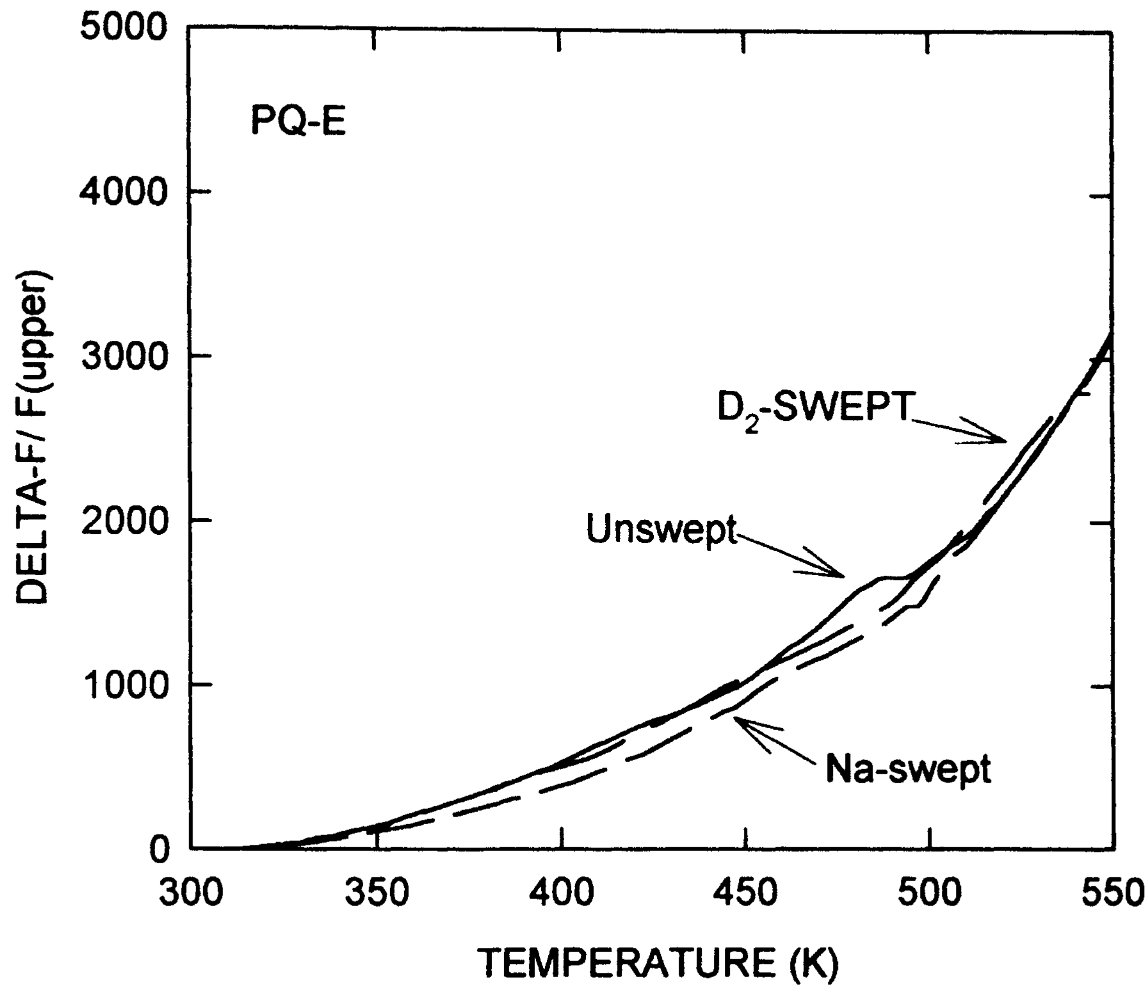

Figure 5. Frequency versus Temperature for PQ-E unswept, Na-swept and D_2-swept resonators.

