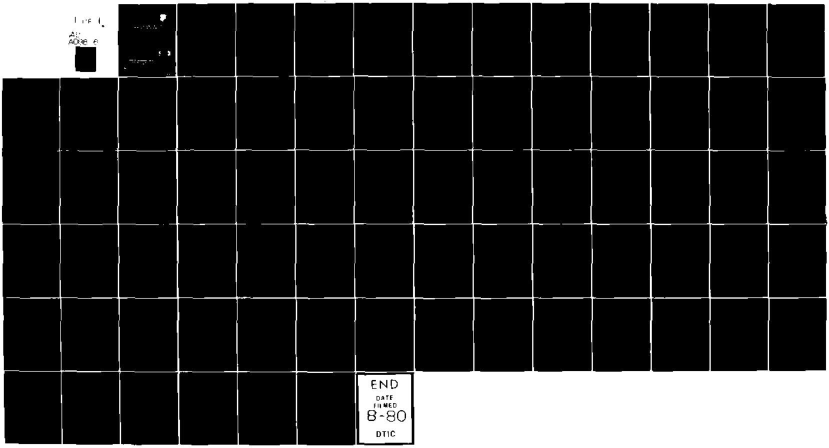
AD-A086 116 OKLAHOMA STATE UNIV STILLWATER DEPT OF PHYSICS F/G 7/4
A STUDY OF THE DEFECTS PRODUCED BY THE IRRADIATION OF QUARTZ.(U)
APR 80 L E HALLIBURTON, J J MARTIN F30602-77-C-0171
UNCLASSIFIED RADC-TR-80-120 NL

1 OF 1
AD
A086116



END
DATE
FILMED
8-80
DTIC

12

RADC-TR-80-120
Final Technical Report
April 1980

LEVEL II

ADA086116

A STUDY OF THE DEFECTS PRODUCED BY THE IRRADIATION OF QUARTZ

Oklahoma State University

Larry E. Halliburton
Joel J. Martin
William A. Sibley

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

DTIC
ELECTE
S JUL 1 1980 D
C

[illegible] FILE COPY

ROME AIR DEVELOPMENT CENTER
Air Force Systems Command
Griffiss Air Force Base, New York 13441

80 6 30 046

This report has been reviewed by the RADC Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

RADC-TR-80-120 has been reviewed and is approved for publication.

APPROVED: Alton F. Armington

ALTON F. ARMINGTON
Project Engineer

APPROVED: Clarence D. Turner

CLARENCE D. TURNER
Acting Director
Solid State Sciences Division

FOR THE COMMANDER: John P. Huss

JOHN P. HUSS
Acting Chief, Plans Office

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(19) REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (14) RADC-TR-80-120 — 2. GOVT ACCESSION NO. AD-A086 116	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) (6) A STUDY OF THE DEFECTS PRODUCED BY THE IRRADIATION OF QUARTZ.	5. TYPE OF REPORT & PERIOD COVERED (9) Final Technical Report, 15 May 77 — 30 Nov 79
	6. PERFORMING ORG. REPORT NUMBER N/A
7. AUTHOR(s) (10) Larry E. Halliburton Joel J. Martin William A. Sibley	8. CONTRACT OR GRANT NUMBER(s) (15) F30602-77-C-0171
9. PERFORMING ORGANIZATION NAME AND ADDRESS Oklahoma State University Physics Department Stillwater OK 74078	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (17) J1 61102F (16) 2306J127
11. CONTROLLING OFFICE NAME AND ADDRESS Deputy for Electronic Technology (RADC/ESM) Hanscom AFB MA 01731	12. REPORT DATE (11) April 1980
	13. NUMBER OF PAGES 67
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Same (12) 74	15. SECURITY CLASS. (of this report) UNCLASSIFIED
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Same

18. SUPPLEMENTARY NOTES

RADC Project Engineer: Alton F. Armington (ESM)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Quartz Crystals	Electrolysis	Sweeping
Radiation Damage	Aluminum-hole center	
Q^{-1} Measurements	OH absorption	
IR Absorption	Na interstitial	
EPR	Mobility	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

We have used infrared absorption (IR), electron spin resonance (ESR), and acoustic loss (Q^{-1}) measurements to investigate the radiation response of high-quality synthetic quartz. Attention was primarily placed on Sawyer Premium Q and Electronic Grade material. Our results show that the radiation-induced mobility of interstitial ions is the principal factor (continued on reverse)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

400790

18

governing the radiation response of quartz. During irradiations below 200 K, IR and ESR results show that hydrogen is the only mobile interstitial. However, if the temperature during irradiation is above 200 K, interstitial sodium and, presumably, the other interstitial alkalis become mobile. This allows Al-OH and $[Al_{e+}]^{o}$ centers to be formed as the Na^{+} ions are removed from the substitutional aluminum sites. Also, the radiation-induced mobility of the Na^{+} ions causes the large frequency shifts observed in unswept quartz-controlled oscillators which are subjected to radiation.

Electrodiffusion (sweeping) removes the interstitial alkali ions from quartz and replaces them with hydrogen, thus forming Al-OH centers and significantly improving the radiation response of the material. Although the hydrogen is trapped at an aluminum site in the absence of a radiation field, it will be mobile during irradiation at any temperature in these swept crystals. This temporary mobility (i.e., displacement from the stable trapping sites during the irradiation and immediate return to these trapping sites upon cessation of the irradiation) contributes to the transient frequency response of quartz oscillators subjected to radiation pulses.

Since the hydrogen content of a quartz crystal after sweeping is controlled by the crystal's aluminum content, we strongly suggest that quartz used in radiation environments be preselected for low aluminum content. Infrared scans at liquid nitrogen temperature before sweeping should be the first step in material selection. Further IR and ESR measurements following the sweeping process give the precise aluminum content of each bar. The ESR measurements also provide a test for the effectiveness (i.e., completeness) of the sweeping process and constitutes the final evaluation of a quartz bar prior to fabrication of the resonator blanks. This latter test is based on the different temperature dependence of the radiation-induced mobility of interstitial hydrogen versus interstitial alkalis and consists of the following steps: 1) Anneal a sample to 500°C for 15 minutes. 2) Irradiate the sample at 77 K and measure the $[Al_{e+}]^{o}$ center concentration with ESR. 3) Irradiate the sample at room temperature and remeasure the $[Al_{e+}]^{o}$ center concentration. 4) Repeat the second step. If the sweeping process is complete, the $[Al_{e+}]^{o}$ center concentration in the second and fourth steps will be the same since there will be no alkalis to displace during the third step.

TABLE OF CONTENTS

*References are numbered separately for each section.

EVALUATION

1. This report is the Final Report on the Contract. It covers research performed on defect formation caused by irradiation of quartz. The objective of the work was the identification of the defects and their effect on quartz oscillator properties. Using radiation, low temperature IR, ESR and acoustic loss measurements, defects associated with aluminum impurities in the lattice have been shown to be detrimental. Some of these defects have been identified.

2. This work is of value because it provided both basic knowledge and an evaluation technique which can identify deleterius defects in quartz used in precision timing and frequency applications. This will be useful for improving the quality of quartz used in frequency and timing applications throughout the Air Force and all of DoD.

Alton F. Armington
ALTON F. ARMINGTON
Project Engineer

I. INTRODUCTION

Because of its piezoelectric properties, quartz has many applications in electronic instrumentation. Examples range from crystal-controlled oscillators and SAW-devices for use in time keeping and communication links to temperature and mass measuring instruments. In many cases, such as precision oscillators in satellites, the operation of quartz-containing devices can be degraded by radiation.[1-3] Thus, the defect structure of crystalline SiO_2 is a subject of considerable importance.

Direct studies of radiation-induced effects in quartz began with the work of Griffiths et al.[5] on the aluminum-associated trapped hole center (now known as the $[Al_{e+}]^o$ center) and the work of Weeks[6] on the oxygen-vacancy-associated trapped electron center (E_1' center). For the $[Al_{e+}]^o$ center, O'Brien[7] successfully interpreted the magnetic resonance data in terms of a model having a hole trapped primarily in a non-bonding orbital of an oxygen ion adjacent to the substitutional aluminum. The comprehensive review by Weil[8] describes additional work on the aluminum-associated hole centers.

All quartz, natural or synthetic, contains aluminum substituting for silicon and thus charge compensators, the most common of which are interstitial H^+, Li^+ and Na^+, are required. It is expected that these interstitials will play a direct role in the response of quartz to radiation and this expectation has been born out by many experiments. As an example, the 50 K acoustic loss peak observed in 5 MHz 5th overtone AT-cut crystals has been attributed to interstitial Na^+ ions and is removed by ionizing radiation.[4]

Interstitial H^+ ions are usually associated with a non-bonding oxygen orbital in the form of OH^- molecules. This association gives rise to infrared absorption which is used to routinely evaluate the quality of quartz.[9-10] If the IR measurements are made at cryogenic temperatures, the absorption bands narrow substantially and allow detailed investigations of the role of OH^- molecules.[11-13] Recent work[14] shows that irradiation of a quartz sample held at liquid nitrogen or liquid helium temperatures breaks up the OH^- radicals and thus reduces the OH^- absorption. On the other hand, irradiation of unswept synthetic quartz while it is at room temperatures does not change the total OH^- absorption compared to before irradiation, but does produce two new bands.

Quartz has relatively large Z-axis channels along which the interstitial ions can move. Kats[11] making use of this characteristic, applied an electric field parallel to the Z-axis while holding the sample temperature in the 400°C to 550°C range. He succeeded in "sweeping" hydrogen and alkali interstitial ions into and out of the sample. Since charge neutrality must be maintained, if one species is removed it must be replaced by a similarly charged species. This technique of changing the relative concentration of hydrogen and alkali ions by sweeping has been used by many investigators and has proven extremely useful in defect identification studies. More importantly, sweeping prior to fabrication has been reported[15] to increase the radiation hardness of quartz crystals used in precision oscillators.

While the aluminum hole and E' centers can be observed with electron spin resonance (ESR) and the OH^- molecules by infrared measurements, direct observation of the alkali interstitials is more difficult. Their presence is known to affect the Q of crystals and, therefore, the frequency stability of the oscillator. For example, Fraser[16] has shown that the 50K loss peak is due to interstitial Na^+ by sweeping Na into natural quartz.

In the present investigation, we have used parallel IR absorption, ESR, and Q^{-1} studies to obtain information about defect formation and migration during irradiation and thermal annealing in quartz. The samples studied were all commercially-available high-quality quartz, thus making our results directly applicable to device operation. The major portion of the paper is concerned with the radiation-induced mobility of interstitial H^+ and Na^+ ions. We find that the H^+ ions are mobile at all temperatures under irradiation but that the Na^+ ions are only mobile above 200K. As an application of these results, we describe a sensitive testing procedure for measuring the extent to which the interstitial Na^+ ions have been removed by the sweeping process.

REFERENCES

1. J. C. King and H. H. Sander, IEEE Trans. on Nuc. Sci. NS-19, 23 (1972).
2. T. M. Flanagan, IEEE Trans. on Nuc. Sci. NS-21, 390 (1974).
3. F. Euler, P. Ligor, A. Kahan, P. Pellegrini, T. M. Flanagan, and T. F. Wrobel, IEEE Trans. on Nuc. Sci. NS-25, 1267 (1978).
4. D. B. Fraser, *Physical Acoustics* (W. P. Mason, ed.) Vol. III-Part A, pp. 1-42, Academic Press, New York, 1966.
5. J. H. E. Griffiths, J. Owen, and I. M. Ward, *Defects in Crystalline Solids* (London, 1955), Bristol Conference, p. 88, Physical Soc.
6. R. A. Weeks, J. Appl. Phys. 27, 1376 (1956).
7. M. C. M. O'Brien, Proc. Roy. Soc. (London) A231, 404 (1955).
8. J. A. Weil, Rad. Effects 26, 261 (1975).
9. D. B. Fraser, D. M. Dodd, D. W. Rudd, and W. J. Carroll, Frequency, 4, 18 (1966).
10. B. Sawyer, IEEE Trans. Sus, SU-19, 41 (1972).
11. A. Kats, Phillips Research Reports 17, 133 (1962).
12. R. N. Brown and A. Kahan, J. Phys. Chem. Solids 36, 467 (1975).
13. H. G. Lipson, F. Euler, and A. F. Armington, "Low Temperature Infrared Absorption of Impurities in High Grade Quartz" Proceedings, 32nd Annual Symposium on Frequency Control, U.S. Army Electronics Command, Fort Monmouth, New Jersey, pp. 11-23 (1978).
14. W. A. Sibley, J. J. Martin, M. C. Wintersgill, and J. D. Brown, J. Appl. Phys. 50, 5449 (1979).
15. B. R. Capone, A. Kahan, R. N. Brown, and J. R. Buckmelter; IEEE Trans. on Nuc. Sci., NS-17, 217 (1970).
16. D. B. Fraser, J. Appl. Phys. 35, 2913 (1964).

II. RECOMMENDATIONS

Our combined IR, ESR, and Q^{-1} results which are described in detail in the final three sections of this report show that even high-quality synthetic quartz is quite variable in aluminum content. For example, we have found aluminum concentrations ranging from approximately 1×10^{16} cm^{-3} to 15×10^{16} cm^{-3} in different Premium Q bars. Furthermore, the sweeping process may also be somewhat variable. To ensure radiation-hardened crystals, only stones with a low aluminum content should be used and they should be completely swept to remove all of the interstitial alkalis. We propose the following quality control tests to screen material intended for use in radiation environments.

