The Anelasticity of Natural and Synthetic Quartz at Low Temperatures*

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Certain imperfections in alpha-quartz are found to introduce anelastic absorption at low temperatures in crystal resonators. For a shear wave of 5 mc, absorption peaks are observed at approximately 20° and 50°K in unirradiated samples. X-irradiation effects a lowering of the amplitude of the 50°K absorption, while a new absorption is introduced at 100°K.

The results of acoustic absorption measurements on a number of selected samples of synthetic quartz resonators suggest that, whereas the 50°K absorption is attributable to excess oxygen, the 100°K defect involves aluminum which is present substitutionally in the crystal structure.

X-irradiation-induced lowering of the resonant frequency of crystal resonators is clearly the result of a lowering of the elastic modulus associated with the 100°K anelastic absorption.

I. INTRODUCTION

Measurements of the internal friction in crystals have revealed mechanical relaxation processes which can be attributed to crystal defects. Bordoni[1] first observed a mechanical relaxation of this kind in a number of metals at low temperatures. The amplitude of the absorption was found to be enhanced by cold work and reduced by annealing. Subsequent measurements of the loss in lead by Bömmel[2] and in copper by Niblett and Wilks[3] served to confirm Bordoni's findings and further to associate the relaxation with the movement of dislocations under the action of an applied shearing stress.

Recently, a study of the low-temperature anelasticity in quartz by Bömmel, Mason and Warner[4] disclosed two structural relaxation proc-

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esses. For a frequency of vibration of 5 mc, one relaxation absorption appears at about 20°K and probably derives from dislocations, while the other, occurring at 50°K, is apparently due to a deformation of the lattice network.

The purpose of the present investigation is two-fold: (a) to probe the nature of the deformation defects in quartz through a study of the dependence of the 50°K absorption on selected natural and synthetic samples, and (b) to determine the relationship between the behavior of quartz crystal resonators at room temperature and the anelastic effects arising from crystal imperfections. In these studies, samples of quartz are subjected to x-irradiation and electrolytic purification. A brief paper describing the dependence of the 50°K absorption in synthetic quartz upon seed plate orientation and the effect of x-irradiation on the amplitude of the 50°K absorption has been published.[5]

II. EXPERIMENTAL PROCEDURE

The experimental technique adopted in this study involves the fabrication of high-Q rotated Y-cut resonators[6] from the quartz to be examined. The Q^{-1} of the crystal unit at resonance is calculated from its equivalent electrical characteristics as determined in a transmission circuit test set. A block diagram of the essential components of the measuring circuit is shown in Fig. 1. The resonant frequency of the crystal unit at minimum impedance* is the frequency of the variable oscillator (frequency synthesizer) adjusted to obtain a peak reading at the detector. For this condition, the equivalent resistance of the crystal unit, R_1, is the value of a resistor which, when substituted for the crystal, gives the same detector reading.

Since the Q for natural quartz thickness shear vibrators can be made as high as several million, it is assumed that Q^{-1} for such resonators is a measure of the internal friction of the quartz itself, i.e., it is independent of the mounting structure. Variations in the frequency-determining

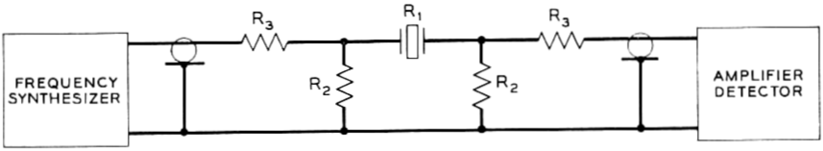

Fig. 1 — Transmission circuit test set used to measure resonator characteristics of quartz.

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* Except for large values of Q^{-1}, the frequency at minimum impedance may be taken to equal the frequency at series resonance.

elastic modulus of quartz due to anelastic processes are reflected as variations in the resonant frequency of vibration.

The crystal and resistance network shown in Fig. 1 are located in a holder assembly (see Fig. 2) which is suspended in a dewar containing liquid helium. The glass envelope surrounding the mounted crystal resonator is filled with helium gas to a pressure of 1 mm Hg at room temperature before it is sealed off. The amount of damping due to this background gas is negligibly small, and the gas provides a thermal lock between the crystal and a copper oven in which the resonator is placed. To maintain the crystal at the helium-bath temperature, a small amount of helium gas is transferred into the sample holder. For operation above 4.2°K, the pressure within the sample holder is reduced to less than 5×10^{-5} mm Hg and a current is passed through the oven winding. For each incremental increase in heater current, the oven will equilibrate at some higher temperature. The equivalent crystal resistance and frequency at resonance is recorded for increasing temperature.

The thermometry below 4.2°K employs the saturated vapor pressure of helium. Between 4.2°K and 30°K a carbon-composition type resistor is used and, above 30°K, a copper-constantan thermocouple. The frequency of the crystal unit is used to indicate whether the quartz sample is at temperature equilibrium with its surroundings. This technique is quite sensitive, because of the large temperature coefficient of frequency above 15°K for the type of crystals investigated.

III. SOME THEORETICAL CONSIDERATIONS

In a non-ideal solid, stress and strain are not uniquely related. This can be demonstrated by observing that, although the stress required to cause an instantaneous strain in a solid is a linear function of the resulting strain, the continued application of stress will cause an additional reversible component of strain to develop. This gradual relaxation of strain for a constant stress can be characterized by a relaxation time. Alternately, if the solid is subjected to a constant strain, the initial stress becomes relaxed to a certain degree. Hence, the mathematical expression for the mechanical behavior of a solid must include the rates of change of stress and strain.

When a solid is made to vibrate at some frequency, f, it can be shown[7] that a relaxation process will cause the stress to be out of phase with the strain by an angle δ and that

$$\tan \delta = \Delta \frac{\omega\tau}{1 + (\omega\tau)^2}, \tag{1}$$

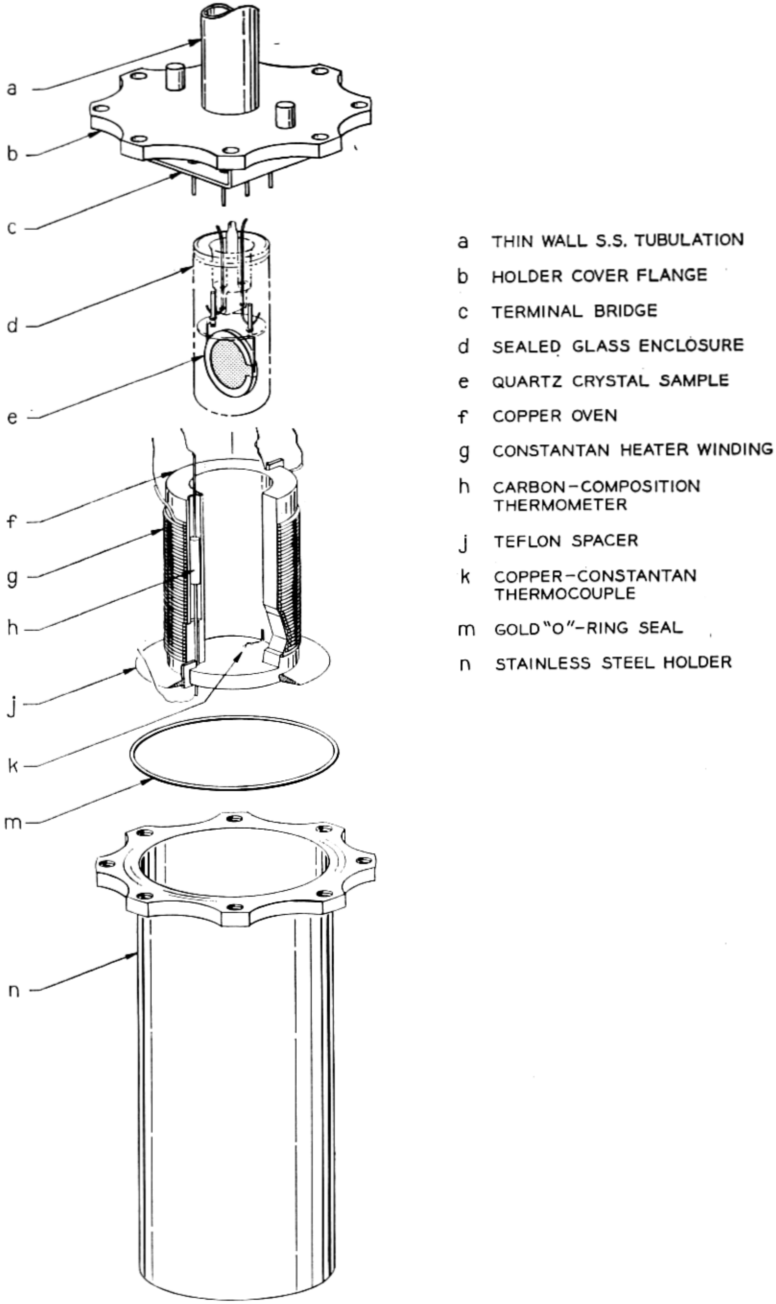

Fig. 2 — Crystal holder assembly used for measurement of internal friction of quartz at low temperatures.

where $\omega = 2\pi f$, τ is the relaxation time for the relaxation process, and Δ, the relaxation strength, is a measure of the relative change due to complete relaxation in the frequency-determining elastic modulus. Tan δ is a measure of the absorption of energy and is equivalent to Q^{-1}. A plot of tan δ vs. ω describes a curve with an absorption maximum equal to $\Delta/2$ when $\omega = 1/\tau$, or

$$Q_{\max}^{-1} = \Delta/2. \tag{2}$$

On either side of the peak, tan δ becomes vanishingly small for $\omega \ll \tau$ and $\omega \gg \tau$. This means that, if the frequency of vibration is either much greater or much less than the jump frequency for the relaxation process given by $1/\tau$, the strain is essentially in phase with the stress. However, when the angular frequency of vibration is equal to $1/\tau$, the phase angle is a maximum, resulting in an absorption peak.