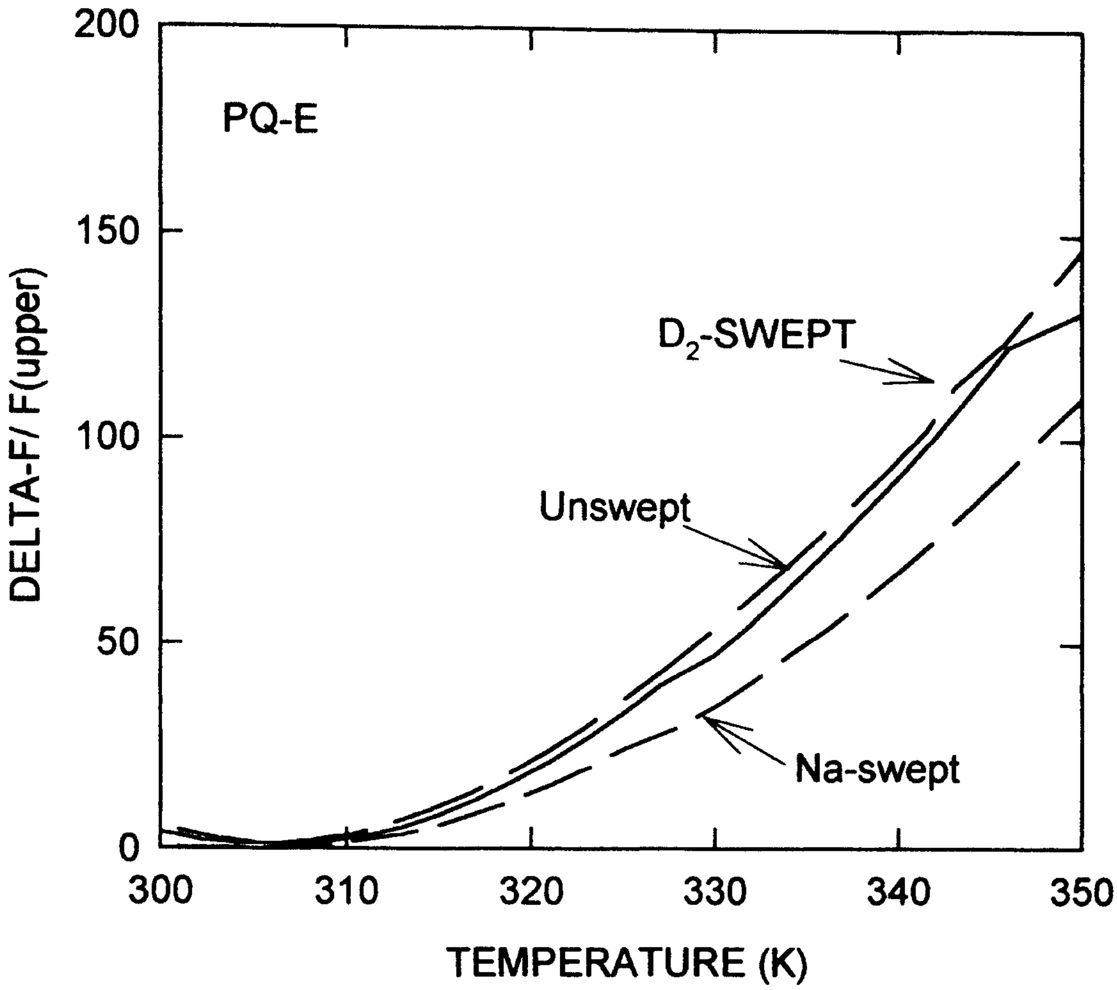

Figure 6. Frequency versus Temperature for PQ-E resonators for temperature range 300k to 350K.