The first test screens material prior to the sweeping process and consists of scanning the lumbered bars in the infrared from 4000 cm^{-1} to 3000 cm^{-1} at a temperature of 80K. Material which shows peaks at 3581 cm^{-1}, 3437 cm^{-1}, and 3400 cm^{-1} with absorption coefficients greater than 0.2 cm^{-1} should be rejected. While these IR peaks do not directly measure the aluminum content, their presence does indicate relatively impure material and crystals fabricated from such material probably will show significant frequency shifts under irradiation. Since the lumbered bar should be polished before sweeping, no real additional sample preparation is required for this initial IR test. An optical Dewar and an IR spectrophotometer are, of course, required. It is also assumed that the bars initially selected have already met the manufacturer's test (usually an IR absorption measurement at a single wavelength) for high-quality quartz.

Quartz bars that pass the first screening test are subsequently swept. Then, the following ESR test is run on a small sample ($8 \times 3 \times 3$ mm^3) cut from the bar to verify the completeness of the sweeping process. This latter test determines to what extent the interstitial alkali ions have been removed from the bar and, also, gives a direct measure of the aluminum content. The ESR screening test is based on the different temperature dependence of the radiation-induced mobility of interstitial hydrogen versus interstitial alkalis and consists of the following steps: 1) Anneal a sample to 500°C for 15 minutes. 2) Irradiate the sample at 77K and measure the $[Al_{e+}]^o$ center concentration. 3) Irradiate the sample at room temperature and remeasure the $[Al_{e+}]^o$ center concentration. 4) Repeat the second step. If the sweeping process is complete, the $[Al_{e+}]^o$ center concentration in the second and fourth steps will be the same since there will be no alkalis to displace during the third step. Swept quartz bars that pass this final test should have much higher probabilities of producing radiation-hardened resonators.

III. PAPERS AND PRESENTATIONS

The following papers and presentations resulted from the present research contract.

1. L. E. Halliburton, B. D. Perlson, R. A. Weeks, J. A. Weil, and M. C. Wintersgill, "EPR Study of the E_4' Center in α-Quartz," Solid State Commun. 30, 575 (1979).
2. W. A. Sibley, J. J. Martin, M. C. Wintersgill, and J. D. Brown, "The Effect of Radiation on the OH^- Infrared Absorption of Quartz Crystals," J. Appl. Phys. 50, 5449 (1979).
3. M. E. Markes and L. E. Halliburton, "Defects in Synthetic Quartz: Radiation-Induced Mobility of Interstitial Ions," J. Appl. Phys. 50, (1979).
4. N. Koumvakalis and M. E. Markes, "Deuterization of Synthetic Quartz," J. Appl. Phys. (in press 1980).
5. S. P. Doherty, J. J. Martin, A. F. Armington, and R. N. Brown, "The Effect of Irradiation and Electrodiffusion on the Sodium Acoustic Loss Peak in Synthetic Quartz Crystals," submitted to J. Appl. Phys.
6. N. Koumvakalis, M. E. Markes, L. E. Halliburton, and J. J. Martin, "Radiation Effects in Crystalline SiO_2: Charge Compensation of Aluminum Ions," submitted to J. Appl. Phys.
7. N. Koumvakalis, "Defects in Crystalline SiO_2: Optical Absorption of the Aluminum-Associated Hole Center," submitted to J. Appl. Phys.
8. L. E. Halliburton, M. Markes, J. J. Martin, S. P. Doherty, N. Koumvakalis, W. A. Sibley, A. F. Armington, and R. N. Brown, "Radiation Effects in Synthetic Quartz: The Role of Electrodiffusion and Radiation-Induced Mobility of Interstitial Ions," IEEE Trans. on Nuc. Sci. NS-26, 4851(1979).
9. J. J. Martin, S. P. Doherty, L. E. Halliburton, M. Markes, N. Koumvakalis, W. A. Sibley, R. N. Brown, and A. F. Armington, "Radiation-Induced Mobility of Interstitial Ions in Synthetic Quartz," Proceedings of the 33rd Annual Symposium on Frequency Control, 134 (1979).

10. M. G. Jani, "Electron Spin Resonance Study of the E'_2 Center in Quartz," Masters Thesis (1979), Oklahoma State University (L. E. Halliburton-supervisor).

11. L. E. Halliburton, "The Defect Structure of Quartz," one hour colloquium, Sandia Laboratories, Albuquerque, N.M., July 13, 1979.

12. L. E. Halliburton, "The Nature and Behavior of Point Defects in Quartz," one hour colloquium, University of Missouri, Columbia, MO, Nov. 14, 1979.

13. L. E. Halliburton, "The Nature and Behavior of Point Defects in Quartz," one hour colloquium, Naval Research Laboratory, Washington, D.C., Feb. 7, 1980.

14. L. E. Halliburton, M. C. Wintersgill, J. J. Martin, W. A. Sibley, and R. A. Weeks, "The E'_4 Center in Quartz," Bull. Am. Phys. Soc. 23, 254 (1978).

15. M. C. Wintersgill, L. E. Halliburton, J. J. Martin, and W. A. Sibley, "Thermal Stability of Defects in Crystalline SiO_2," Bull. Am. Phys. Soc. 23, 255 (1978).

16. J. Isoya, B. D. Perlson, J. A. Weil, and L. E. Halliburton, "Spin-Hamiltonian of the E'_4 Center in α-Quartz," Bull. Am. Phys. Soc. 24, 375 (1979).

17. M. E. Markes and L. E. Halliburton, "Radiation-Induced Mobility of Interstitial Ions and Production of Hole Centers in Quartz," Bull. Am. Phys. Soc. 24, 449 (1979).

18. S. P. Doherty, J. J. Martin, and A. F. Armington, "Acoustic Loss in Irradiated 5 MHz 5th Overtone Quartz Crystals," Bull. Am. Phys. Soc. 24, 449 (1979).

19. W. A. Sibley, J. J. Martin, M. C. Wintersgill, and D. Brown, "The Effect of Radiation on the OH^- Infrared Absorption of Quartz Single Crystals," Bull. Am. Phys. Soc. 24, 449 (1979).

20 L. E. Halliburton, "Point Defects in Crystalline SiO_2," presented at the Southeastern Section meeting of the American Physical Society, Nov. 8-10, 1979.

21. J. J. Martin and S. P. Doherty, "Radation Effects on the Na Loss Peak in 5 MHz AT-Cut Quartz Resonators," presented at the Southeastern Section meeting of the American Physical Society, Nov. 8-10, 1979.

IV. INFRARED ABSORPTION

A. INTRODUCTION

High precision quartz oscillator clocks and filters are widely used in satellite communication and guidance systems. Since the stability of the precision oscillators used in these systems becomes of greater importance as usage increases, a continual effort must be made to develop oscillators that are stable for long periods.[1] Considerable work has been done in the past on the effect of radiation on SiO_2 crystals.[2-10] However, because of the difficulty of obtaining crystals with homogeneous impurity concentrations or even samples with known impurity content, an understanding of how radiation damage affects the oscillation frequency has not yet been obtained. It is clear from previous research that impurities do play an important role. Changes in impurity states could most certainly affect the frequency stability of oscillators, since radiation and stress can affect impurity valence states and mobilities, it is not surprising that both can cause instability in oscillation frequency.

When an ionic or covalent material is exposed to radiation, two types of response can occur:[11] i) ionizing radiation can cause changes in valence states which may result in mobility of impurities; ii) incident particles can displace ions if energy transfer from the bombarding particle is sufficiently great. High energy electrons or protons are most effective for ionic displacements, whereas ionizing radiation creates electron-hole pairs which give rise primarily to valence changes. The displacement cross section for 1-2 Mev electrons impinging upon ions is sufficiently small that except at very large doses, few ionic displacement type defects are present. On the other hand, if hydrogen or alkali atoms have the appropriate valence state, it is possible that, at sufficiently high temperatures, they can be mobile. Thus, ionizing radiation can "trigger" motion of these impurities along the open channels of crystalline SiO_2. This motion will be temperature dependent.

In our work, optical absorption studies of unirradiated and irradiated quartz have been made using ultraviolet, visible and infrared light. A number of electron paramagnetic resonance (EPR) studies have also been made by our co-workers, Markes and Halliburton.[12] The latter spectra are complex but do yield valuable information on the redistribution of electrons and holes by radiation. This work will concentrate on infrared absorption data. However, attempts will be made to correlate the infrared measurements with both EPR and visible optical absorption results where possible. The purpose of this paper is to present data corroborating some of the existing information available on OH^- infrared transitions in SiO_2 crystals and to give additional results on the mobilities and locations of impurities in SiO_2.

B. EXPERIMENTAL PROCEDURE

Single crystal ingots of both Electronic and Premium Q material were purchased from Sawyer Research Products, Inc. Specimens were cut such that the c-axis was parallel to the incident beam of the monitoring light. In this case the electric vector of the incident light, E, was always perpendicular to the c-axis ($E \perp c$). After the crystals were cut and polished, infrared absorption was measured on a Beckman 4240 spectrophotometer. The visible and ultraviolet spectral ranges were measured using a Cary 14 spectrophotometer. A cryostat equipped with CaF_2 windows and capable of reaching 7K with temperature controllable to ±2K was utilized.

Irradiations were made with a Van de Graaff electron accelerator. Most often the irradiations were done with 1.6 Mev electrons and a current of approximately 0.2 A/cm^2 on the samples. Since the penetration depth of these electrons is about 2mm in SiO_2, samples with greater thickness were irradiated on both sides. The radiation port for the cryostat consisted of a 5 mil aluminum window.

C. RESULTS

The differences in the infrared optical properties of Sawyer Electronic Grade and Sawyer Premium Q grade quartz are illustrated in Fig. 1. The data are for the case $E \perp c$. From the figure it can be seen that the spectrum typical of Premium Q samples exhibits primarily rather broad intrinsic quartz lattice mode overtone absorption at $3200cm^{-1}$, $3300cm^{-1}$ and $3400cm^{-1}$. Other extrinsic bands are also present around $3400cm^{-1}$ since there are changes in this region with radiation dose. The OH^- stretching modes are evidenced by the sharp peaks and are obviously much less intense in the Premium Q specimens (dashed line) than in the Electronic Grade material (solid line). Table I lists the wavelengths, widths at half maximum, H, and the maximum absorption coefficient for the most prominent bands in the two materials. In the past both Kats[3] and Bates and Perkins[13] have found relationships which connect the concentration of hydrogen ions per cm^3, N_H, with the maximum absorption coefficient, $\alpha_m(cm^{-1})$, and the halfwidth, $H(cm^{-1})$, with the various OH bands. They determined that $N_H = 1.8 \times 10^{16} H\alpha_m cm^{-3}$. The data in Table I suggest that Premium Q crystals contain less than $3 \times 10^{16} cm^{-3}$ hydrogens participating as OH^-, whereas the Electronic Grade material contains approximately 4×10^{17} hydrogens/cm^3 in this state. The measurements illustrated in Fig. 1 were made at 77K. As has been shown by Lipson, et al.[14] the OH bands are very temperature sensitive. In fact, for our samples measurements at 300K show only intrinsic SiO_2 overtone bands. There is a considerable change in the intensity of the OH bands over the temperature range 7K to 77K. It is imperative that infrared measurements be made at 77K or lower if defect bands are to be monitored.

When samples are irradiated at either 10K or 77K with low doses of electrons (an absorbed energy of about 500 Joules/cm^3), few changes are observed. In the Electronic Grade crystals the $3581cm^{-1}$ band decreases and the small $3367cm^{-1}$ band disappears. No other noticeable effects are observed. For larger doses