The relationship between relaxation time and temperature is provided by the distribution of energy levels. Most often this distribution is an Arrhenius type such that

$$\tau = \tau_0 e^{E/RT}, \tag{3}$$

where τ_0 is a constant, E is the activation energy for the relaxation and R is the gas constant. The absorption curve plotted as a function of temperature for a simple relaxation process, i.e., involving a single activation energy, is given in Fig. 3.

The effect which structural relaxation has upon the frequency-deter-

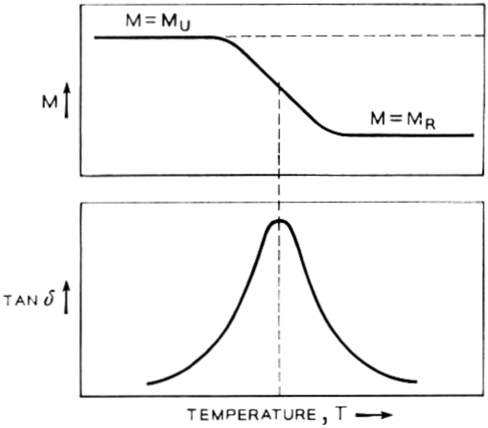

Fig. 3 — Variation of internal friction and real modulus with temperature for simple relaxation process.

mining elastic modulus M is given by

$$M = M_U - \frac{M_U - M_R}{1 + (\omega\tau)^2}, \tag{4}$$

where $M = M_U$ when $\omega \gg \tau$, and $M = M_R$ when $\omega \ll \tau$. Thus, when the frequency of vibration is much greater than the relaxation time, there occurs no delayed elastic response in the medium. The modulus for this condition is therefore unrelaxed and denoted by M_U. However, when $\omega \ll \tau$ there is sufficient time between reversals in the direction of the stress for the delayed elastic response to be effective. The result of complete relaxation causes the modulus to be lowered to M_R.

The change in the modulus with temperature is also given in Fig. 3. It will be observed that the inflection temperature in the curve of M vs. T is the same as that corresponding with tan $\delta_{\max}$. The mechanical behavior of a solid at temperatures below a given relaxation absorption peak is, therefore, unaltered by anelastic effects attending the relaxation process.

The terms in (3) can be rearranged in the following manner:

$$\frac{M_U - M}{M_R} = \frac{M_U - M_R}{M_R} \Big/ 1 + (\omega\tau)^2. \tag{5}$$

The expression $(M_U - M_R)/M_R$, giving the relative change in the modulus due to complete relaxation, has been previously denoted as the relaxation strength Δ.

According to the above analysis, if a relaxation process is induced by some means in a solid, then the elastic modulus at temperatures where ω is greater than τ will be lowered. On the other hand, if a defect which introduces a structural relaxation is eliminated, then the elastic modulus for the solid will be increased at temperatures where ω is greater than τ.

IV. ANELASTIC ABSORPTION IN QUARTZ

There are at least three basic types of crystal defects which can contribute to the anelasticity of quartz:

(a) impurity ions, which can break away from attracting centers and diffuse from one equivalent interstitial site to another within the crystal;

(b) a deformation of the normal crystal network, allowing for the oscillation of segments of the crystal lattice between positions of equal potential energy and

(c) rows of atoms comprising dislocation lines, which move in the crystal glide planes.

The indicated motions for the above defects are thermally activated and, therefore, at a given temperature the structural elements involved surmount an energy barrier, whose height is given by E in (3), with a jump frequency, $1/\tau$, characteristic of the process. If, by subjecting quartz to a stress, there results an energy bias of the potential wells between which the defect element moves, then the defect population density in the position of lowest energy will preferentially increase. Thus, there occurs a delayed elastic response.

We will limit this report to an examination of the anelasticity of quartz arising from the deformation-type defects.

AT-cut* overtone crystal units have been fabricated using electrical grade Brazilian quartz and various samples of synthetic quartz. In view of the dependence of a number of the physical properties of synthetic quartz upon the direction of crystal growth, the synthetic crystal units will be classified according to the particular seed surface on which the quartz is grown. Thus, resonators obtained from growth on a z-minor rhombohedron are termed z-face or z-minor samples. Samples taken from growth on a basal cut or from the Z-growth region on a Y-bar seed crystal are denoted as Z-growth sample resonators.

In Fig. 4 the internal friction at 5 mc in natural and synthetic quartz at low temperatures is shown by the curves of Q^{-1} vs. T for representative crystal units. In these samples two absorption peaks are immediately evident, one in the neighborhood of 20°K and the other at 50°K. In the case of natural quartz these absorptions have been attributed to structural relaxations. The relaxation frequencies for the two mechanisms are reported[4] to be

$$\tau_{20^\circ\mathrm{K}} = 7.7 \times 10^{-10}\, e^{155/RT} \tag{6}$$

and

$$\tau_{50^\circ\mathrm{K}} = 10^{-13}\, e^{1300/RT}. \tag{7}$$

An examination of the magnitudes of τ_0 and E for the two absorptions suggests that the 20°K relaxation mechanism involves the motion of dislocations and that the 50°K relaxation process is probably due to a deformation of the crystal lattice.

As may be observed in Fig. 4, the synthetic samples representative of both z-face and Z-growth material exhibit an extremely large absorption at 50°K.[5] (Henceforth, the same two samples of synthetic quartz will be used for all reported resonator measurements unless specified otherwise.) In comparison with natural quartz, it is common to find the 50°K absorption peak in z-face and Z-growth quartz almost three and two

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* A Y-cut plate rotated about the X-axis by an angle $\theta = +35^\circ\ 15'$.

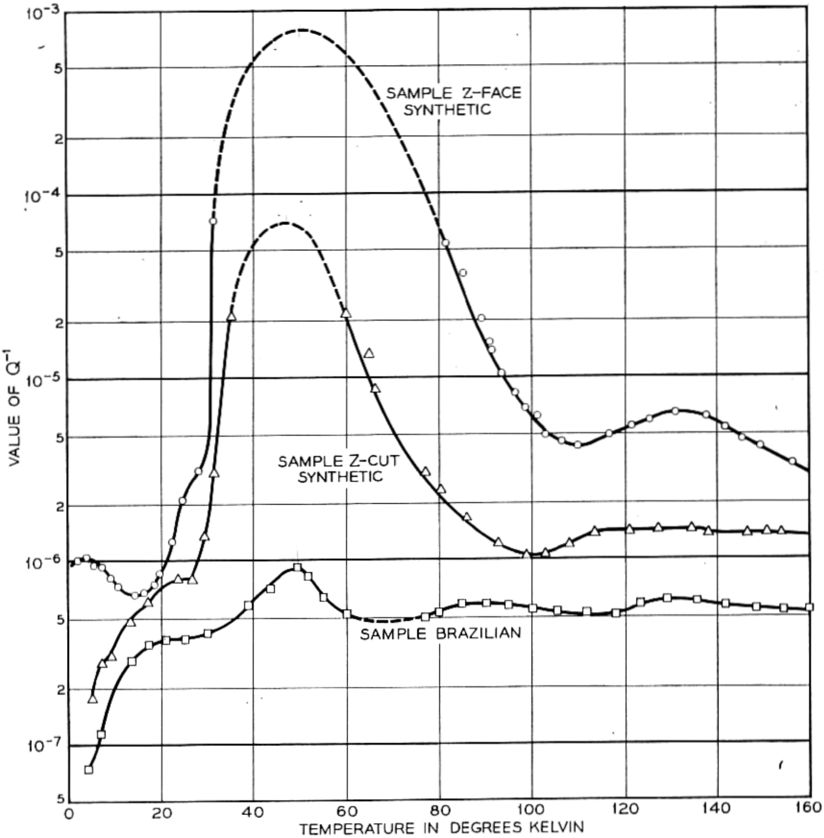

Fig. 4 — Internal friction at 5 mc for thickness shear vibration (AT-cut) in natural quartz and two representative samples of z-face and Z-growth synthetic quartz at low temperatures.

decades higher respectively. It is apparent that the concentration of crystal defects responsible for the 50°K peak is (a) commonly greater in synthetic quartz and (b) dependent upon the crystallographic orientation of the seed plate. It must be noted that other growth conditions besides seed orientation can affect the 50°K defect concentration.

Assuming that the 50°K relaxation process derives from some impurity or combination of impurities, a spectrochemical analysis of the z-face and Z-growth samples should reveal large differences in the impurity concentration between the two materials. In Table I may be seen the emission analysis* of two quartz samples taken from the same mother

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* Analysis made by the Spectrographic Services and Research at the Naval Gun Factory Laboratory, Washington, D. C.

TABLE I — CONCENTRATION OF IMPURITIES IN PPM

Impurities	z-face	Z-growth
Al	30	10
Fe	10	10
Mg	0.3	0.3
Na	3	3
Cu	0.1	<0.1
Li	1	0.3
Ni	10	<10

crystals from which the z-face and Z-growth specimens (Fig. 4) were obtained.