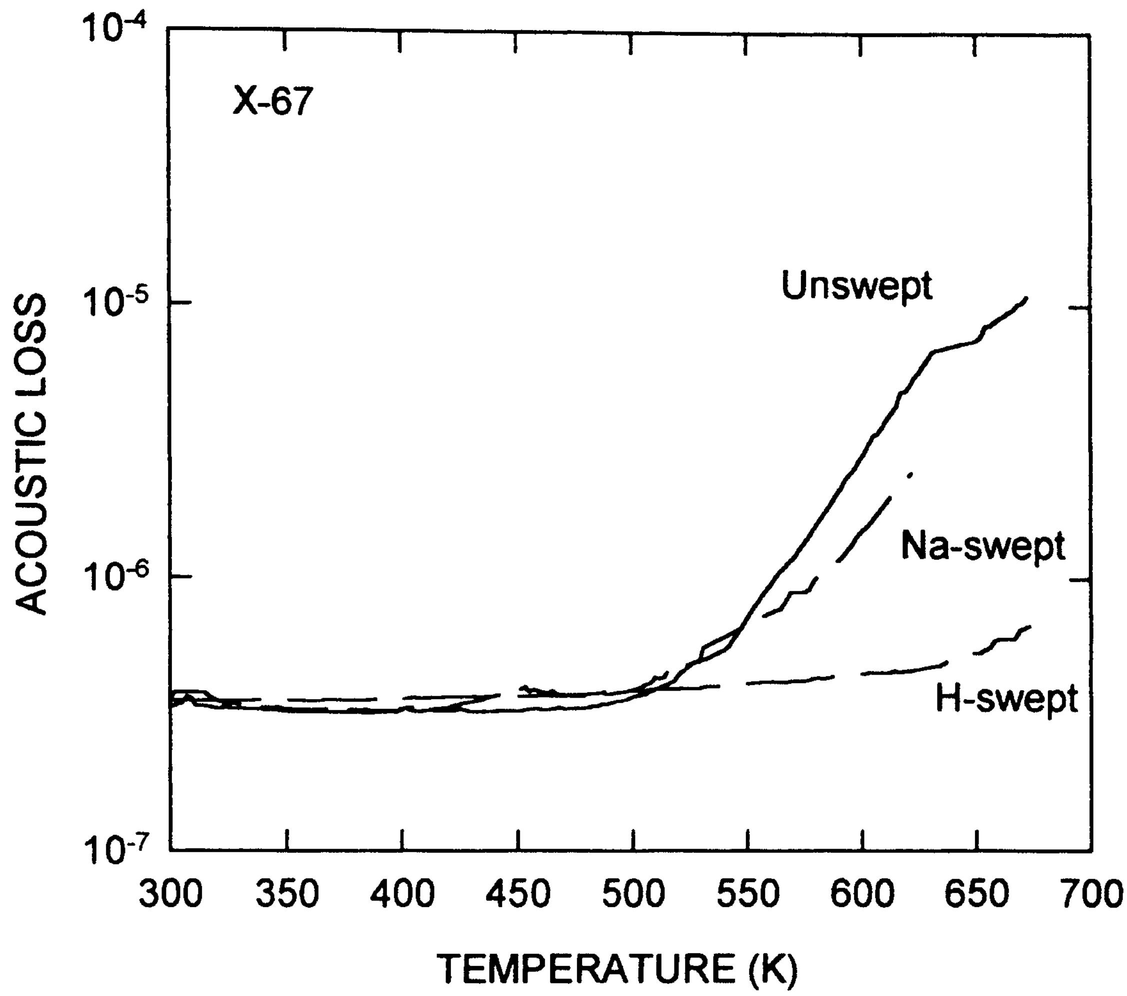

Figure 7. Acoustic Loss versus Temperature for X-67 unswept, H-swept and Na-swept resonators.

range. The acoustic loss in the unswept and Na-swept resonators is constant for the temperature values between 300K to 500K. For the temperature values higher than 500K the acoustic loss increases rapidly with increasing temperature. This increase in loss is due to the alkali ion motion in the z-axis channel.

This rapid increase at higher temperature in acoustic loss is smaller than that seen in the PQ-E samples. This is a reasonable result because X-67 quartz has only 0.11ppm Al and therefore, associated alkalis while PQ-E quartz has 10 to 12ppm Al. Consequently, the mobile alkali loss should be much less in the X-67 samples. Figure 8 shows that the acoustic loss of the unswept and Na-swept increases exponentially in T^{-1} at the higher temperatures. Figure 9 shows the acoustic loss versus 1000/T(K) curves for the unswept and Na-swept samples on an expanded scale. The slopes of these curves yielded activation energies of 0.72eV and 0.88eV for the unswept and Na-swept samples. These values are in reasonable agreement with our results for the unswept and Na-swept PQ-E samples and Fraser's results on Li- and Na-doped quartz. Table III summarizes the activation energy results.