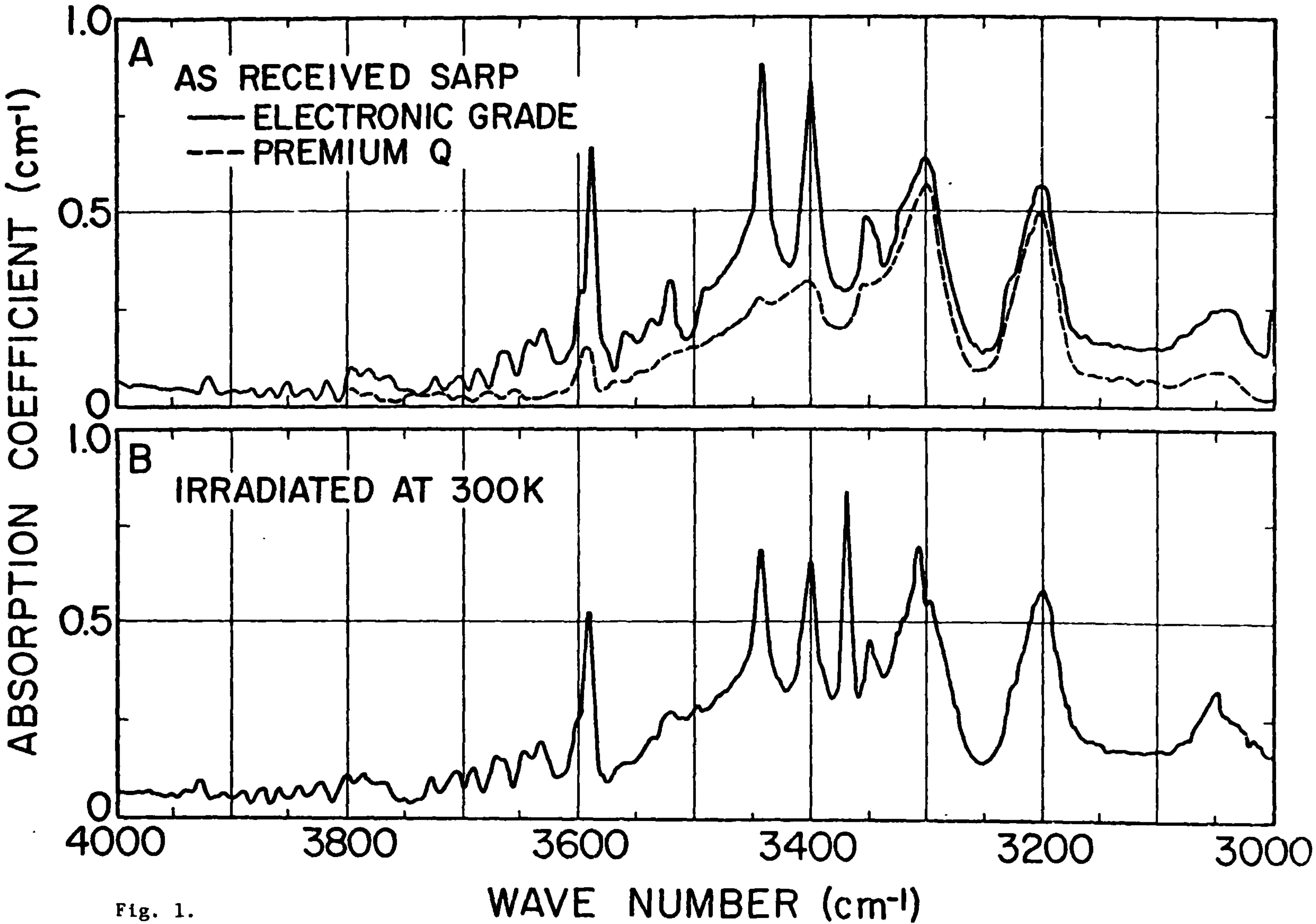


Fig. 1.
In A, the upper solid curve shows the infrared absorption taken at 77K for a SARP Electronic Grade sample in the as-received condition. The dashed curve shows the results for a SARP Premium Q sample. In B, the infrared absorption in the Electronic Grade sample after a 300K irradiation to a dose of 2000 Joules/cm^3 is shown. This irradiation has produced the bands at 3306cm^{-1} and 3367cm^{-1}.

TABLE I. Prominent OH Bands as Measured at 77K for Electronic Grade Quartz.

Wavenumber (cm^{-1})	α_m(cm^{-1})	H(cm^{-1})	Comments
3581	0.61(0.06)*	6	Unirradiated
3437	0.71(0.04)	12	"
3400	0.75	12	"
3348	0.25	16	"
3367	0.61	7	Irradiated at 300K
3306	0.23	7	"

---

*The values in parentheses are for a Premium Q sample.

all the bands decrease markedly and for doses greater than 2000 Joules/cm^3 ($\sim 10^8$ Rads) all bands disappear. The bands only partially recover their original strength upon annealing to room temperature.

If instead the material is irradiated at 300K to a dose of about 2000 Joules/cm^3 and then measured at 77K, it is found that the original OH bands have decreased and two intense bands appear at $3367cm^{-1}$ and $3306cm^{-1}$ with the total area under the OH bands remaining constant. The lower curve in Fig. 1 shows this behavior for a SARP Electronic Grade sample. It should be noted that the intensity of the $3306cm^{-1}$ band is considerably less than that of the $3367cm^{-1}$ band for a 300K irradiation. However, the intensity ratio of these two bands depends on the radiation temperature and dose.

If a sample which has been irradiated at 300K to produce the two bands at $3367cm^{-1}$ and $3306cm^{-1}$ is given a brief low dose irradiation (500 Joules/cm^3) at either 77K or 10K, the $3367cm^{-1}$ band decreases and the $3306cm^{-1}$ band increases as shown in curve A of Fig. 2. If the sample is then isochronally annealed, the two bands retain their relative strengths until 230K is reached. Above 230K they quickly recover the original intensities produced by the 300K irradiation. The recovery is essentially complete by 270K. The sharpness with which this recovery takes place suggests that the process is not a migration event governed by Boltzmann statistics. A higher dose (2000 Joules/cm^3) irradiation at 77K suppresses both bands. Upon annealing, both bands recover with nearly equal strength at 110K, as shown in curve B of Fig. 2. The recovery is essentially complete by 200K and the rearrangement process described above again takes place between 230K and 270K.

The production of the $3306cm^{-1}$ and $3367cm^{-1}$ bands under electron irradiation is strongly temperature dependent. Figure 3 shows the production of these two bands versus the irradiation temperature. The bands are not formed when the irradiation takes place at temperatures below 180K. Above 180K the

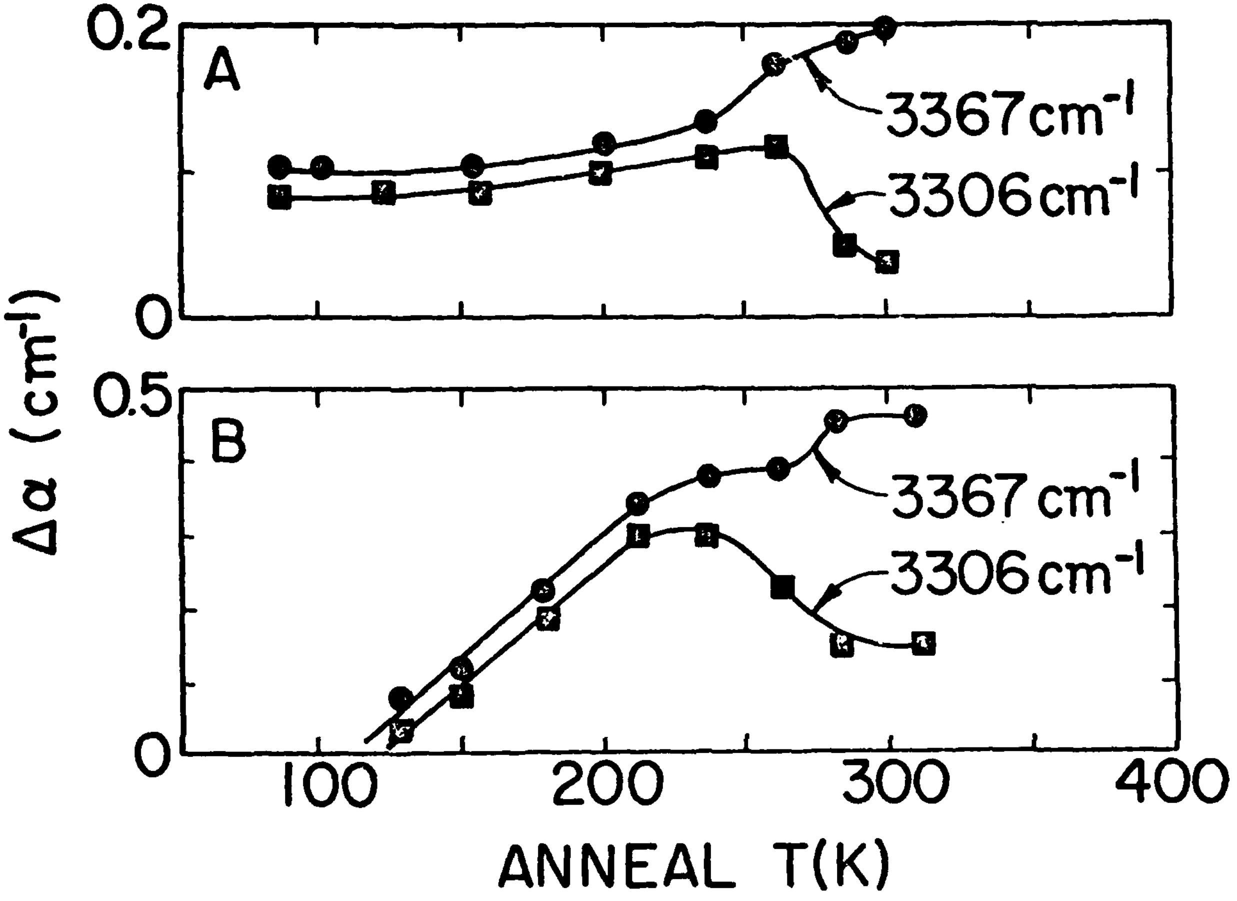


Fig. 2.
The absorption coefficients of the 3306cm^{-1} and 3367cm^{-1} bands are shown as functions of isochronal anneal temperature following a 77K irradiation. Curve A is for a sample irradiated to a dose of 500 Joules/cm^3, and Curve B is for a sample irradiated to a dose of 2000 Joules/cm^3.

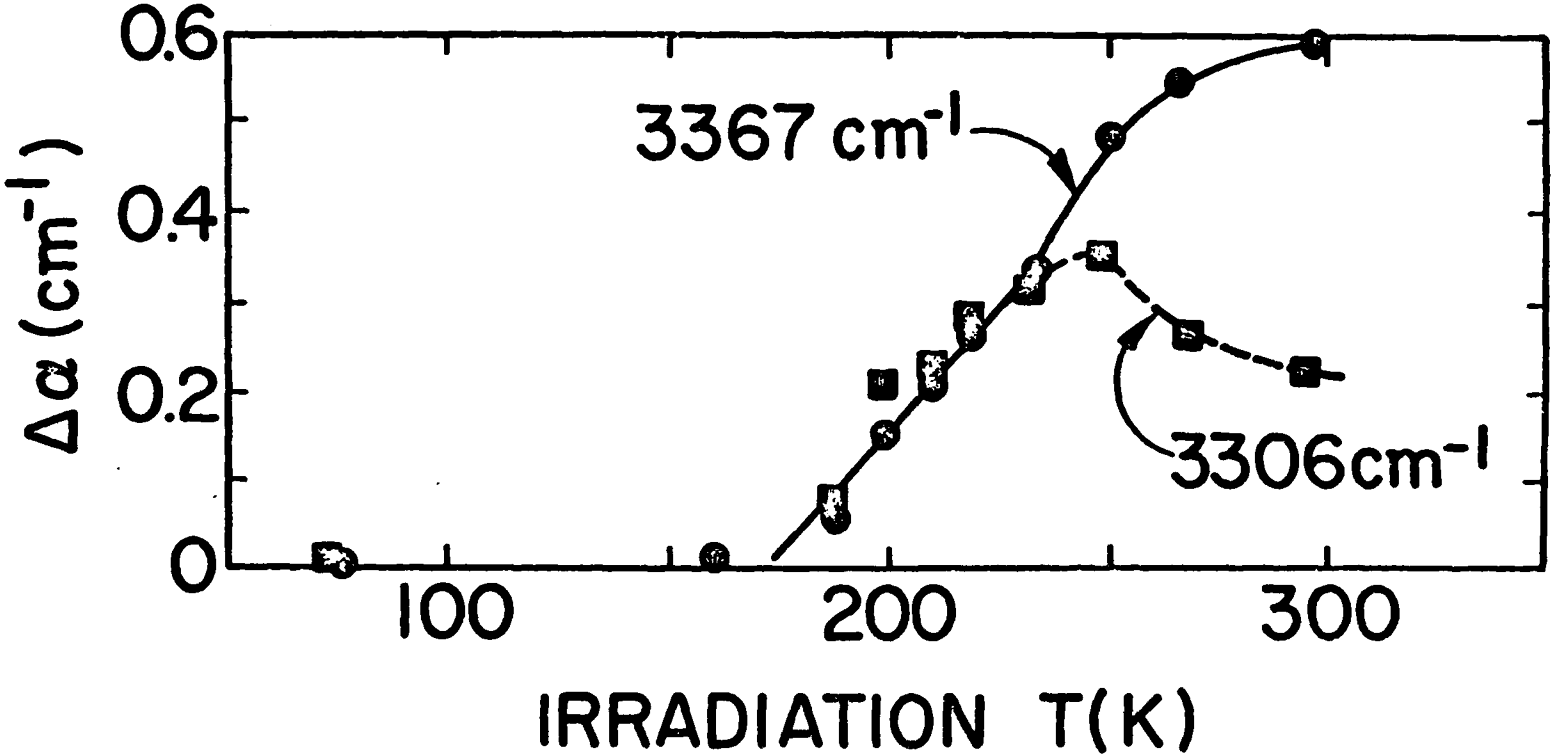


Fig. 3.
The production of the 3306cm^{-1} and 3367cm^{-1} bands as a function of sample temperature during irradiation is shown.

bands grow in with nearly equal intensities up to about 230K. Above this temperature, as mentioned above, the distribution of the defect centers quickly changes to the ratio established by a 300K irradiation.

The high temperature annealing of the irradiation induced $3306cm^{-1}$ and $3367cm^{-1}$ bands is portrayed in Fig. 4. Both bands are stable to 600K and disappear by 740K. In this treatment the crystals were held for 10 min. at temperature and then quenched in liquid nitrogen. After the annealing series was complete, the samples were reirradiated at room temperature. In this case the $3306cm^{-1}$ and $3367cm^{-1}$ bands both reappeared in the same proportion as before annealing. As mentioned above, when samples are irradiated at 300K to relatively higher doses ($2K$ Joules/cm^3), the infrared bands at $3581cm^{-1}$; $3439cm^{-1}$; $3400cm^{-1}$ decrease by about a factor two. Larger doses can eliminate them completely. These bands regain their initial intensity when the irradiated specimens are annealed at 740K.