The obvious similarity of the synthetic samples regarding the concentration of impurities, together with their vastly different 50°K absorption presents a rather strong argument against associating the 50°K defect with impurities in quartz. The spectrographic analysis, of course, does not rule out the possibility that the 50°K defect might involve an excess or deficiency of oxygen. A defect structure involving the former will be considered in Section V.

Significant differences between natural and some synthetic quartz crystals have also been noted in the AT-cut frequency-temperature characteristics.[8,9,10,11] The variation of frequency with temperature between $-60°$ and 100°C for a series of crystal units fabricated from the Z-growth quartz is shown in Fig. 5. From the AT-cut family of curves two identifiable characteristics may be determined by graphical analysis. One is the angle of rotation, θ_0, for which the frequency excursion over the temperature range is a minimum and the other is the inflection temperature, T_i, of the f-T curve for a crystal cut at $\theta = \theta_0$. For natural and Z-growth quartz θ_0 and T_i are nearly the same and given by $35°20' \pm 1'$ and $30°\text{C} \pm 2°\text{C}$ respectively. Departures from the above characteristics occur in z-face quartz, where θ_0 is found to be some four minutes larger and T_i is shifted to 40°C. In all samples of quartz examined there is a unique concurrence of shifts in the frequency-temperature characteristics with amplitude of the 50°K relaxation absorption.

The resonant frequency of a rotated Y-cut crystal is given by:

$$f = \frac{1}{2t}\sqrt{\frac{c_{66}'}{\rho}}. \tag{8}$$

In this expression, t is the resonator thickness, ρ is the density of quartz and c_{66}', the effective elastic constant, is

$$c_{66}' = c_{66}\cos^2\theta + c_{44}\sin^2\theta - c_{14}\sin 2\theta, \tag{9}$$

where c_{ij} are the elastic constants.

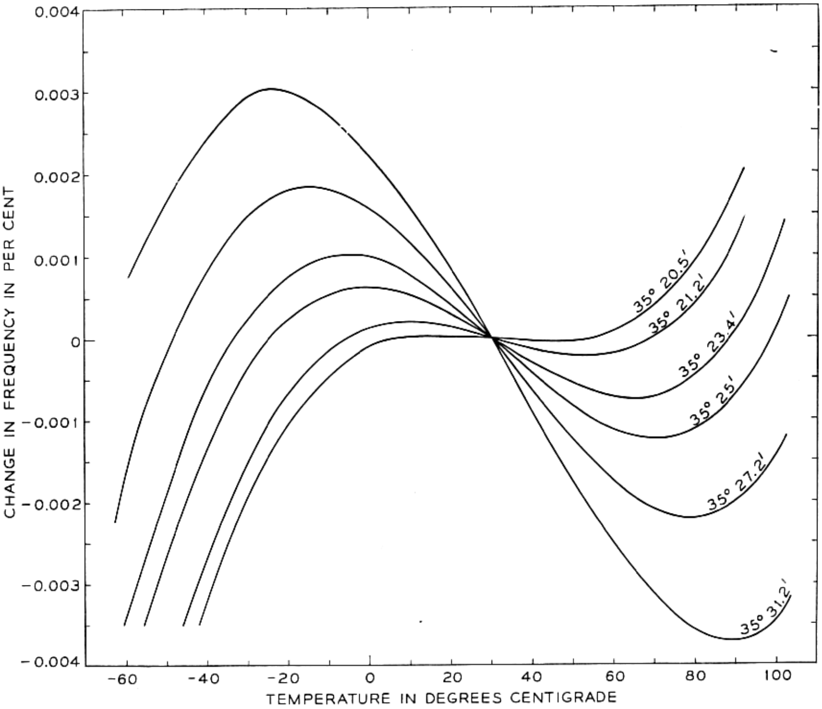

Fig. 5 — Frequency vs. temperature curves between −60° and 100°C for a group of AT-cut resonators fabricated from the Z-growth synthetic crystal.

From (8) the change in frequency attending a small variation in c_{66}' is found to be

$$df = \frac{f}{2} \frac{dc_{66}'}{c_{66}'} . \tag{10}$$

It was pointed out in the previous section that a relaxation process will cause a lowering of the elastic modulus, for a given frequency of vibration, at temperatures above the relaxation absorption. If dc_{66}' in (10) is taken as the change in the elastic modulus due to complete relaxation, then

$$\frac{\Delta f}{f} = \frac{\Delta}{2}, \tag{11}$$

or

$$\frac{df}{f} = Q_{\max}^{-1} . \tag{12}$$

Thus, the relative change in f attributable to the complete relaxation of a simple relaxation process, is just equal to the maximum value of the associated absorption.

Neglecting the normal variations of frequency with temperature, the effect described above should alone account for a difference of frequency of approximately 1,000 ppm between otherwise identical natural and z-face quartz AT-cut resonators above 50°K. It is suggested that the observed variations in the f-T characteristics between natural and synthetic AT-cut resonators arise from a change of one or more of the elastic constants comprising c_{66}', attending the relaxation of the 50°K defect.

The dielectric loss in quartz at low temperatures has been reported by Volger, et al.[12] The loss in natural quartz and samples of z-face and Z-growth quartz at 32 kc is described in Fig. 6. A number of the dielectric loss peaks in quartz have been associated[12] with the relaxation of specific crystal defects. The activation energy and relaxation time τ_0 for the dielectric loss which appears at 38°K in Fig. 6 are reported to be 1,270 cal/gm mole and 2×10^{-13} sec. These values compare closely with those for the 50°K mechanical relaxation. Furthermore, the relative possition of the dielectric tan δ values for the z-face and Z-growth specimens is in general agreement with the mechanical absorption at 50°K for similar samples. It appears definite, therefore, that the 50°K defect gives rise to an orientational electric polarization.

Volger, et al. have suggested that the 38°K dielectric absorption is caused by what is referred to as a B-center type defect, namely $^{2\text{Al}}\text{B}$. A two-dimensional schematic representation of the $^{2\text{Al}}\text{B}$ defect, along with others which will be of interest in Section V, is shown in Fig. 7.* The association of the $^{2\text{Al}}\text{B}$ defect with the 38°K dielectric absorption peak in synthetic quartz is based primarily on an observed higher concentration of Al in the synthetic material. In view of the emission analysis given in Table I and the measured mechanical absorption in comparable synthetic samples, the above interpretation is subject to some doubt.

V. EFFECT OF X-IRRADIATION

A number of samples of natural and synthetic AT-cut crystal units have been irradiated with 50-kv X-rays from a tungsten target tube op-

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* In a recent communication Dr. Stevels now contends that $^{\text{Al}}_{\text{H}}\text{P}$ defects are responsible for the 38°K dielectric absorption rather than $^{2\text{Al}}\text{B}$ defects. The $^{\text{Al}}_{\text{H}}\text{P}$ defect is similar to $^{\text{Al}}_{\text{Na}}\text{P}$ shown in Fig. 7(c), except that Na^+ is replaced by H^+.

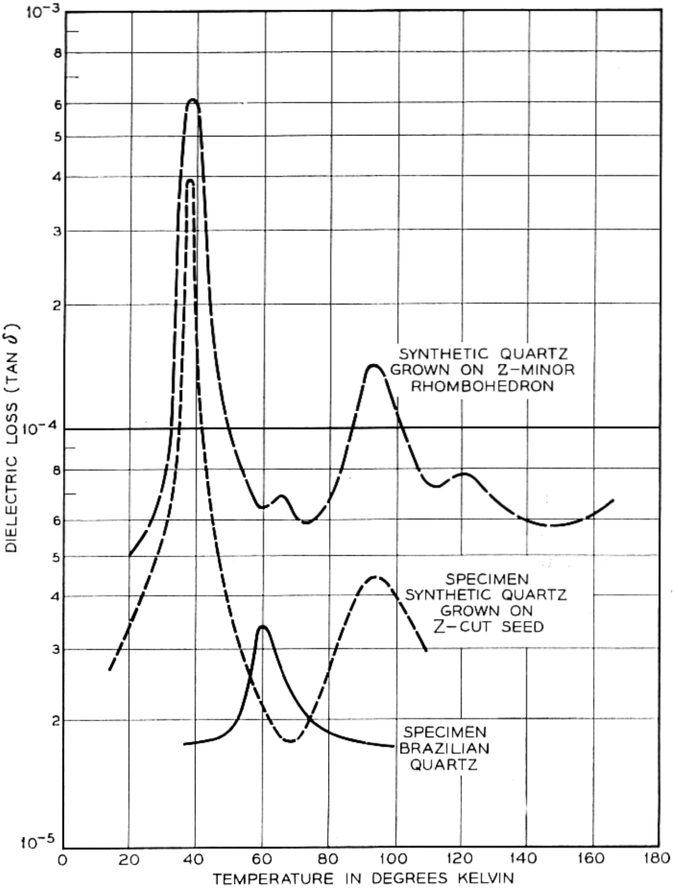
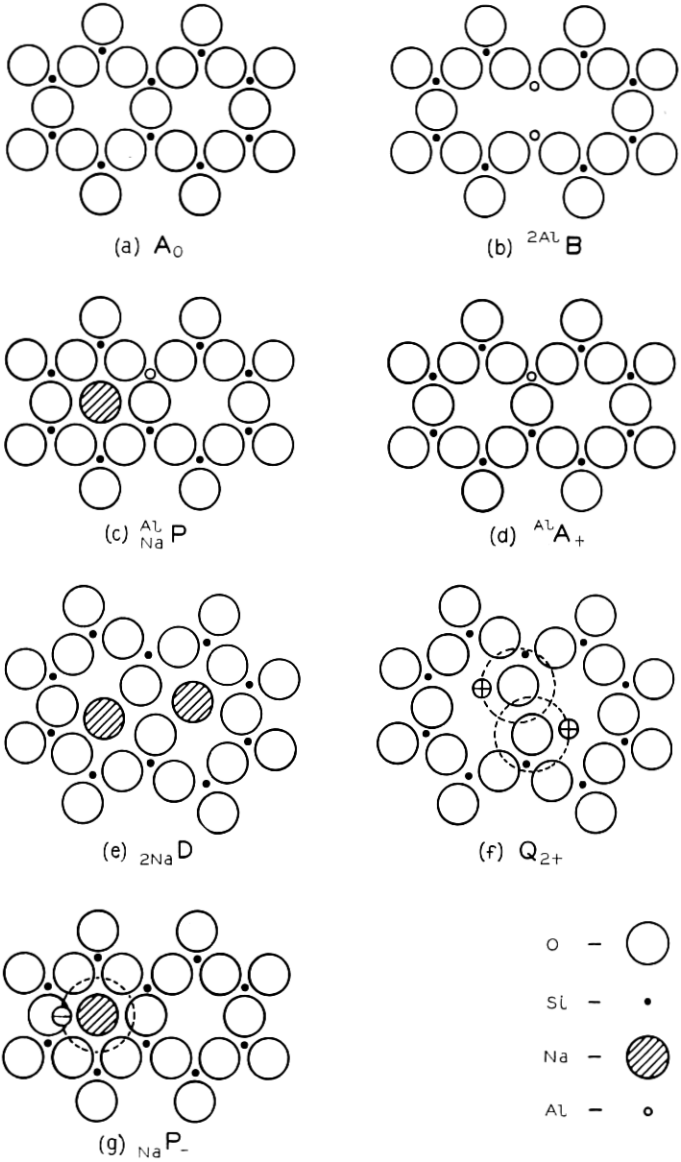