Figure 10 shows that the fractional frequency offset from the upper turnover frequency versus temperature curves are nearly the same for all three X-67 resonators. Figure 11 shows these curves on an expanded scale. The effects of sodium are less in these low aluminum content samples.

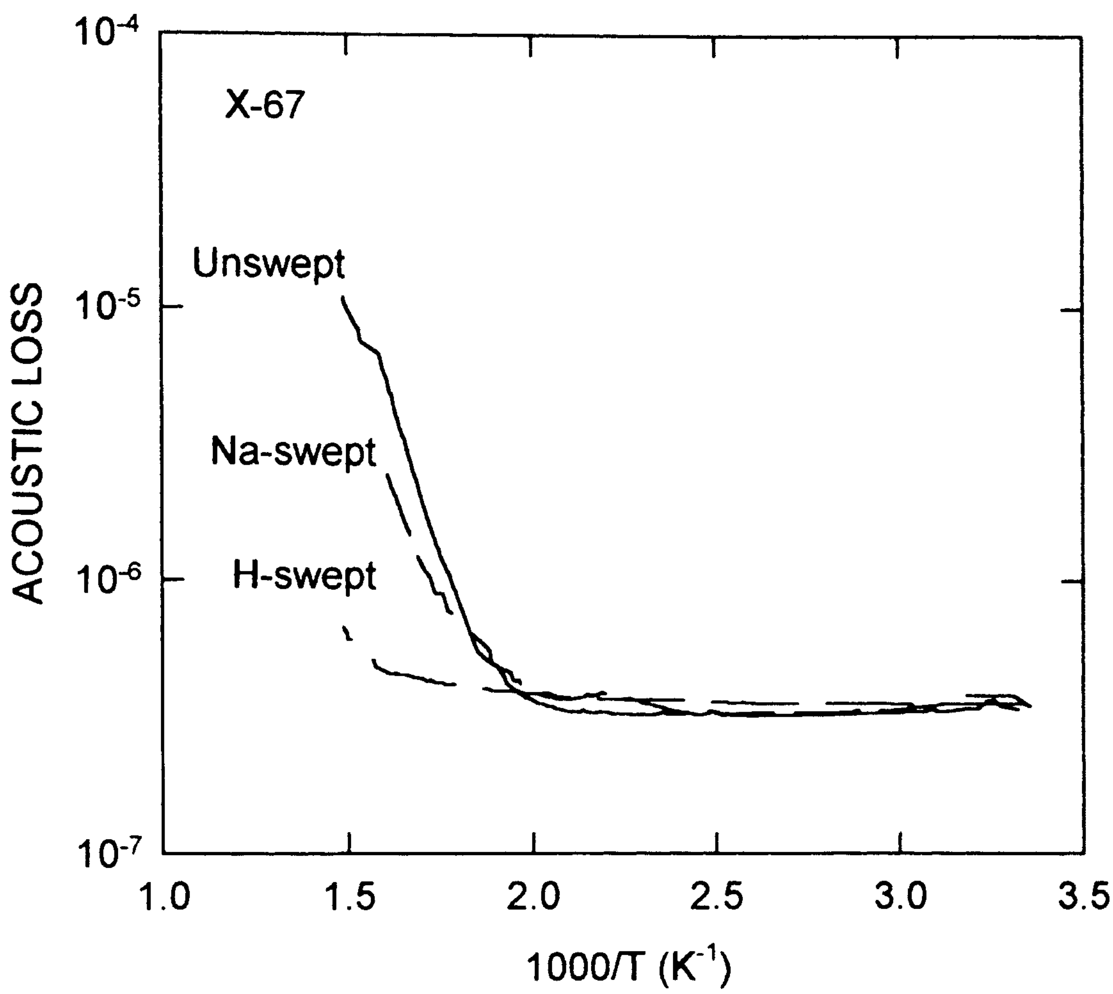

Figure 8. Acoustic Loss versus 1000/T(K) for X-67 unswept, H-swept and Na-swept resonators.