D. DISCUSSIONS

In the past, excellent research on the infrared absorption of quartz has been done by Kats,[3] Brown and Kahan[9] and Lipson, et al.[14] Kats' work is encyclopedic. He studied a large number of quartz samples, both natural and synthetic, and attempted to correlate their infrared absorption at low temperature with impurities detected by chemical analyses. From this work Kats tentatively identified certain absorption peaks with the presence of alkali and Al^{3+} ions. Many of these same bands were observed by Brown and Kahan[9] in purer samples. Recently Lipson, et al.[14] have found that four bands, $3348cm^{-1}$, $3396cm^{-1}$, $3437cm^{-1}$, and $3581cm^{-1}$, are present in both SARP Electronic Grade and Premium Q specimens. Kats earlier identified bands at $3400cm^{-1}$ as due to OH^- perturbed by Li^+ and at $3581cm^{-1}$ as due to OH^- in the vicinity of K^+. The relative intensities of the bands in Electronic Grade and Premium Q samples

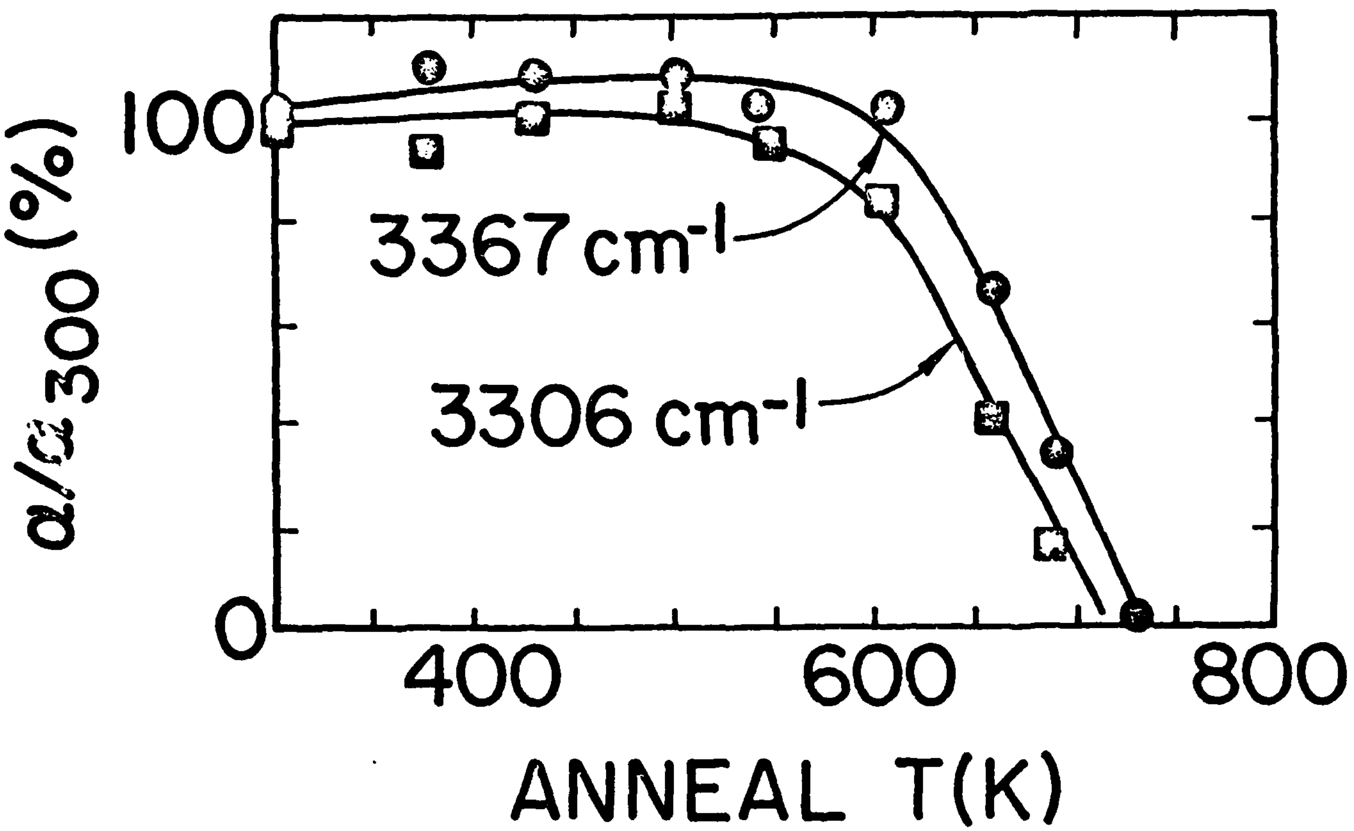


Fig. 4.
The **high** temperature annealing behavior of the 3306cm^{-1} and 3367cm^{-1} bands is shown. The initial absorption coefficients were 0.21cm^{-1} and 0.58cm^{-1}, respectively. The sample was held at each temperature for 10 minutes and then quenched in liquid nitrogen.

are given in Table I. Some caution must be used in evaluating both the absorption and the impurity analyses since Lipson, et al.[14] have illustrated that impurities can be inhomogenously distributed in these crystals. Despite the fact that Kats[7] was tentatively able to identify many of the infrared absorption peaks with the presence of alkali impurity ions such as Na^+ and Li^+, it has not been possible in the purer materials to find evidence of his series of bands. In fact, at this stage it is not possible to identify conclusively any of the bands observed in either the Premium Q or the Electronic Grade samples.

On the other hand, the observation that the OH absorption bands decrease with radiation dose even at 15K indicates that some form of hydrogen is mobile in quartz even at these low temperatures. If this effect was due to only a "local" mobility of the hydrogen or proton, then it might be expected that with warming of the sample the infrared spectrum would return to its pre-irradiated appearance. Since this does not happen until very high temperatures, there must be long-range mobility.

This result is consistent with the EPR studies of Markes and Halliburton[12] on similar samples. They have observed atomic hydrogen, H^o, and several other H related centers following a low temperature irradiation. Their results show that the hydrogen atoms anneal out near 120K but that the other H related EPR centers do not decay until much higher temperatures are reached.

Even though hydrogen may be mobile in a radiation field at low temperatures, alkalis are not. However, there is indirect evidence that alkali atoms are mobile in a radiation field at temperatures above 180K. The absorption bands at $3306cm^{-1}$ and $3367cm^{-1}$ appear with irradiation at temperatures above 180K as shown in Figure 3. Kats[3] postulated that these two bands were due to OH^- ions in the vicinity of Al^{3+} ions with no alkali ions nearby. If this model is correct, then the appearance of the $3306cm^{-1}$ and $3367cm^{-1}$ bands would result from the following process. Alkali ions are near Al^{3+} ions where they act as charge compensators. In a radiation field the alkalis migrate away and are replaced by H^+ ions or holes trapped in the non-bonding orbitals of neighboring oxygen ions.

Markes and Halliburton[12] have found an enhanced production of the $[Al_{e^+}]^o$ center by low temperature irradiation if the sample was first irradiated above 200K. This result is consistent with the model of the high temperature radiation induced motion of the alkali away from the Al^{3+} impurity which then traps an H^+ ion. During the subsequent low temperature irradiation the H^+ is moved away from the Al^{3+} and a hole is trapped there for charge compensation. It is already well known that when crystals are placed in an electric field of 10^3 Volts/cm at 775K these same $3306 cm^{-1}$ and $3367 cm^{-1}$ bands appear.[3] It is believed that alkali ions are "swept" out of the crystals in this process. Thus, it appears that electron irradiation at temperatures above 180K generated alkali atom motion and the resulting affect is much like that produced by the "sweeping" process.

However, the $3306 cm^{-1}$ and $3367 cm^{-1}$ bands do not grow together with radiation as has been suggested in the past. They are probably due to OH^- ions in two different but closely related site symmetries. The fact that the transfer from one site to another occurs so sharply around 240K suggests that a phonon-assisted process is involved. In particular, if a bending or rotational mode of vibration of the $SiOH^-$ or $AlOH^-$ type defects has the appropriate phonon frequency to shift hydrogen from one site to the other site, then this type of sharp transformation might be expected.

The high temperature annealing of irradiated quartz reestablishes the original distribution of hydrogen and alkalis at various sites in the material. This redistribution of hydrogen at high temperatures is not unexpected. Similar behavior is observed in MgO where changes from brucite $Mg(OH)_2$ precipitates to isolated $MgO(OH)_2$ molecules in the lattice occur due to various heat treatments.[15]

The irradiated quartz samples were also investigated for visible and ultraviolet absorption. Some workers in the past have attributed the smokey quartz coloration to so-called $[Al_{e^+}]^o$ trapped centers[16] mentioned earlier. In our investigation of both Electronic and Premium Q SARP samples no smokey coloration is observed. Nassau and his collaborators[17] have indicated in the past that there is no connection between the Al-hole centers and visible absorption.

Jones and Embree[18] recently suggested a correlation between a luminescence band and the presence of oxygen vacancies which were detected by means of ultraviolet absorption. We have not observed any increase in the UV absorption for the radiation doses used in our experiments. For the 1.6 MeV electrons and doses of up to 2000 Joules/cm^3 only very few radiation oxygen vacancies would be produced. It is planned to irradiate to the higher doses needed to produce oxygen vacancies and to look for the associated UV absorption and luminescence.

E. <u>SUMMARY</u>

In summary we have found the following:

1. The OH^- infrared bands in quartz are strongly temperature dependent. Consequently, they must be studied at temperatures of 77K or below.

2. Prolonged low temperature irradiation suppresses all of the OH bands. They recover upon annealing to 740K.

3. Irradiation at room temperature lowers the original OH bands and produces a strong band at 3367cm^{-1} and a less intense band at 3306cm^{-1}. A subsequent irradiation at 77K switches these two bands to a nearly equal intensity. Upon annealing they recover their original strengths near 240K.

F. REFERENCES

1. C. Audoin and J. Vanier, J. Phys. E. 9, 697 (1976).
2. A. Kats and Y. Haven, Phys. and Chem. of Glasses 1, 99 (1960).
3. A. Kats, Phillips Research Reports 17, 133 (1962).
4. R. A. Weeks, Phys. Review 130, 570 (1963).
5. D. M. Dodd and D. B. Fraser, J. Phys. and Chem. Solids 26, 673 (1965).
6. D. B. Fraser, Physical Acoustics, (Ed. W. P. Mason), Vol. 5, Chapter 2, Academic Press, New York, 1968.
7. J. H. Mackey, J. W. Boss and D. E. Wood, J. Magnetic Resonance 3, 44 (1970).
8. J. A. Weil, Radiation Effects 26, 261 (1975).
9. R. N. Brown and A. Kahan, J. Phys. and Chem. Solids 36, 467 (1975).
10. G. B. Krefft, Radiation Effects 26, 249 (1975).
11. E. Sonder and W. A. Sibley, Point Defects in Solids, (Ed. J. H. Crawford and L. M. Slifkin), Vol. 1, Chapter 4, Plenum Press, New York, 1973.
12. M. Markes and L. E. Halliburton, to J. Appl. Phys. (December, 1979).
13. J. B. Bates and R. A. Perkins, Phys. Review 1316, 3713 (1977).
14. H. G. Lipson, F. Euler and A. F. Armington, "Low Temperature Infrared Absorption of Impurities in High Grade Quartz," Proceedings, 32nd Annual Symposium on Frequency Control, U.S. Army Electronics Command, Fort Monmouth, New Jersey, pp. 11-23 (1978).
15. B. Henderson and W. A. Sibley, J. Chem. Phys. 55, 1276 (1976).
16. R. Schnadt and J. Schneider, Phys. Kunden-Materie 11, 19 (1970).
17. K. Nassau and B. E. Prescott, Phys. Stat. Sol. (a)29, 259 (1975); Mineralogical Magazine 41, 301 (1977); Am. Mineralogist 62, 589 (1977) and 63, 230 (1978).
18. C. E. Jones and D. Embree, J. Appl. Phys. 47, 5365 (1976).

V. ELECTRON SPIN RESONANCE

A. INTRODUCTION

Because of its piezoelectric properties, quartz has many applications in electronic instrumentation. Examples range from crystal-controlled oscillators and SAW-device filters for use in communication links to temperature and mass-measuring instruments. In many cases, such as precision oscillators in satellites, the operation of quartz-containing devices can be degraded by radiation.[1-3] Thus, the defect structure of crystalline SiO_2 is a subject of considerable importance.

Fundamental studies of radiation-induced effects in quartz began with the work of Weeks[4] on the oxygen-vacancy-associated trapped electron center (E_1' center) and the work of Griffiths et al.[5] on the aluminum-associated trapped hole center (now known as the $[A\ell_{e^+}]^o$ center). The initial work by Weeks on the E_1' center was extended by Silsbee,[6] who determined the g matrix and the ^{29}Si hyperfine matrices. More recently, the excellent theoretical work of Feigl, Fowler, and Yip[7] has provided insight to the electronic and ionic structure of the E_1' center. For the $[A\ell_{e^+}]^o$ center, O'Brien[8] successfully interpreted the magnetic resonance data in terms of a model having a hole trapped primarily in a non-bonding orbital of an oxygen ion adjacent to the substitutional aluminum. The comprehensive review by Weil[9] describes additional work on the aluminum-associated hole centers.