Fig. 6 — Low-temperature dielectric absorption at 32 kc in natural quartz and two samples of synthetic quartz.

erating at 48 ma. The exposure in all cases amounts to approximately 10^6 r. Two effects of considerable interest are observed: (a) in all samples, the 50°K defect is virtually eliminated and (b) an absorption at 100°K is induced in samples which color with irradiation. The effect listed under (a) will be considered first.

An example of the profound change in the concentration of 50°K defect with x-irradiation is shown in Fig. 8. Here the curves of Q^{-1} and $\Delta f/f$ before and after x-irradiation are given for the Z-growth sample (Δf is equal to $f - f_T$, where f is the frequency of the crystal unit at room temperature and f_T is its frequency at temperature T). Before irradiation,



(a) A_0

(b) ^{2Al}B

(c) $^{Al}_{Na}P$

(d) $^{Al}A_+$

(e) $_{2Na}D$

(f) Q_{2+}

(g) $_{Na}P_-$

Fig. 7 — Two-dimensional schematic representation of some defects believed to occur in alpha-quartz.

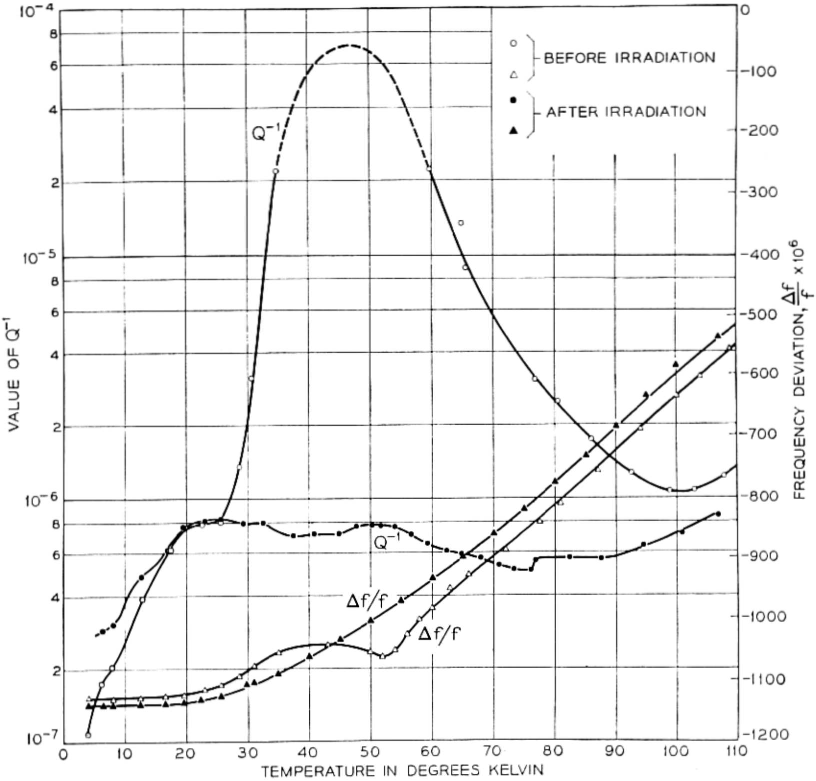


Fig. 8 — Internal friction and frequency deviation at low temperatures for 5-mc thickness shear vibration in Z-growth synthetic quartz before and after x-irradiation.

the change in frequency of the crystal above approximately 30°K is determined not only by the temperature dependence of the parameters at the right in (8) but also by:

$$\frac{df}{f} = \frac{Q_{\max}^{-1}}{1 + (\omega\tau)^2}. \tag{13}$$

Here, $Q_{\max}^{-1}$ and τ relate to the 50°K relaxation process. Since the 50°K defects are all but eliminated with x-irradiation, the $\Delta f/f$ vs. T curve after irradiation in Fig. 8 describes the change of frequency with temperature, exclusive of any change in c_{66}' due to stress relaxation. Therefore, a difference curve of $\Delta f/f$, before and after irradiation, should resemble the curve of M vs. T shown in Fig. 4. Such a curve is plotted in Fig. 9 for the Z-growth specimen, with relative frequency change converted to read per cent change in c_{66}'. The dotted curve is derived from (5), with τ given by (6) and Δ, the change in c_{66}' due to complete relaxation, taken to be the difference between points A and B in Fig. 9. (The value of Δ, computed in this manner, can be used to approximate $Q_{\max}^{-1}$, provided the relaxation process is one involving at most a very narrow distribution of activation energies.) A correction of the frequency measurements to read in terms of frequency at resonance rather than at minimum impedance would cause the calculated change in c_{66}' to coincide more nearly with the theoretical curve. The difference curve below 35°K, contrary to expectations, does not fall on the zero reference line. This can be interpreted to signify that the 50°K defect not only contributes to the crystal's anelasticity but also alters bonds in the crystal structure sufficiently to cause a change in the unrelaxed c_{66}' and in dc_{66}'/dt.

If, as suggested in Section IV, shifts in the f-T characteristics of AT-cut resonators can be traced to the 50°K defect, then it must follow that x-irradiation will cause synthetic quartz to acquire the f-T behavior of natural quartz. In Fig. 10 the f-T curves for the z-face specimen before and after irradiation are shown between −60° and 100°C. It is observed that the curve after irradiation assumes nearly the same form as that for a natural specimen having the same angle θ.

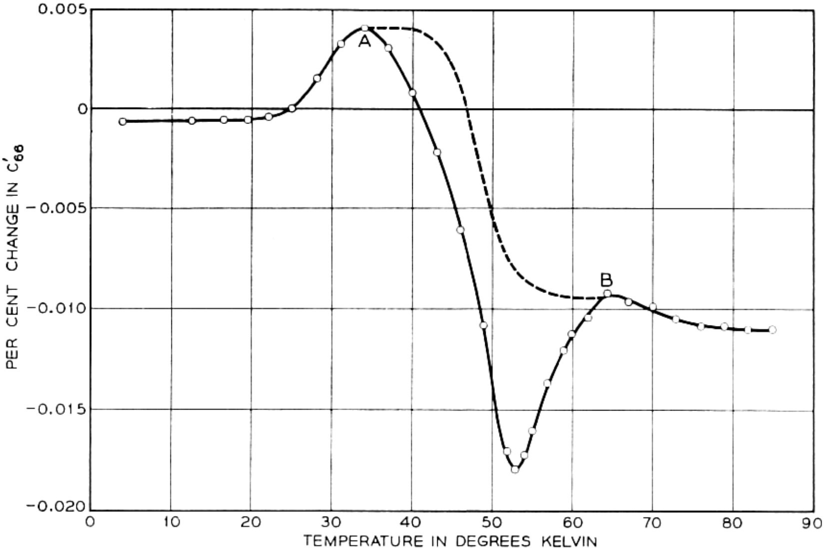


Fig. 9 — Variation of c_{66}' with temperature for 5-mc thickness shear vibration in unirradiated Z-growth resonator relative to c_{66}' after x-irradiation; dotted line describes the theoretical curve for a simple relaxation process.