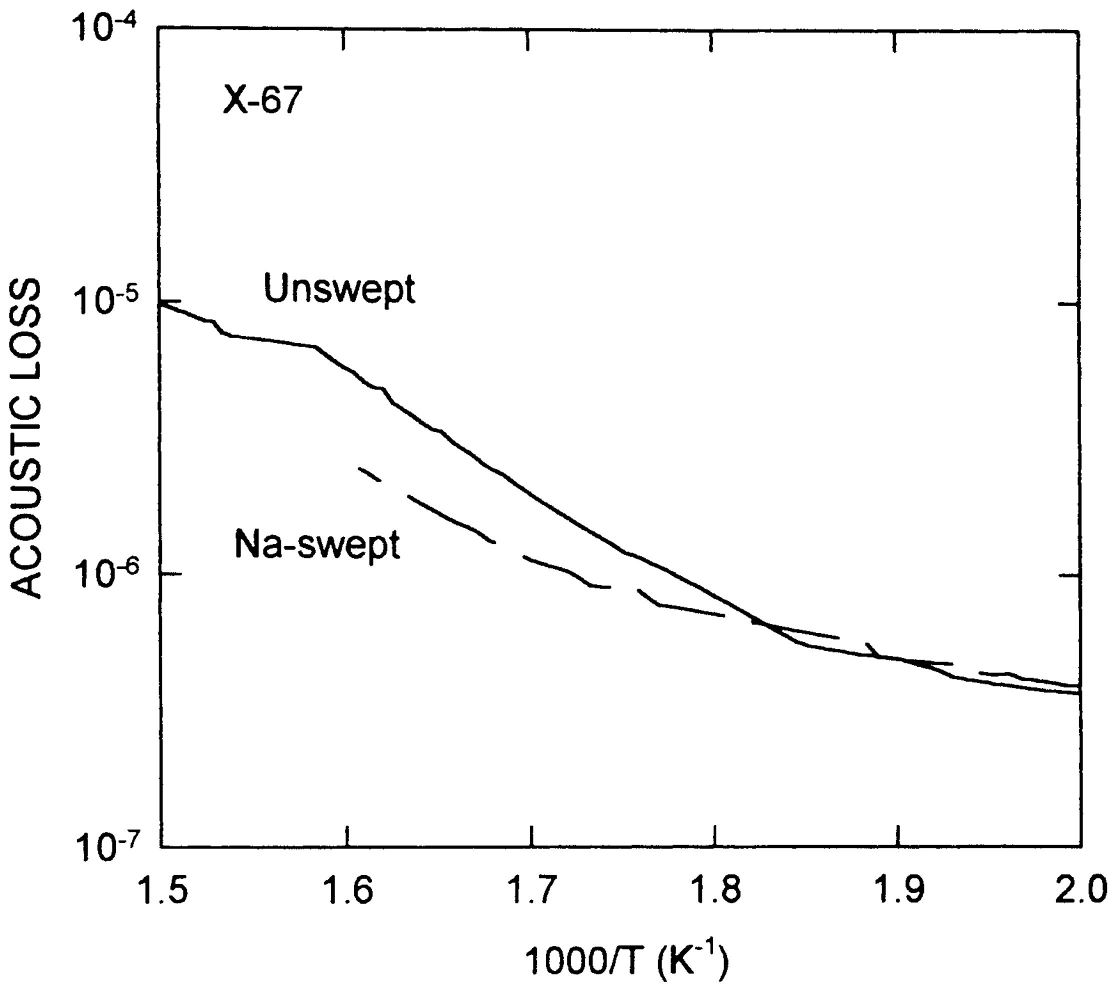

Figure 9. Acoustic Loss versus 1000/T(K) for X-67 unswept and Na-swept resonators.