All quartz, natural or synthetic, contains aluminum substituting for silicon and thus charge compensators, the most common of which are H^+, Li^+ and Na^+ interstitial ions, are always present. It is expected that these interstitial ions will play a direct role in the response of quartz to radiation, and this expectation has been born out by many experiments. Anderson and Weil,[10] and later Mackey,[11] studied Li^+ and Na^+-associated electron-like germanium centers in quartz. More complex $GeHLi_2$ and GeH_3 centers have been reported by Weil[12] and Laman and Weil,[13] respectively. Mackey[11] and Mackey _et al._[14] have characterized a family of $[Al_{e^+}/M^+]^+$ centers where M^+ represents an interstitial cation. These latter centers were created below room temperature when a radiation-produced hole is stabilized adjacent to the complex formed by a substitutional aluminum ion and its neighboring H^+, Li^+ or Na^+ interstitial charge compensator. Additional complexities in the kinetics of defect formation and annealing in quartz, including secondary reactions, have been amply demonstrated by Mattern _et al._[15]

Quartz has relatively large c-axis channels along which the interstitial ions can move. Kats,[16] making use of this characteristic of quartz, applied an electric field parallel to the c-axis while maintaining the sample temperature in the 400°C to 550°C range and succeeded in "sweeping" hydrogen and alkali interstitial ions into and out of the sample. Since charge neutrality must be maintained, if one species is removed from the sample another similarly charged species must be taken into the sample. This technique of changing the relative concentration of hydrogen and alkali ions by sweeping has been subsequently used by many investigators and has proven extremely useful in defect identification studies. More importantly, sweeping prior to fabrication has been reported[3] to increase the radiation hardness of quartz resonators used in precision oscillators.

In the present investigation, we have used the electron spin resonance (ESR) technique to obtain information about defect formation, anneal, and migration effects in quartz. The samples studied were all commercially-available high-quality quartz, thus making our results directly applicable to device operation. A number of previously unreported defects have been observed and their production and decay properties are described. However, the major portion of the paper is concerned with the radiation-induced mobility of interstitial Na^+ ions. In as-received unswept quartz grown using sodium carbonate as the mineralizer, the majority of aluminum ions are charge-compensated by neighboring interstitial Na^+ ions. If irradiations are performed at temperatures above 200 K, these interstitial Na^+ ions are removed from the aluminum sites and $[Al_{e^+}]^o$ centers are created. Subsequent heating of the samples to above 600 K causes these interstitial alkali ions to return to the aluminum sites. The radiation-induced mobility of the interstitial hydrogen ions occurs at lower irradiation temperatures, even at 77 K, in contrast to the 200 K onset of radiation-induced mobility of the interstitial Na^+ ions. As an application of these results, we describe a sensitive testing procedure for measuring the extent to which the interstitial Na^+ ions have been removed from a synthetic quartz sample by the sweeping process.

B. EXPERIMENTAL PROCEDURE

The synthetic crystals of α-quartz used in this study were purchased from Sawyer Research Products[17] after being grown by the hydrothermal process using sodium carbonate as the mineralizer (a small amount of lithium carbonate was also included in the solution). The crystals were received in the form of lumbered bars ($1.5 \times 1.8 \times 17.7$ cm^3) containing only pure Z-growth material. Magnetic resonance samples ($2 \times 3 \times 8$ mm^3) for use in the individual experiments were then cut from the bars with a diamond saw.

Sawyer produces Electronic Grade and Premium Q quartz, and swept and unswept samples of both types of material were included in this investigation. All sweeping of samples (except one sample described in Sec. III) was done by Sawyer and both SARP I and SARP II processes were represented. The autoclave run numbers and the sweeping run numbers and dates, as supplied by Sawyer, are given in Table II for our lumbered quartz bars. Each bar is specified as either Electronic Grade or Premium Q by the label EG or PQ, respectively. Different bars of the same class are then distinguished by a letter and different samples cut from the same bar are distinguished by a number. For example, crystal EG-E37 is the 37th small sample to be cut from the Eth bar of Electronic Grade material.

The first two bars listed in Table II EG-E and EG-F, are from a single original bar which had been cut in half by Sawyer, with one-half being swept and the other half remaining unswept. Similarly, bars PQ-E and PQ-F are from a Premium Q bar which had been cut in half and only one part swept. These two pair-bars, half swept and half unswept, provide a direct means to characterize the effect of the Sawyer sweeping process.

All the irradiations were 4 minutes in duration and used 1.7 MeV electrons from a Van de Graaff accelerator. The current on the sample was approximately 0.2 $\mu A/cm^2$. During a 77 K irradiation, the sample was immersed directly in liquid nitrogen. For an intermediate temperature irradiation, the sample was placed in a styrofoam tube and nitrogen gas of the chosen temperature was passed by the sample. Following each irradiation, the sample was either returned to, or kept at, 77 K and then placed in a spring-loaded Delrin sample holder while remaining under liquid nitrogen. The sample and holder were quickly transferred into a liquid nitrogen-filled finger Dewar which, in turn, was inserted in a Varian V-4531 rectangular cavity. All the ESR spectra described in this paper were taken at 77 K.

The ESR spectrometer used in this work consisted of a home-built homodyne microwave bridge (operating at 9.133 GHz) and a 9-inch Fieldial-regulated Varian magnet. The magnetic field modulation frequency was 100 kHz. A Varian Variable Temperature Accessory V-4557 was used for the thermal anneal studies below room temperature. The sample was removed from the microwave cavity and heated in a separate furnace for each step of the anneals above room temperature. An NMR proton probe and microwave frequency counter were used to measure the g values.

C. IMPURITY ANALYSIS

A limited number of samples were analyzed for impurity content and the results, expressed in μg/g, are presented in Table III Atomic absorption

TABLE II. Autoclave and sweep run identification numbers as supplied by Sawyer for quartz samples used in the present investigation.

BAR	AUTOCLAVE RUN	SWEEP RUN
EG-E	E 1-8	unswept
EG-F	E 1-8	I/A May 23, 1975 Bar No. I3A
EG-C	unknown	unswept
EG-D	E 42-9	M/D Jan. 18, 1978 Bar No. M18D
PQ-E	K 19-5	unswept
PQ-F	K 19-5	H/Y May 31, 1978 Bar No. H6Y

TABLE III. Impurity analysis (μg/g) of Electronic Grade and Premium Q quartz grown by Sawyer. (Analysis was done by the Analytical Chemistry Division at Oak Ridge National Laboratory.)

	Li	Na	K	Aℓ	Fe
			Atomic Absorption		
PQ-E2	<1	3.4	<1	<10	<10
EG-E37	<1	7.6	2	<10	<10
EG-E43	<1	<1	<1	<10	<10
			Mass Spectroscopy		
PQ-E3				7	70
EG-E39				2	30
EG-E42				3	20

was used to monitor Li, Na, K, Aℓ, and Fe in the samples PQ-E2, EG-E37, and EG-E43. The dominant alkali impurity in these samples was Na, while Li was below the limits of detectability in all three samples. The sample EG-E43 was swept at Oklahoma State University prior to the impurity analysis, which explains the reduction in Na and K content relative to sample EG-E37. This particular sweep was done in vacuum at 530°C with graphite electrodes and consisted of 15 hours at 1500 volts/cm and another 18 hours at 1850 volts/cm. Presumably, this sweeping replaced the alkalis in sample EG-E43 with hydrogen initially present either in the graphite electrodes or in the residual atmosphere.

Mass spectroscopy was used to determine the Aℓ and Fe content of the samples PQ-E3, EG-E39, and EG-E42, none of which had been swept. The results show that the aluminum concentration in the Premium Q sample was greater than in the two Electronic Grade samples, which agrees very well with the ratio of the maximum $[A\ell_{e+}]^0$ center concentration induced by radiation (see Table V) in the PQ-E and EG-E samples. The consistency in the relative aluminum concentration as determined by mass spectroscopy and electron spin resonance is reassuring. On the other hand, the atomic absorption and mass spectroscopy values for Fe content are not in agreement and, furthermore, no electron spin resonance spectra due to Fe^{3+} have been observed before or after irradiation.

Also of interest, infrared absorption in unswept samples from these same bars shows that the EG-E samples contain approximately 2-3 times more OH^- ions than the PQ-E samples. Thus, the OH^- content correlates, to first order, with the alkali content.

D. RESULTS

In quartz, many of the electron-like paramagnetic defects have very long spin-lattice relaxation times at 77 K and thus are difficult to observe with a homodyne ESR spectrometer operating in the absorption mode. At the beginning of this investigation, it was found that these defects with long spin-lattice relaxation times would give reasonably intense signals if the spectrometer's phase-sensitive detector were adjusted "out-of-phase". On the other hand, the hole-like centers invariably have very short spin-lattice relaxation times at 77 K and can easily be observed with an "in-phase" setting of the spectrometer. Figure 5 shows the "in-phase" and "out-of-phase" response for the as-received unswept Electronic Grade sample EG-E37 irradiated at 77 K and maintained at this low temperature. No ESR signals were observed in this or any of the other samples before irradiation.

The "in-phase" and "out-of-phase" responses in Fig. 5 contain previously unreported ESR spectra. One of these unidentified spectra is hole-like and has been designated U-1 in Fig. 5a. This notation is arbitrary and only meant to be used until a model, and thus a more precise label, can be assigned to the defect. Additional unlabeled and unidentified hole-like spectra occur in Fig. 5a. Several electron-like spectra tentatively labeled U-2, U-3, and U-4 are found in Fig. 5b. The U-2 and U-3 spectra both exhibit a doublet nature strongly suggestive of a hyperfine interaction with a 100% abundant $I = 1/2$ nucleus. The doublet separation when the magnetic field is parallel to the c-axis is 13.6 gauss and 5.7 gauss for the U-2 and U-3 centers, respectively. The U-4 spectrum appears as a broadened single line in Fig. 5b but may actually be a slightly-split doublet or may be overlapped by one or more lines from different spin species such as the E_1' and E_2' centers. Another spectrum present in the sample following irradiation at 77 K but not shown in Fig. 5 is the widely-split doublet due to atomic hydrogen.[18] The c-axis g values for the unidentified centers as well as other previously-identified paramagnetic centers found in Sawyer quartz are tabulated in Table IV.

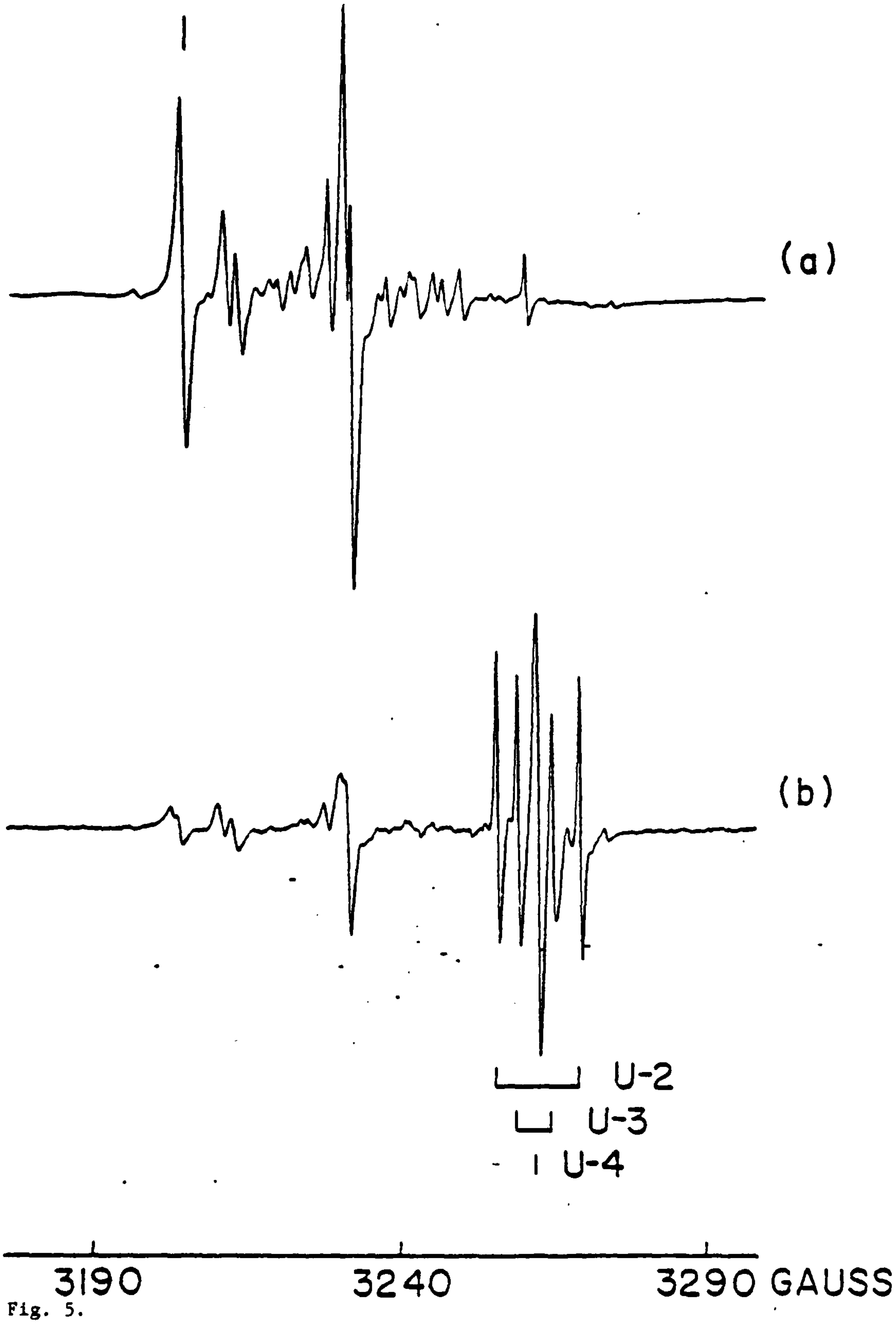


Fig. 5.
(a) "In-phase" response and (b) "out-of-phase" response of the ESR spectrometer for unswept Electronic Grade sample EG-E37 following the initial irradiation at 77K.