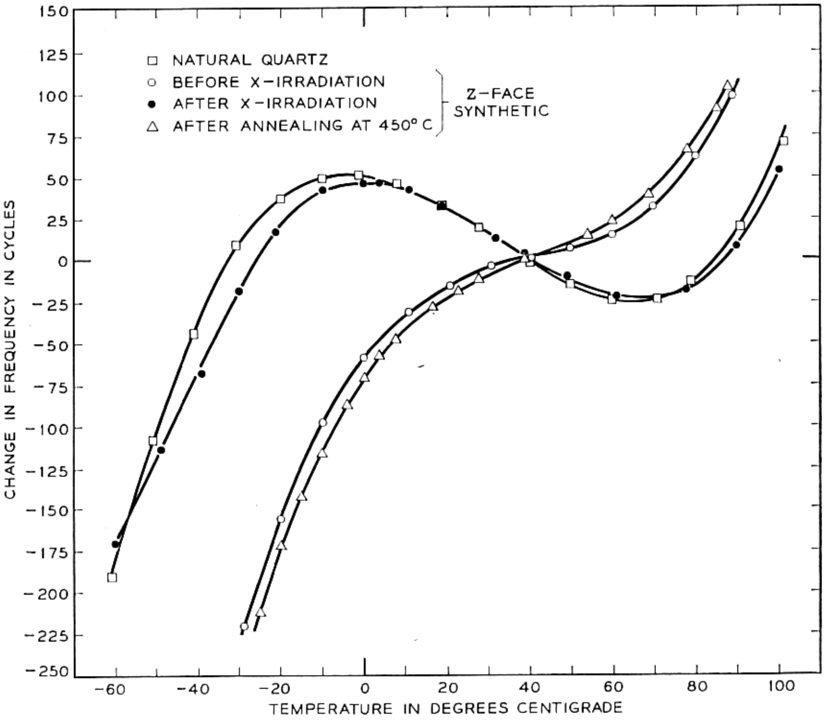


Fig. 10 — Frequency vs. temperature curves between −60° and 100°C for 5-mc AT-cut z-face synthetic resonator before and after x-irradiation and after annealing.

Annealing of x-irradiated synthetic resonators at 500°C for several minutes causes the return of the 50°K absorption to the same amplitude it had prior to irradiation. Therefore, annealing should also cause the *f-T* characteristics of the x-irradiated z-face sample to return to the form it had before irradiation. By referring to Fig. 8, this can be observed to occur. Chi[13] has examined the effects of x-irradiation on the AT-cut *f-T* characteristics of various samples of synthetic quartz.

The effective elimination by X-rays of the anelasticity associated with the 50°K defect requires that the underlying defect be readily altered by ionizing irradiation. The $^{2\text{Al}}$B defect, however, represents a particularly stable configuration. This consideration, together with a lack of correlation between Al content and the 50°K absorption, does not favor designating the B-center as the responsible defect. A discriminative study of defect centers likely to occur in quartz and which are better able to account for phenomena associated with the 50°K absorption, suggests considering the Q_{2+} defect [Fig. 7(f)].

A Q-center is simply a site at which an excess oxygen atom enters the lattice structure and forms a nonbridging oxygen defect. In the Q_{2+} defect, only one orbital electron from each of the nonbridging oxygen atoms is paired with an electron from the nearest silicon atom. If an ionizing radiation is sufficiently energetic to remove a paired electron from one of the nonbridging oxygen atoms, then the oxygen atom is effectively removed from the center. The remaining nonbridging oxygen atom may then cross-link with the silicon atom formerly associated with the freed oxygen and thereby reduce the center to the normal structure represented by A_0 in Fig. 7(a). Thus, by a process not unlike x-irradiation, induced cross-linking occuring between polymer chains, Q-centers in quartz may be transformed to A_0-centers.

The inclusion of an extra oxygen atom in the crystal lattice will cause a corporate distortion of bond angles in the vicinity of the defect, as suggested by the disposition of the atoms about the center in Fig. 7(f). It is certain that other structure-sensitive properties of quartz will therefore be influenced by the presence of Q-centers. Berman[14] has shown that the low-temperature thermal conductivity of quartz is quite sensitive to the degree of crystal perfection. If it is assumed that, in the region immediately surrounding Q-centers, the crystal lattice is somewhat similar to the close-range misorientation within the silica tetrahedra of fused quartz, then it follows that the low-temperature thermal conductivity of quartz will be decreased by an amount dependent upon the Q-center concentration. Measurements of the thermal conductivity of a sample of natural and Z-growth quartz by Berman* are given in Fig. 11. It is observed that the thermal conductivity of a Z-growth specimen is very little like that of a single crystal since the conductivity peak is depressed by more than a decade and shifted toward higher temperatures. This alteration of the conductivity peak is characteristic of an increase in thermal resistance caused by phonon-defect interaction. Indeed, the conductivity of Z-growth quartz approaches that of neutron irradiated quartz.

In line with the suggestion that Q-centers contribute to the low-temperature thermal resistance in quartz, it is of considerable interest to examine the effect of X-rays on the thermal conductivity of a synthetic sample. With the exception of Q-centers, it is unlikely that the defects in quartz could be modified by X-rays so as to effect an increase in ther-

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* R. Berman has kindly communicated the results of his measurements on synthetic specimens provided by the author.

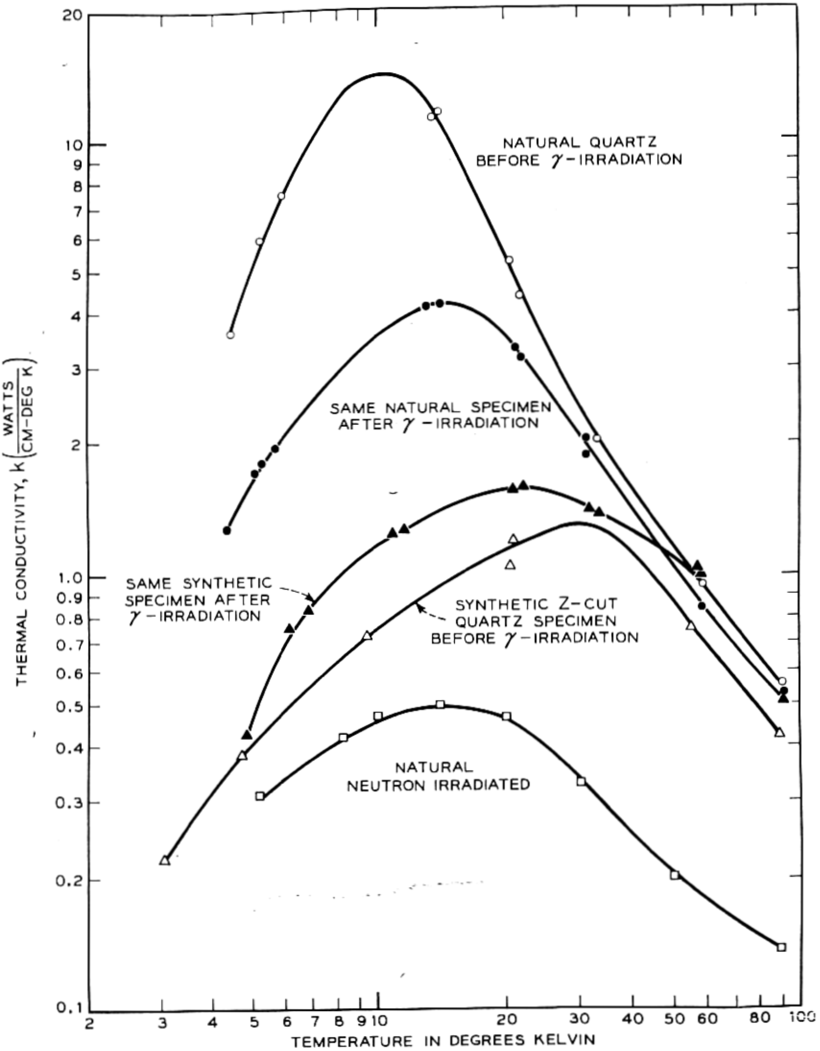

Fig. 11 — Low-temperature thermal conductivity of natural and synthetic quartz before and after gamma irradiation (neutron-irradiated natural sample is included for comparison).

mal conductivity. Hence, it is not surprising to find that, whereas irradiation causes an impairment of the conductivity of natural quartz (see Fig. 11), the conductivity of the irradiated synthetic specimen increases. It is reasonable to expect that γ-modified imperfections contributing to the increase of thermal resistance in natural quartz are probably also present in the Z-growth sample. In spite of such defects, however, the thermal conductivity of the synthetic specimen is improved with irradiation.

The observed low-temperature conductivity in natural and synthetic quartz before and after γ-irradiation is thus found to be in general agreement with speculations based upon the Q-center model.