TABLE III

ACTIVATION ENERGIES

SAMPLE	UNSWEPT (Li)	Na-SWEPT
PQ-E	0.78eV	0.88eV
X-67	0.72eV	0.88eV
FRASER	0.72eV	0.77eV

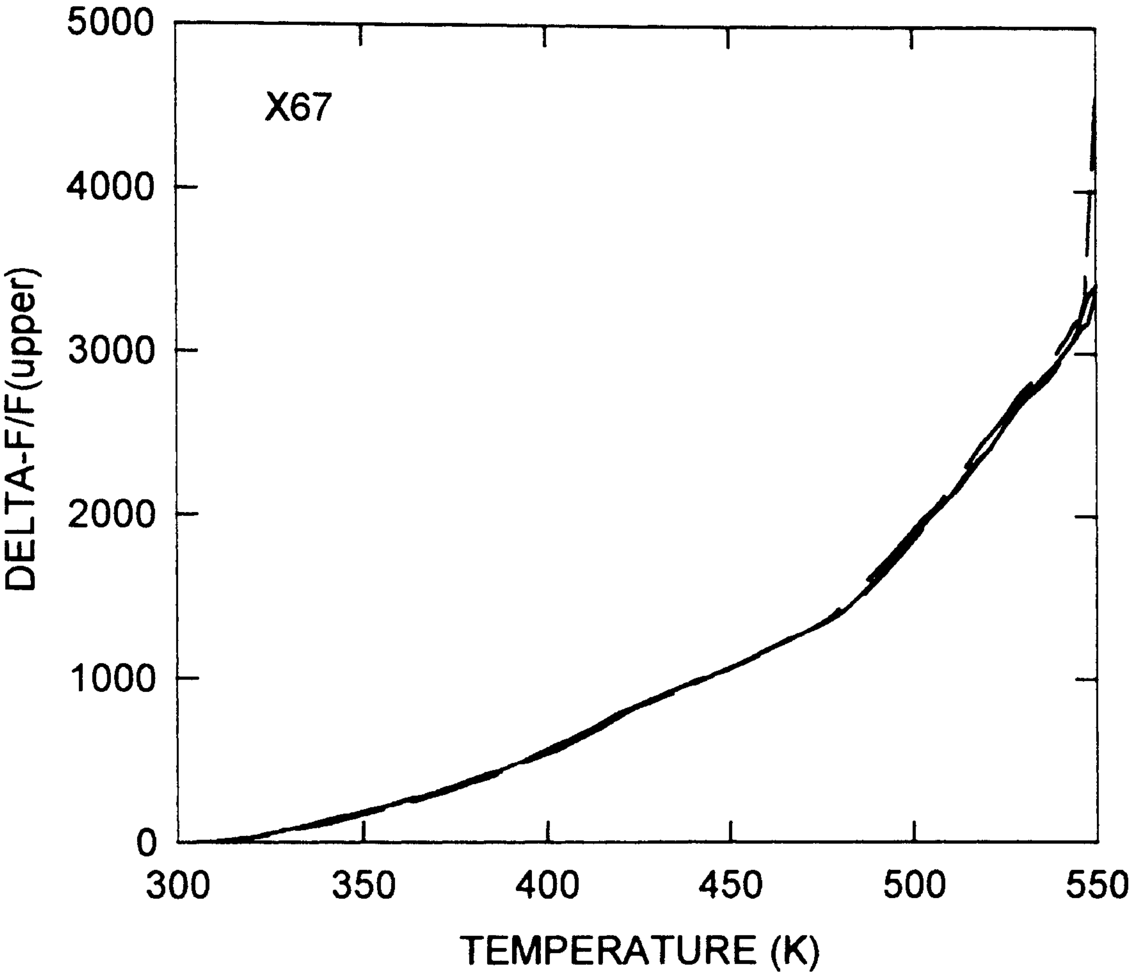

Figure 10. Friequency versus Temperature for X-67 unswept, H-swept and Na-swept resonators.