TABLE IV The c-axis g values for paramagnetic defects produced by electron irradiation of Sawyer synthetic quartz. The first three centers have been previously observed. The last four centers are reported in this paper for the first time and remain to be identified.

CENTER	g_c
$[\mathrm{A}\ell_e{+}]^o$	2.0183
E_2'	2.0005
E_4'	2.0011
U-1	2.0379
U-2	2.0005
U-3	2.0008
U-4	2.0005

As illustrated in Fig. 5 a number of paramagnetic defects were created by the initial irradiation of the as-received unswept Electronic Grade sample at 77 K; however, all except one of these centers were destroyed by warming the sample to room temperature. Figure 6 shows the thermal stability of these various defects during a series of 5 minute pulse anneals at progressively higher temperatures. The monitoring temperature during this sequence was 85 K. In this particular sample, EG-E37, a very few $[A\ell_{e^+}]^o$ centers were created by the initial low temperature irradiation and they thermally decayed between 90 K and 110 K as did the unidentified hole center U-1. In this same temperature range, 90-110 K, the hydrogen atom H^o and the U-3 signals grew as the U-2 signal decreased. The hydrogen atom, H^o, was thermally destroyed between 115 K and 135 K while at the same time, the U-2 and U-3 centers both increased. The U-2 and U-3 centers finally disappeared over the 135 K to 170 K temperature range. Very little change in the U-4 spectrum was observed between 77 K and room temperature.

After the initial 77 K irradiation, a subsequent irradiation at room temperature of this same unswept Electronic Grade sample (EG-E37) produced the "in-phase" and "out-of-phase" responses shown in Fig. 7 The spectrum in Fig. 7a is due to the $[A\ell_{e^+}]^o$ center while the spectra in Fig. 7b are attributed to the E_2' center[19] and the E_4' center.[20-22] These same three spectra are also found in other similar samples that have received only the room temperature irradiation and not the initial 77 K irradiation. The c-axis g values for these three centers are given in Table IV.

Following the initial 77 K irradiation and subsequent room temperature irradiation, the unswept Electronic Grade sample EG-E37 was then re-irradiated at 77 K. The "in-phase" responses of the spectrometer following each of the three irradiations are shown in Fig. 8 for comparison. The dominant feature of this irradiation sequence is the large enhancement of the $[A\ell_{e^+}]^o$ center

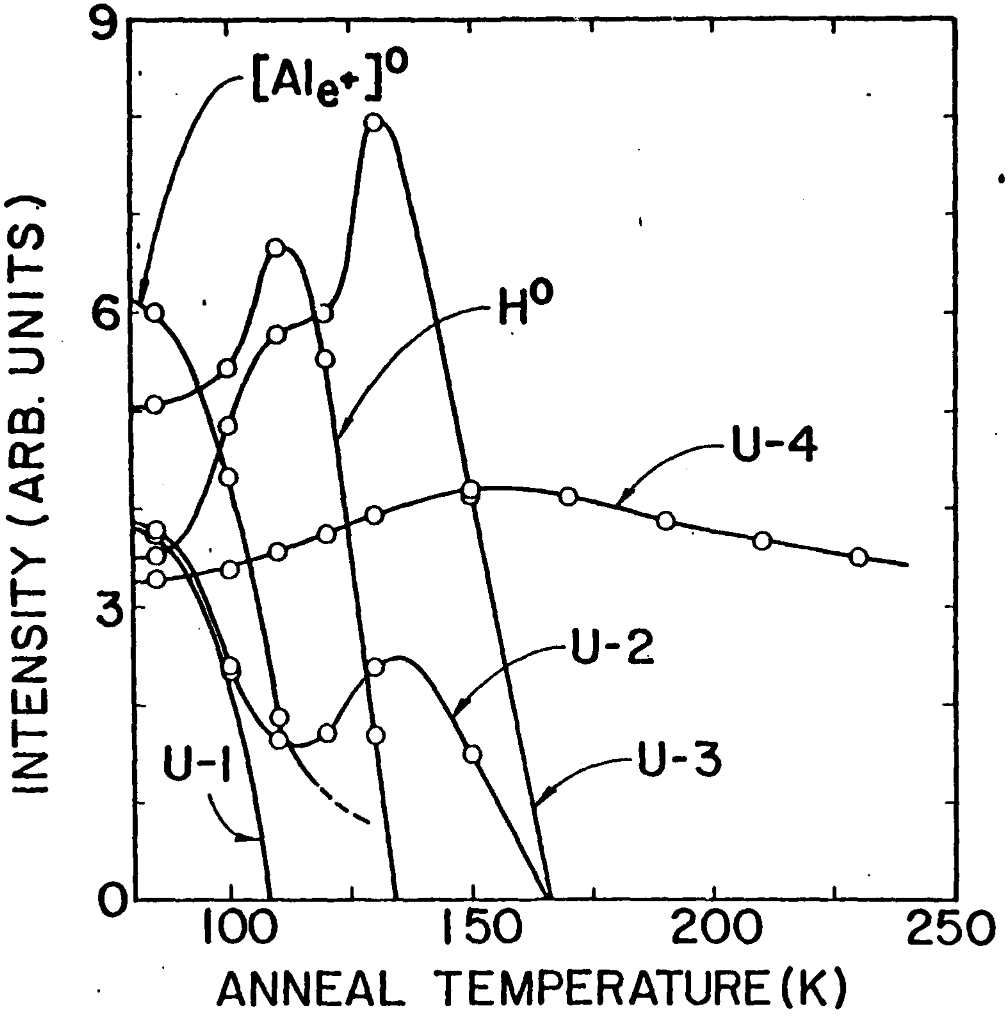


Fig. 6.
Pulsed thermal anneal of unswept Electronic Grade sample EG-E37 following the initial irradiation at 77 K. The pulse durations were 5 minutes and the monitoring temperature was 85 K.

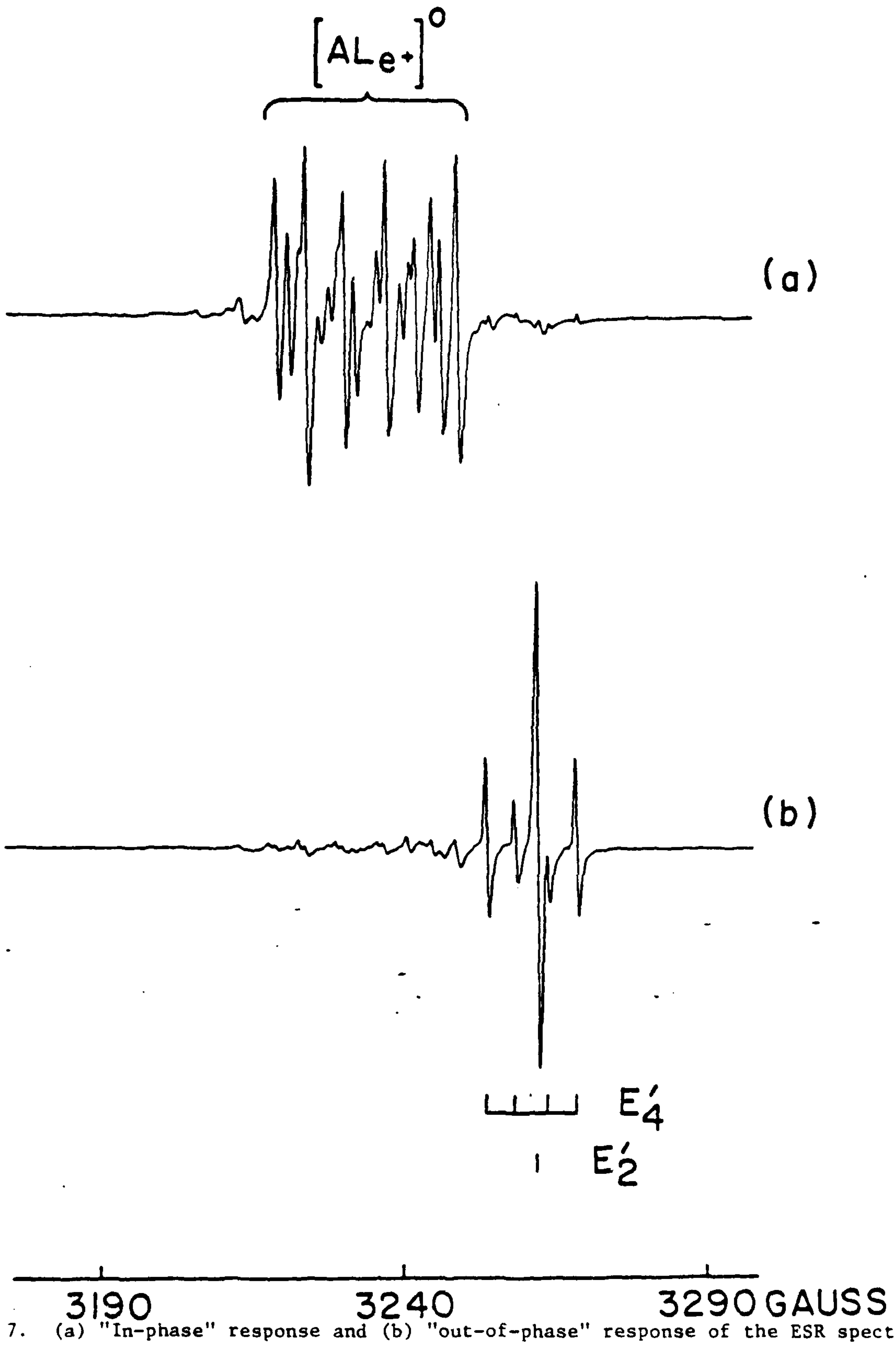


Fig. 7. (a) "In-phase" response and (b) "out-of-phase" response of the ESR spectrometer for unswept Electronic Grade sample EG-E37 following irradiation at room temperature.

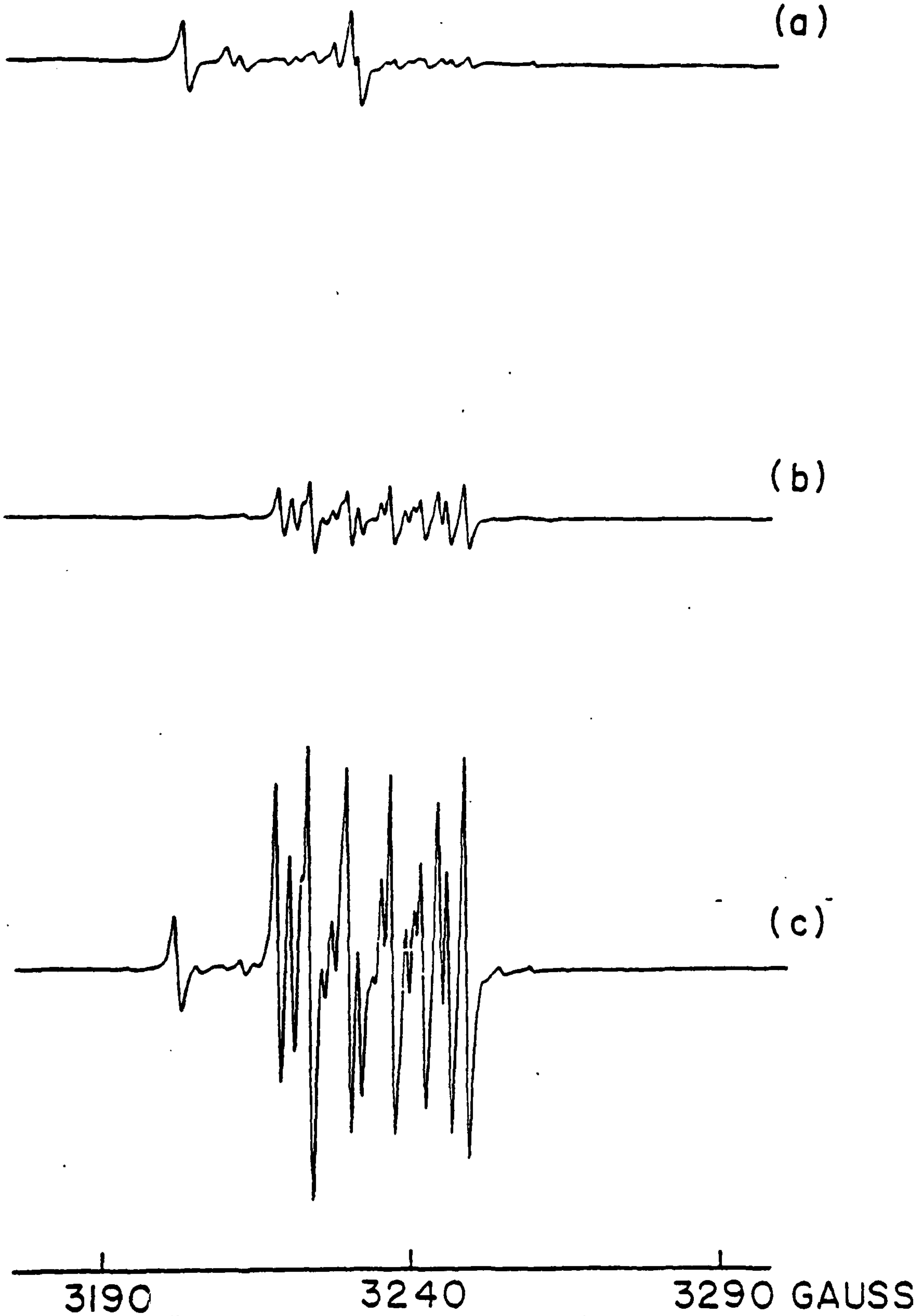


Fig. 8. "In-phase" response of the ESR spectrometer for unswept Electronic Grade sample EG-E37 after each irradiation in the following series; (a) irradiation at 77 K with no previous irradiation, (b) irradiation at room temperature, and (c) re-irradiation at 77 K. All three traces were taken with identical spectrometer setting.

concentration by the room temperature irradiation and the further increase during the second 77 K irradiation. A pulse anneal of sample EG-E37 following this second 77 K irradiation gave the results shown in Fig. 9 The atomic hydrogen center H^{0} and the U-1, U-2, and U-3 centers show the same behavior during this anneal as in the initial anneal described in Fig. 6 The major new features are the appearance of the E_2' and E_4' centers above 20 K and the failure of the $[\mathrm{A}\ell_{e^+}]^{0}$ centers to disappear.