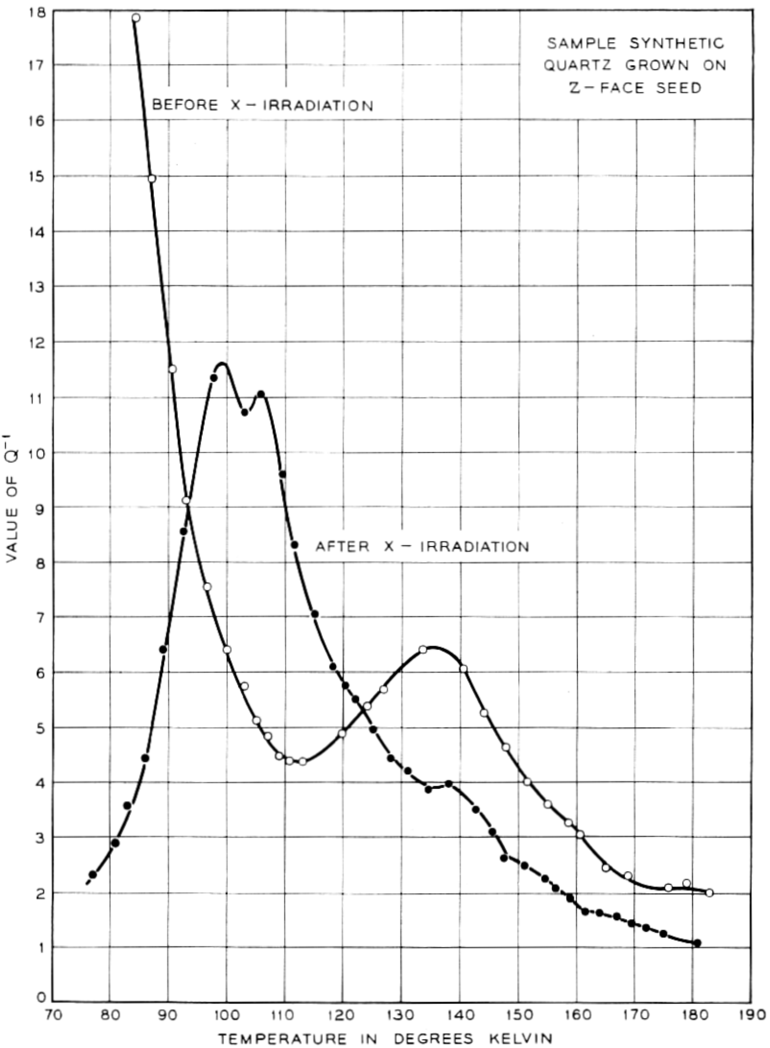

Fig. 12 — Internal friction vs. temperature for AT-cut z-face synthetic sample operating at 5 mc before and after x-irradiation. Note the radiation-induced absorption centered about 100°K.

Let us turn now to effect (b) above, which concerns the X-ray induced internal friction, appearing at 100°K.

In the course of examining the anelasticity of x-irradiated z-face quartz, a well-defined absorption peak centered about 100°K was observed. The curves of Q^{-1} vs. T for the z-face sample before and after x-irradiation are shown over the temperature range of interest in Fig. 12. The 100°K absorption is obviously nonexistent in the unirradiated sample, emerging only as the result of x-irradiation. (The precipitous increase in absorption below 100°K in the sample prior to irradiation is simply the high-temperature tail of the 50°K absorption.) The induced internal friction may be characterized as consisting primarily of two absorption peaks of nearly equal amplitude in the neighborhood of 100°K.

Operation of the z-face sample at its third, fifth and ninth overtone frequencies show the absorption peak to be displaced to higher temperatures with increase in frequency, indicative of a relaxation process. A plot of log ω as a function of $1/T_{\max}$, where $T_{\max}$ is the temperature at which the lower temperature component of the 100°K absorption occurs for a given frequency of vibration, is given in Fig. 13. Over this somewhat narrow frequency range a straight line can be drawn through the plotted points. The slope of the line, according to (3), is proportional to the ac-

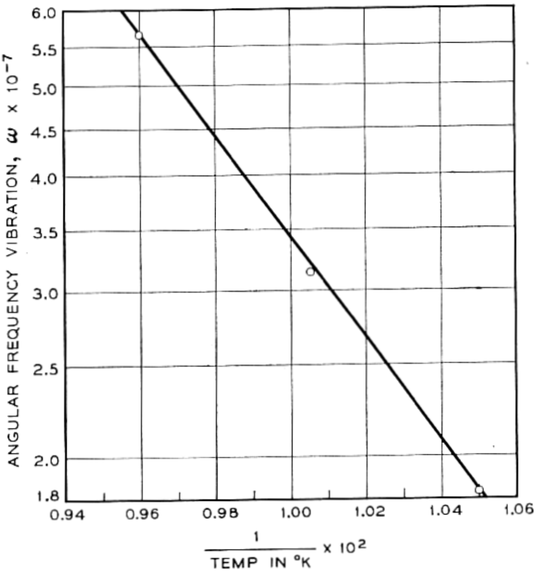

Fig. 13— Frequency of vibration plotted as a function of temperature at which maximum occurs in irradiation-induced absorption.

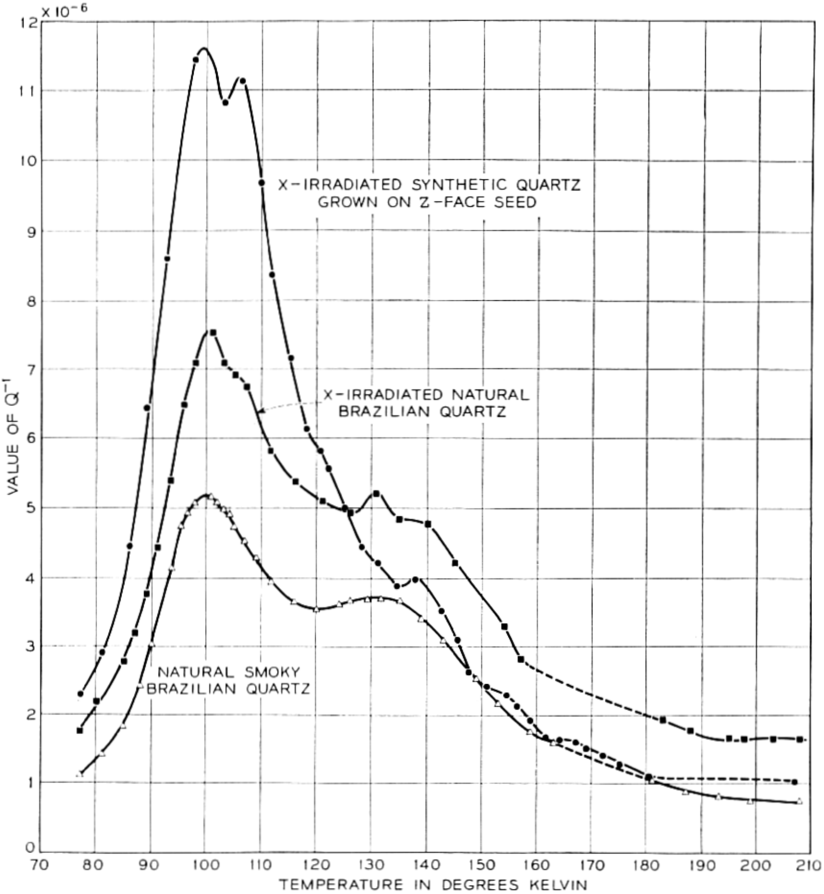

Fig. 14 — Comparison of x-irradiation-induced relaxation absorption in z-face synthetic and natural quartz resonators. Bottom curve is absorption in natural smoky Brazilian quartz.

tivation energy for the relaxation process. For some relaxation frequency, $1/\tau$, (3) then yields the value of τ_0. Accordingly, E and τ_0 for the lower temperature component of the 100°K absorption are calculated to be 2,450 cal/gm mole and 1.6×10^{-13} sec respectively.

At first thought, it might appear that the 100°K defect is simply the 50°K defect modified by the ionizing radiation, since the 100°K absorption "grows" at the expense of the 50°K absorption in the z-face sample. In order to test this proposition, a natural quartz sample having a small 50°K absorption was x-irradiated. The resulting Q^{-1} vs. T curve for the irradiated natural specimen, together with that for the z-face sample, is shown in Fig. 14. Although the absorptions at 50°K in these two crystal units prior to irradiation differ by some three decades, in the region of 100°K after irradiation they still agree to within an order of magnitude. This fact tends to refute any suggested relationship between the 50° and 100°K defects.

Crystal units fabricated from natural smoky Brazilian quartz also exhibit essentially the same absorption characteristics through 100°K (see bottom curve in Fig. 14), as induced by x-irradiation of clear quartz.

A visual examination of the three specimens used in Fig. 14 revealed their color density to be roughly proportional to the height of the 100°K absorption. Furthermore, the 100°K absorption is removed by annealing in much the same manner that the induced smoky color is eliminated. These observations naturally suggest that the so-called A-band optical absorption and the 100°K mechanical absorption in quartz derive from a common crystal defect. This argument is strengthened by measurement of the absorption in a sample of Z-growth quartz. (It is known[15] that Z-growth quartz shows only a very slight tendency to darken with irradiation.) In Fig. 15 it is quite clear that an absorption at 100°K is just barely detectable above background in an irradiated Z-growth specimen.

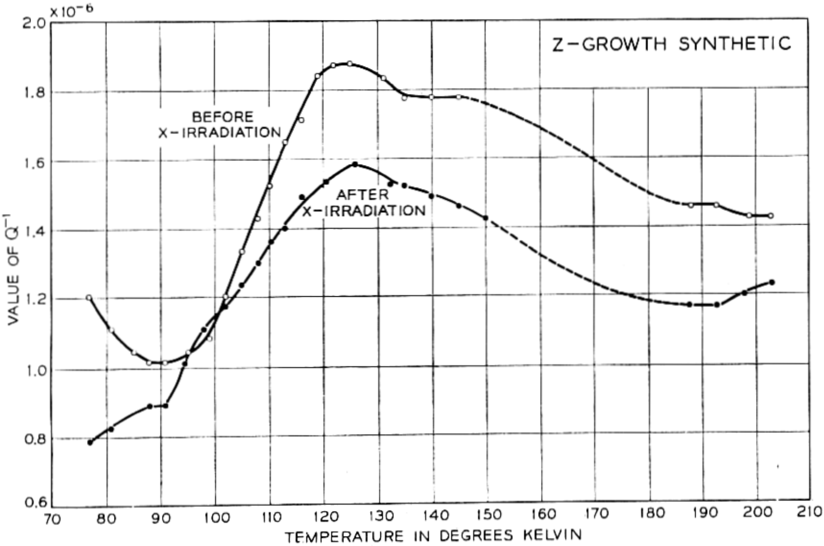

Fig. 15 — Internal friction vs. temperature for AT-cut Z-growth synthetic sample operating at 5 mc before and after x-irradiation.