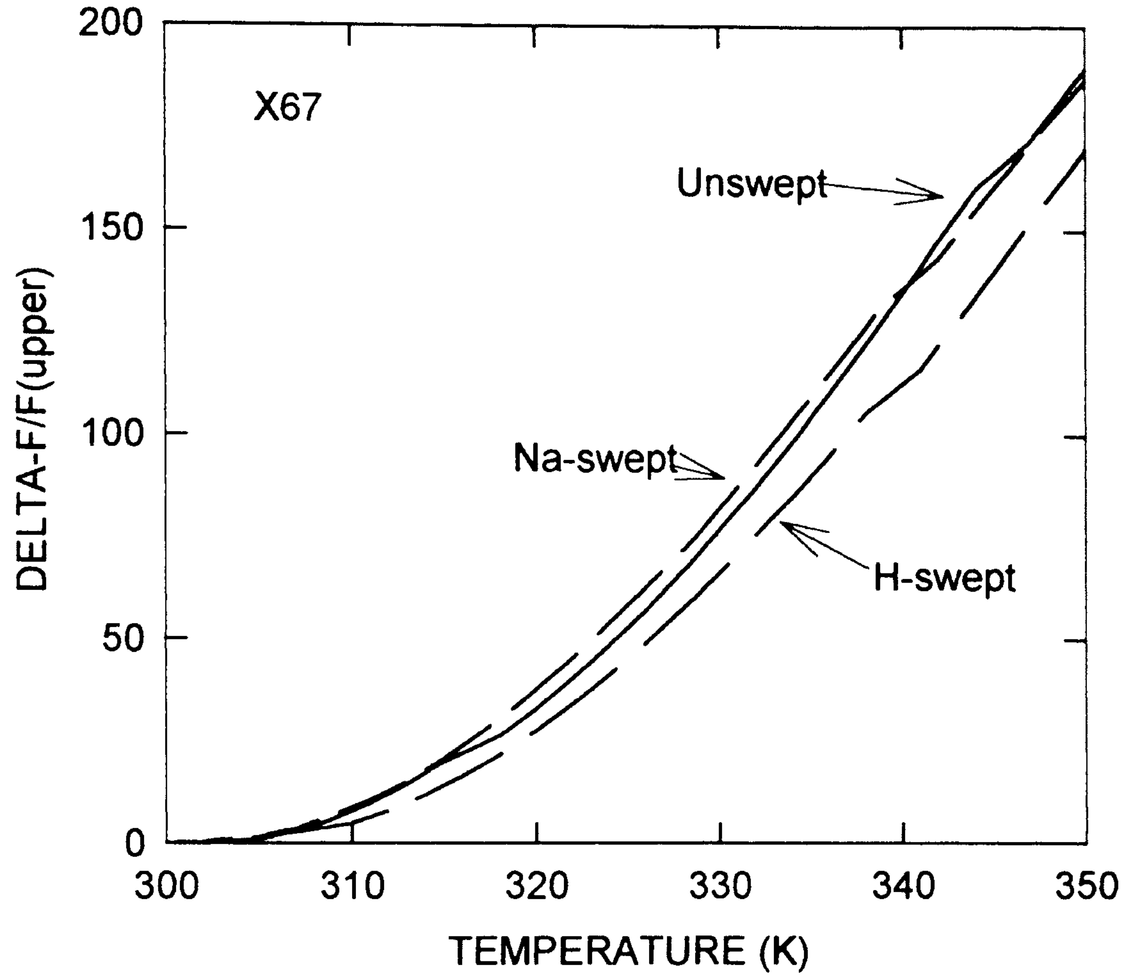

Figure 11. Frequency versus Temperature for X-67 resonators for temperature range 300K to 350K.

CHAPTER V

CONCLUSION

The acoustic loss of unswept (Li), Na-swept and H- or D2- swept 5MHz 5th overtone AT-cut quartz resonator blanks was measured over the 300K to 700K temperature range. The unswept and Na-swept resonators showed a thermally activated acoustic loss at higher temperatures. Activation energies of 0.72 to 0.77 eV were found for the unswept samples. An activation energy of 0.88eV was found for both the Na-swept crystals. The acoustic loss of the H-swept and D_2-swept samples remained small over the entire temperature range.

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