An as-received Electronic Grade sample (EG-F12) which had been swept by Sawyer gave quite different results when subjected to the same sequence of irradiations as the unswept sample EG-E37. These two samples were taken from the separate halves, half swept and half unswept, of an original single bar and thus, any major differences in their behavior must be attributed to the sweeping process. Figure 10 shows the "in-phase" and "out-of-phase" spectrometer responses following the initial 77 K irradiation, the subsequent room temperature irradiation, and finally the second 77 K irradiation. The initial 77 K irradiation produced a factor of 25 increase in the $[\mathrm{A}\ell_{e^+}]^{0}$ center concentration in the swept sample EG-F12 (Fig. 10a) as compared to the unswept sample EG-E37 (Fig. 8a). The production of $[\mathrm{A}\ell_{e^+}]^{0}$ centers in the two samples was very similar for the room temperature irradiation (Figs. 8b and 10c) and the second 77 K irradiation (Figs. 8c and 10e). The production of the U-1, U-2, U-3, U-4, E_2' and E_4' centers was also very similar in the swept and unswept samples as shown in Fig. 5b Fig. 7b and Figs. 10b, d, and f.

The enhancement of the $[\mathrm{A}\ell_{e^+}]^{0}$ center concentration by room temperature irradiation is also observed in the unswept Premium Q sample PQ-E5 as illustrated in Fig. 11. The "in-phase" responses of the spectrometer following the initial 77 K irradiation, the subsequent room temperature irradiation, and finally the second 77 K irradiation are shown in Figs. 11a, b, and c, respectively.

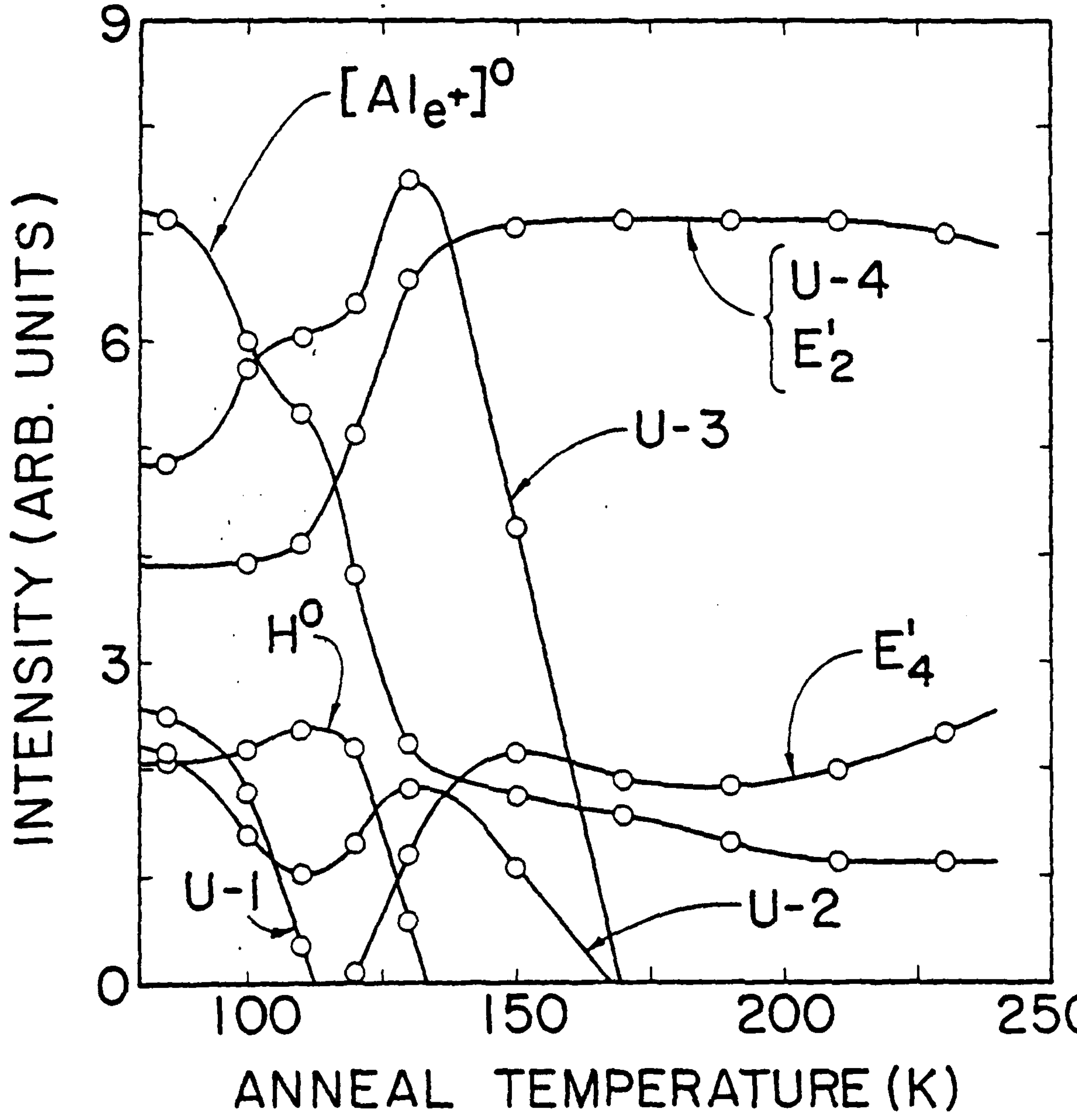


Fig. 9. Pulsed thermal anneal of unswept Electronic Grade sample EG-E37 after being irradiated at room temperature and then re-irradiated at 77 K. The pulse durations were 5 minutes and the monitoring temperature was 85 K.

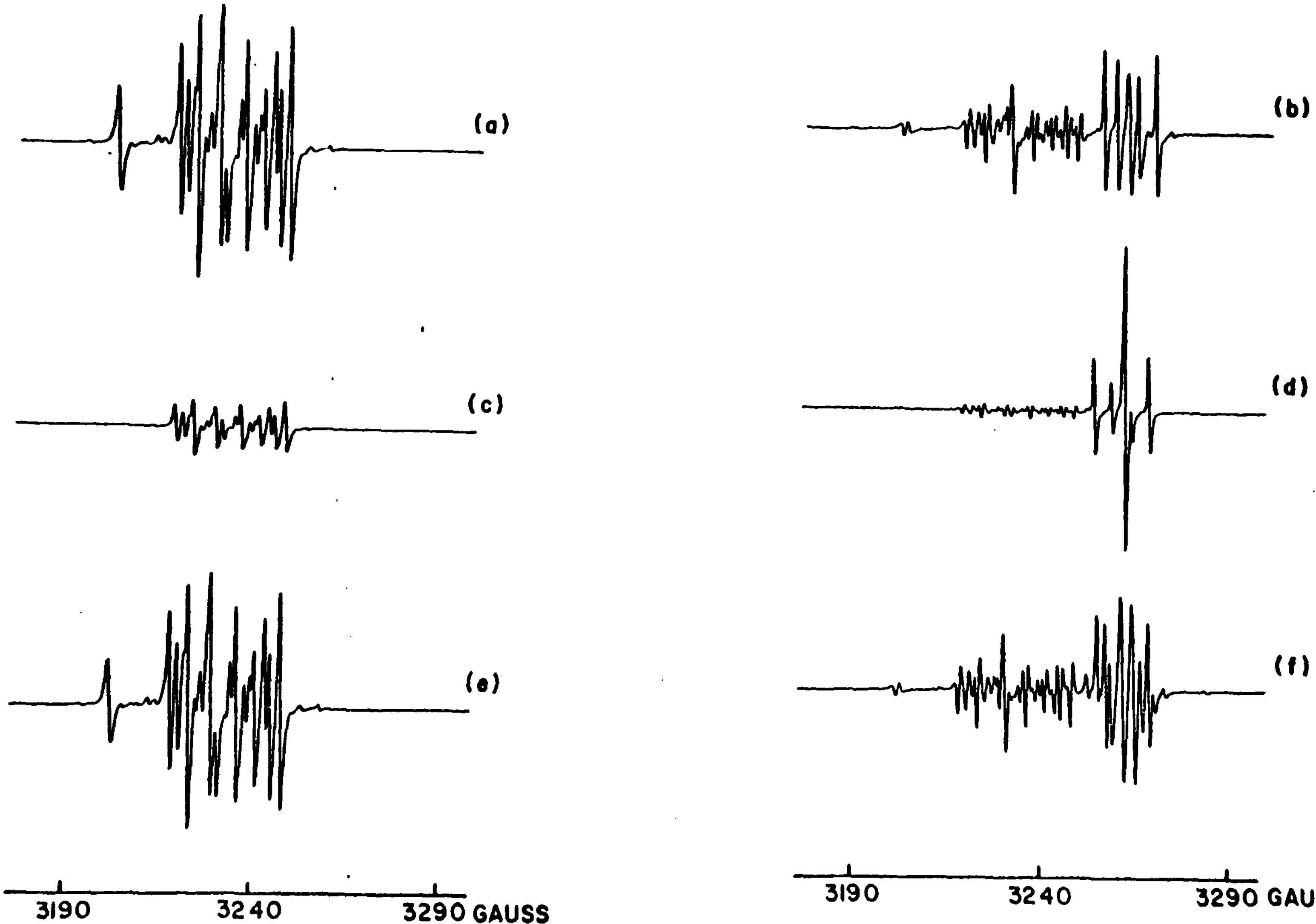


Fig 10. ESR spectra from Sawyer-swept Electronic Grade sample EG-F12. (a) "In-phase" and (b) "out-of-phase" response follow irradiation at 77 K with no previous irradiation. (c) "In-phase" and (d) "out-of-phase" response following irradiation at rc temperature. (e) "In-phase" and (f) "out-of-phase" response following re-irradiation at 77 K. All "in-phase" traces were ta with the same spectrometer settings and all "out-of phase" traces were taken with the same spectrometer settings.

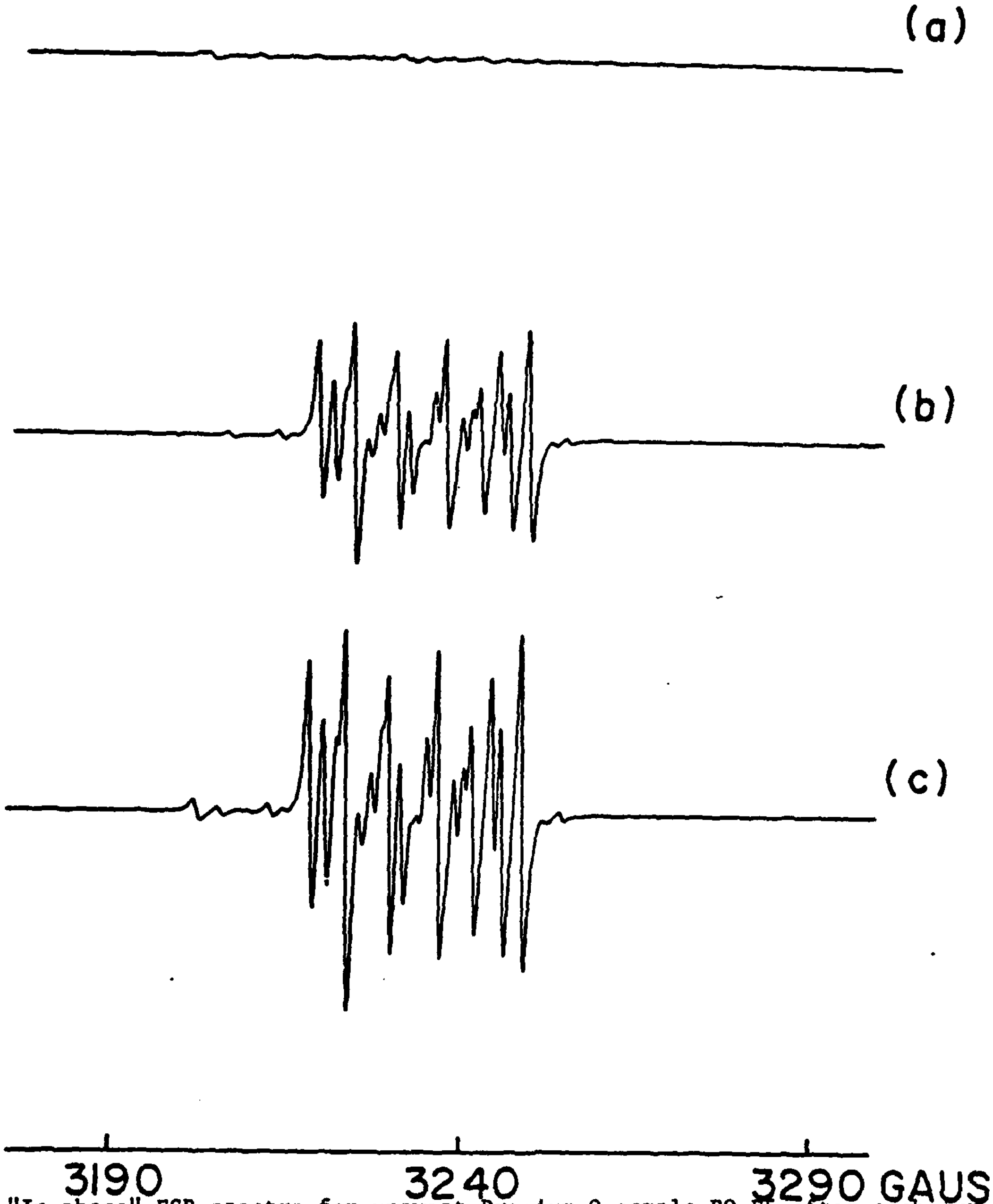


Fig. 11. "In-phase" ESR spectra for unswept Premium Q sample PQ-E5 after each irradiation in the following series; (a) irradiation at 77 K of a previously unirradiated sample, (b) irradiation at room temperature, and (c) re-irradiation at 77 K. All spectrometer settings remained the same for the three traces.