The resonant frequency of natural AT-cut samples is found to be lowered by some 20 ppm as a result of the x-irradiation. This effect is explicable in terms of a reduction of the elastic modulus through the mechanical relaxation of the 100°K defect. The increase in modulus attending the elimination of the comparatively large 50°K defect in synthetic quartz precludes observing the above effect in most irradiated z-face and Z-growth samples.

Fondel[16] noted that the average resonant frequency of BT-cut* resonators is lowered by 200 ppm after they are subjected to x-irradiation. The change in frequency appears to be proportional to the density of the induced smoky color. It was proposed[16] that the X-rays cause a change in the basic properties of the quartz. It can now be stated that this change involves the introduction of 100°K defects.

On the basis of the average frequency change for the BT-cut it is anticipated that $Q^{-1}_{\max}$ for the 100°K absorption in the average BT-cut will be in the vicinity of 10^{-4}. In Fig. 16 are shown the variations of the internal friction and resonant frequency of a natural BT-cut crystal unit down to the temperature of liquid nitrogen. This particular sample is not representative of the average natural quartz specimen since the induced frequency lowering amounts to only 47 ppm, nevertheless

i. the onset of the frequency change coincides with the absorption at 100°K and

ii. the sum of df/f, computed according to (12), for the two absorption peaks comprising the 100°K absorption is roughly equivalent to the observed frequency shift.

Upon substitution of the values of θ equal to 35° 15′ and $-49°$ for the AT and BT-cut respectively into (9), the expressions for c_{66}' are

$$c_{66}' \text{ (AT)} = 0.333\, c_{44} + 0.666\, c_{66} - 0.943\, c_{14}\,, \tag{14}$$

$$c_{66}' \text{ (BT)} = 0.570\, c_{44} + 0.428\, c_{66} + 0.990\, c_{14}\,. \tag{15}$$

Since the term containing c_{14} is negative for the AT-cut, the value of c_{66}' (AT) would in fact be increased if a mechanical relaxation affected only c_{14}. Instead, c_{66}' (AT) is lowered approximately $\frac{1}{10}$ as much as c_{66}' (BT) by x-irradiation. The 100°K defect must, therefore, lower not only c_{14} but also one, or perhaps both, of the other elastic constants. Bottom[17] has measured the frequency constant of AT-cut, BT-cut and Y-cut crystals before and after irradiation. Through the use of these three orientations, Bottom has estimated that changes of -0.07 per cent,

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* A Y-cut plate rotated about the X-axis by an angle $\theta = -49°$.

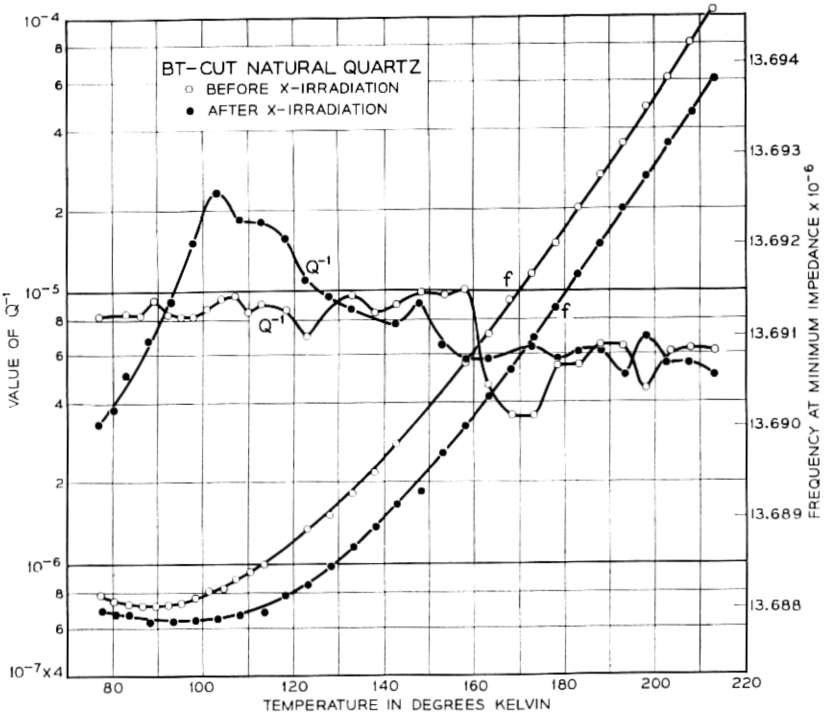

Fig. 16 — Internal friction and frequency of vibration at low temperatures for BT-cut natural quartz resonator before and after x-irradiation.

-0.03 per cent and -0.02 per cent occur in c_{14}, c_{44} and c_{66} respectively as a result of x-irradiation.

VI. DEFECT UNDERLYING THE 100°K ABSORPTION

In the preceding section evidence is presented which demonstrates the close relationship between a deformation-type structural relaxation and color centers. It is well established that the ability of a crystal to darken with x-irradiation is the necessary and sufficient condition for the appearance of a unique relaxation absorption. Henceforth, it will be assumed that the optical and associated mechanical absorption derive from the same crystal imperfection.

A number of investigations have been undertaken to define the nature of the A-band defect. Brown and Thomas[15] found that Z-growth colored much less readily when exposed to X-rays than did natural quartz. Later, Mitchell and Paige[18] showed that the A-band was probably associated with some impurity, which Ditchburn, et al.[19] tentatively identified as substitutional aluminum. Griffiths, Owen and Ward[20] discovered a spin resonance absorption in quartz which also appears to originate from a defect center consisting of substitutional aluminum. More recently, Mitchell and Paige[21] have described some experimental work which indicates that the magnetic effect and the A-band can be traced to the same defect.

A defect model, adjusted to account for the observed paramagnetic resonance absorption in smoky quartz, has been described by O'Brien and Pryce.[22] In it, an Al atom acquires a co-ordination number of four by accepting an extra electron, becoming Al^-. The Al^- may then enter the crystal structure at a Si lattice site. In order to maintain electroneutrality, a monovalent cation such as Na^+, Li^+ or H^+ must be in close association with the Al^-. It is proposed[22] that the effect of an ionizing irradiation on this center is to remove an orbital electron, most often from one of the oxygen atoms adjacent to the Al^-. The cation is then no longer bound to the defect center and hence diffuses away, becoming an electron trap. A two-dimensional schematic representation of this defect, before irradiation, is shown in Fig. 7(c). It is denoted as ${}^{\mathrm{Al}}_{\mathrm{Na}}\mathrm{P}$. The probable interaction between this defect and an ionizing radiation is given by

$$ {}^{\mathrm{Al}}_{\mathrm{Na}}\mathrm{P} + \gamma = {}^{\mathrm{Al}}\mathrm{A}_{+} + {}_{\mathrm{Na}}\mathrm{P}_{-} \,. $$

The ${}^{\mathrm{Al}}\mathrm{A}_{+}$ defect, Fig. 7(d), is quite similar to the A_0 structure except that an Al^- resides at a Si site and the defect contains an unpaired electron. As the cation migrates from the A-center, it probably picks up an electron and becomes a ${}_{\mathrm{Na}}\mathrm{P}_{-}$ defect, Fig. 7(g). The ${}^{\mathrm{Al}}\mathrm{A}_{+}$ defect is considered to be responsible for both the magnetic and optical effects.

The observed correlation between A-band and 100°K absorption simply means that x-irradiation of a defect in quartz produces other defects which provide the mechanisms for both optical and mechanical effects. The original defect is doubtless ${}^{\mathrm{Al}}_{\mathrm{Na}}\mathrm{P}$ and, on the basis of the above-cited investigations, the color center can be traced to the ${}^{\mathrm{Al}}\mathrm{A}_{+}$ defect.

The problem remaining is to determine whether it is the ${}^{\mathrm{Al}}\mathrm{A}_{+}$ or the ${}_{\mathrm{Na}}\mathrm{P}_{-}$ defect which is responsible for the mechanical relaxation. An interesting approach to the solution of this problem involves the removal of mobile impurity ions from quartz. When a sample of quartz is placed in an electric field, directed along the Z-axis and heated to approximately 500°C, a deposit is observed to collect at the cathode surface.[23] The main constituent of the deposit on a sample of natural quartz has been identified as Na.[23] It is apparent, therefore, that impurity ions, which are

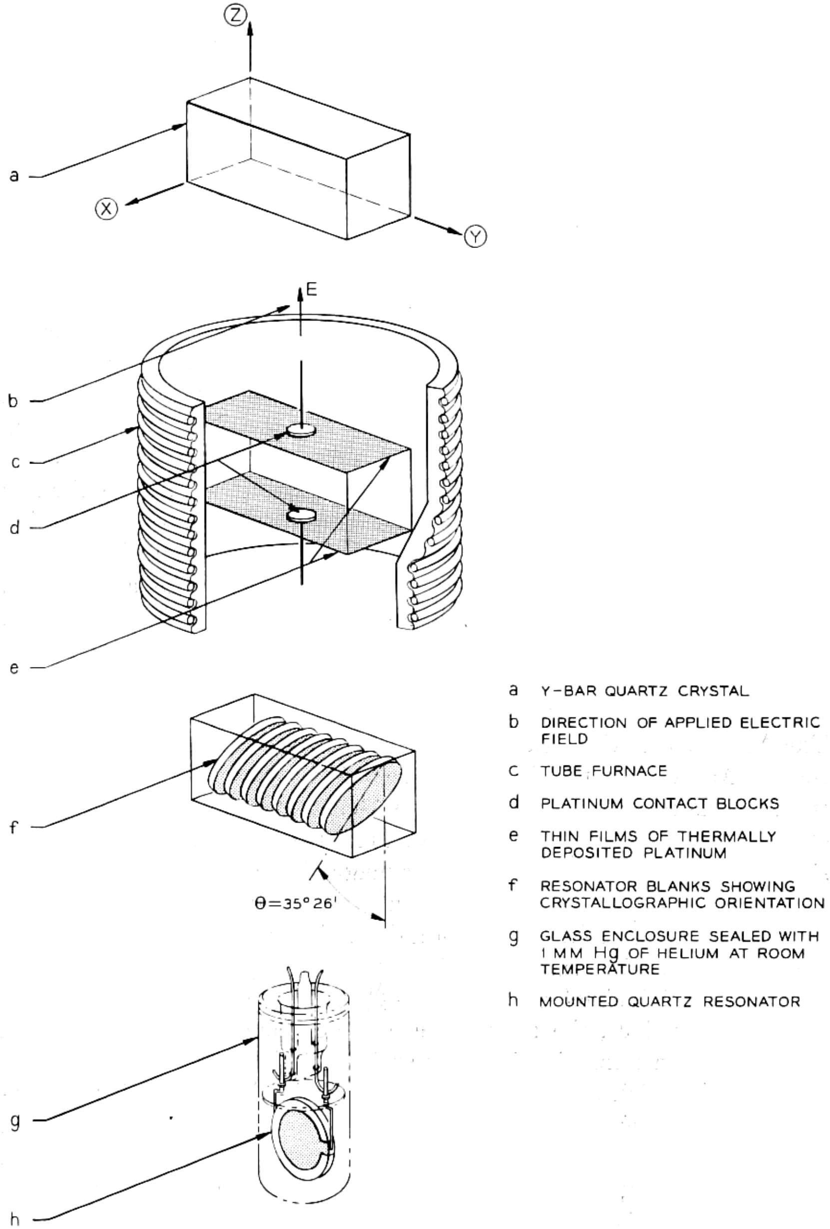

Fig. 17 — Process steps for the preparation of thermoelectrically treated quartz resonators.

known to have a high mobility along the optic axis, can be effectively swept from quartz.

Consider the effect of electrolytic purification on the ${}^{\mathrm{Al}}_{\mathrm{Na}}\mathrm{P}$ defect. In view of the foregoing, it is reasonable to expect Na^+ to be stripped from P-centers and collected at the cathode surface. As a result, the ${}^{\mathrm{Al}}_{\mathrm{Na}}\mathrm{P}$ defects are reduced to ${}^{\mathrm{Al}}\mathrm{A}_-$ which, except for an excess electron, closely resembles the structure of the irradiation-induced ${}^{\mathrm{Al}}\mathrm{A}_+$ defect. The incidence of ${}_{\mathrm{Na}}\mathrm{P}_-$ defects in the swept quartz should be quite rare. There are, therefore, two alternatives:

i. If the 100°K absorption is due to ${}^{\mathrm{Al}}\mathrm{A}_+$ rather than ${}_{\mathrm{Na}}\mathrm{P}_-$ defects, an absorption similar to the one at 100°K should be observed in thermoelectrically treated quartz, or

ii. If an absorption akin to the 100°K absorption cannot be generated by sweeping the material, the 100°K absorption probably involves the ${}_{\mathrm{Na}}\mathrm{P}_-$ defect.

A number of test resonators were fabricated from a natural quartz crystal. Half the units were untreated and used for control purposes, while the rest were thermoelectrically treated. The process steps involved in the preparation of the treated crystal units are shown in Fig. 17. A plot of the mechanical loss at 5 mc in a representative treated sample, before and after x-irradiation, is compared in Fig. 18 with an untreated x-irradiated sample. It is obvious immediately that the absorption centered about 85°K in the swept quartz is strikingly similar to the 100°K absorption. Both have roughly the same amplitude and are characterized by two absorption peaks. Measurements at other frequencies demonstrate that the absorption at 85°K is due to a relaxation process with a τ_0 of the same order of magnitude as that for the 100°K relaxation process and an activation energy of approximately 2,000 cal/gm mole. The necessary conditions for the first alternative given above are satisfied; therefore, it is concluded that the *irradiation-induced defect underlying the relaxation process whose absorption peak occurs at 100°K for a frequency of 5 mc is the* ${}^{\mathrm{Al}}\mathrm{A}_+$ *defect.* Conversely, the above observations and analysis can be effectively used to argue the propriety of relating the A-band absorption to ${}^{\mathrm{Al}}\mathrm{A}_+$.

The lower activation energy for the thermoelectrically induced relaxation is perhaps attributable to the excess negative charge carried by the ${}^{\mathrm{Al}}\mathrm{A}_-$ defect. The ${}^{\mathrm{Al}}\mathrm{A}_-$ defects in treated quartz could presumably be easily converted to ${}^{\mathrm{Al}}\mathrm{A}_+$ defects by x-irradiation. However, A-band absorption cannot be induced in swept quartz* and, significantly, neither

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* It appears that V. E. Bottom (Final Report, U. S. Army Signal Corps Contract DA-36-039 sc-66, 30 June 1953) first reported this effect.

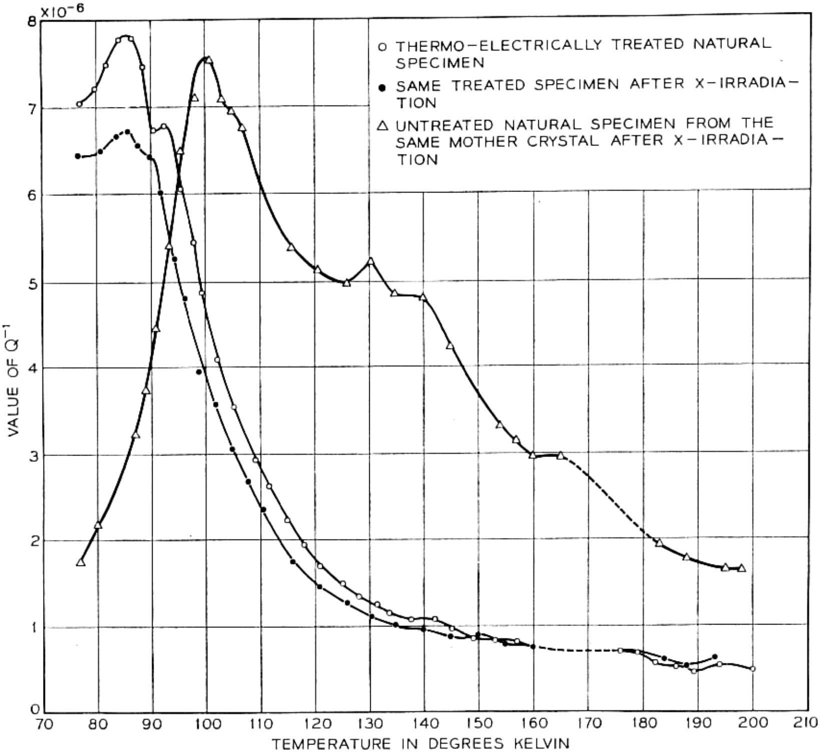

Fig. 18 — Comparison of relaxation absorption in sample of thermo-electrically treated natural quartz and x-irradiation-induced absorption in natural quartz.

can the 100°K absorption (see the curve for x-irradiated treated quartz in Fig. 18.) It is conceivable that removing Na^+ in treated quartz effectively eliminates electron traps in the material. Consequently, electrons ionized off $^{Al}A_{-}$ defects by x-irradiation will readily diffuse back to these centers and thus negate the irradiation effect.

VII. CONCLUSIONS

The concentration of deformation defects underlying the relaxation absorption, which occurs at 50°K for a frequency of 5 mc, has been found to be several decades higher in synthetic quartz than in the natural material. The characteristic lowering of the elastic modulus in the region of stress relaxation is observed as a decrease in the resonant frequency of AT-cut resonators at temperatures above 50°K. It is apparent that the 50°K defect also alters the *f-T* characteristics of the AT-cut.

The singular lack of correlation between concentration of impurities in quartz and the amplitude of the mechanical absorption at 50°K argues against proposing that the responsible lattice deformation derives from some specific impurity. This observation, together with the fact that x-irradiation effectively eliminates the 50°K absorption, suggests that the deformation defect consists of excess oxygen, forming nonbridging oxygen defects.

It has been demonstrated that x-irradiation induces a 100°K relaxation absorption at 5 mc in quartz which darkens with irradiation. The 100°K absorption is not found in clear quartz. Although a lowering of the frequency of crystal resonators which have been subjected to x-irradiation has been previously observed, it is now possible to attribute the change to a decrease of the elastic modulus caused by the relaxation of the 100°K defect. Since the amplitude of the 100°K absorption is proportional to the color density of the irradiated sample, the defect responsible for this relaxation could conceivably be either $^{\mathrm{Al}}\mathrm{A}_+$ or $_{\mathrm{Na}}\mathrm{P}_-$. Measurements of the mechanical absorption in electrolytically purified sample resonators clearly favor selecting $^{\mathrm{Al}}\mathrm{A}_+$ as the responsible defect.

VIII. ACKNOWLEDGMENTS

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