When subjected to the same sequence of irradiations, the swept Premium Q sample PQ-F10, whose "in-phase" responses are shown in Fig. 12 exhibited an $[\mathrm{A}\ell_{e^+}]^0$ center production similar to the swept Electronic Grade sample EG-F12.

In addition to the previously described Electronic Grade and Premium Q samples, another unswept Electronic Grade sample (EG-C4) and a swept Electronic Grade sample (EG-D2) were cycled through the sequence of three irradiations and anneals. The relative concentration of the $[\mathrm{A}\ell_{e^+}]^0$ centers following each step in the sequence is tabulated in Table V for each of the six samples examined in detail. None of the six samples had received any radiation prior to the beginning of the sequence described in Table V. From this data, it is clear that the number of $[\mathrm{A}\ell_{e^+}]^0$ centers produced by the initial irradiation at 77 K (STEP 1) of as-received samples is strongly dependent on whether the samples are swept or unswept. Following the second 77 K irradiation (STEP 4), all of the samples, whether swept or unswept, are at or near their maximum $[\mathrm{A}\ell_{e^+}]^0$ center concentration. Thus, for unswept samples, both Electronic Grade and Premium Q, an intermediate room temperature irradiation leads to an enhanced $[\mathrm{A}\ell_{e^+}]^0$ center concentration following the second 77 K irradiation.

A series of irradiations at progressively higher temperatures between 77 K and 300 K determined the critical temperature range needed in order for the intermediate temperature irradiation to enhance the production of $[\mathrm{A}\ell_{e^+}]^0$ centers by the second 77 K irradiation in unswept samples. The results for the unswept Electronic Grade sample EG-E34 are shown in Fig. 13 Following each irradiation between 77 K and 300 K, the unswept sample was returned to 77 K and reirradiated to insure filling all electron traps before measuring the $[\mathrm{A}\ell_{e^+}]^0$ center ESR spectrum. It is the intensity of this 77 K irradiation-produced $[\mathrm{A}\ell_{e^+}]^0$ center spectrum which is plotted versus intermediate irradiation temperature in Fig. 13 The onset of $[\mathrm{A}\ell_{e^+}]^0$ center enhancement

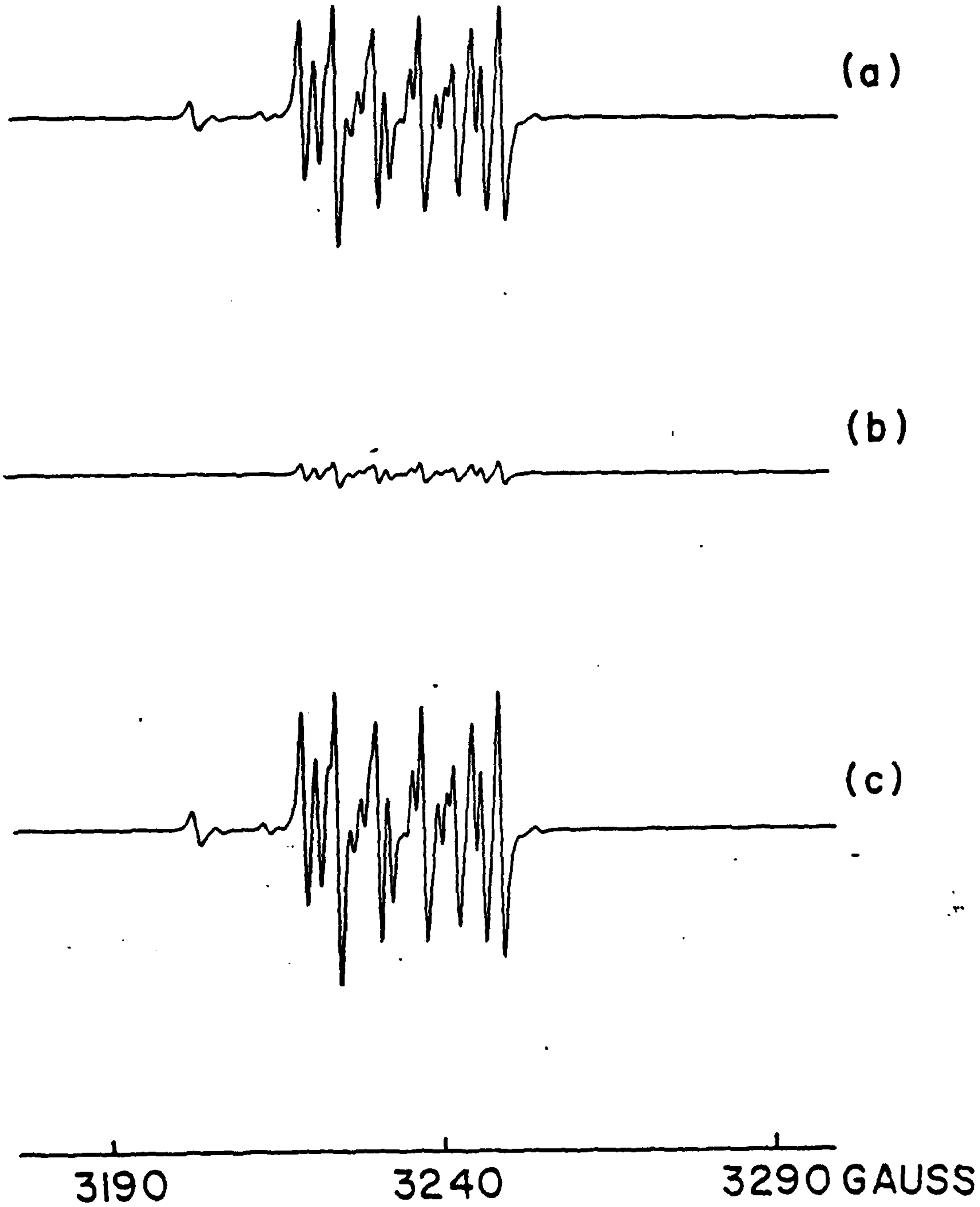


Fig. 12. "In-phase" ESR spectra for Sawyer-swept Premium Q sample PQ-F10 after each irradiation in the following series; (a) irradiation at 77 K of a previously unirradiated sample, (b) irradiation at room temperature, and (c) re-irradiation at 77 K. All spectrometer settings remained the same for the three traces.

TABLE V. Relative concentration of the $[Al_{e^+}]^o$ centers as determined by ESR following each step of a sequence of irradiations and thermal anneals. One unit is approximately 4 x 10^{13} unpaired spins.

	EG-E37 (unswept)	EG-F12 (swept)	EG-C4 (unswept)	EG-D2 (swept)	PQ-E5 (unswept)	PQ-F10 (swept)
STEP 1 Irradiate at 77 K.	6	153	28	418	4	330
STEP 2 Anneal to room temperature.	0	12	7	48	1	44
STEP 3 Irradiate at room temperature.	29	33	23	50	311	33
STEP 4 Irradiate at 77 K.	180	141	188	331	496	413
STEP 5 Anneal to room temperature.	42	18	93	74	281	75

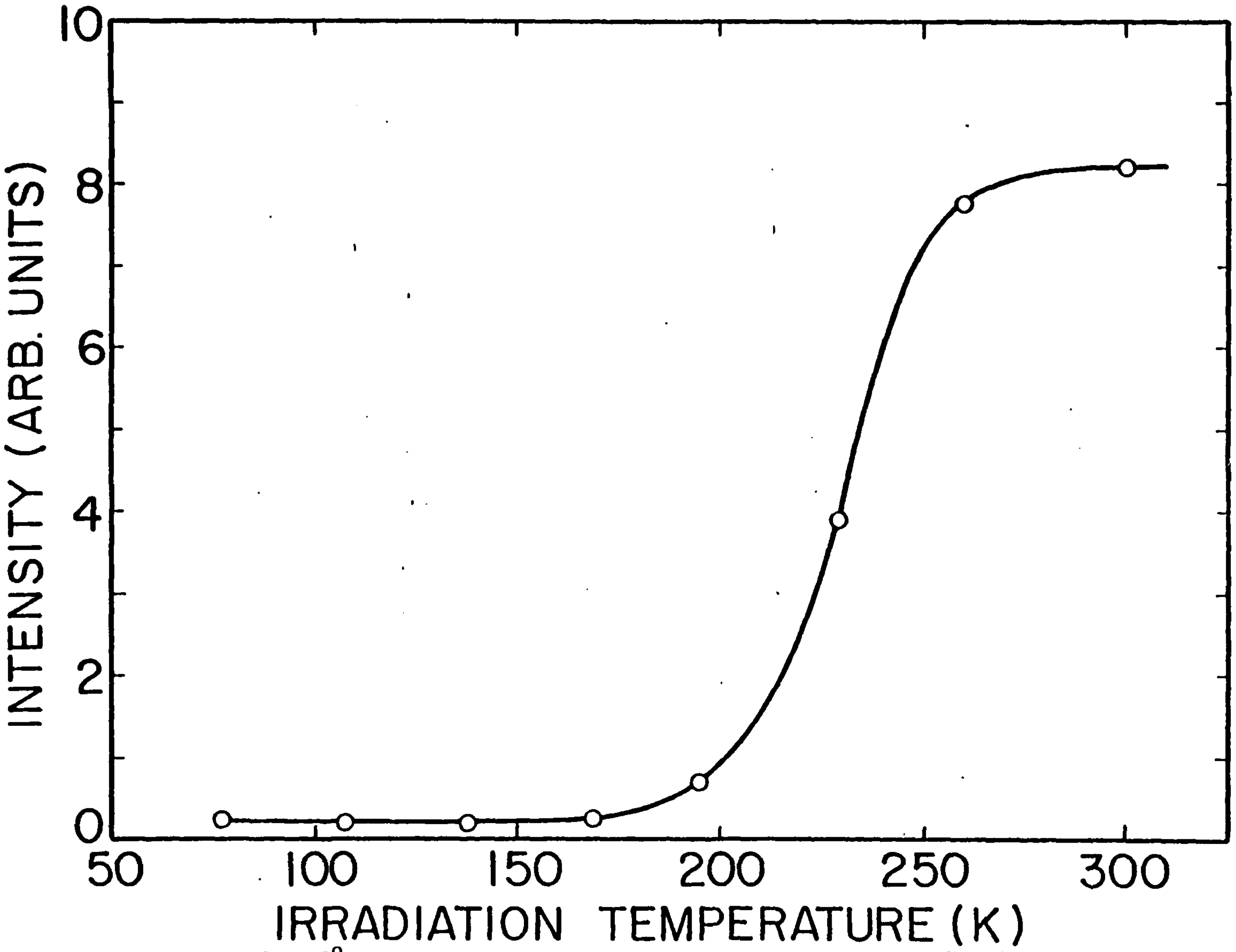


Fig. 13. Concentration of $[Al_{e^+}]^o$ centers as a function of irradiation temperature for the unswept Electronic Grade sample EG-E34.

in the unswept samples occurs for intermediate irradiations above 200 K.

To determine if the unswept samples could be returned to the as-received state (i.e., where $[\mathrm{A}\ell_{e^+}]^0$ centers are not easily created by 77 K irradiations) after being irradiated at room temperature, a sequence of high temperature anneals and re-irradiations were carried out. The results are shown in Fig. 14 for the unswept Electronic Grade sample EG-E38. This sample was first irradiated at room temperature and then irradiated at 77 K to establish an initial monitoring value for the $[\mathrm{A}\ell_{e^+}]^0$ center concentration (corresponding to the 295 K data point in Fig. 14). A series of 15 minute anneals at progressively higher temperatures followed. After each anneal step, the sample was re-irradiated at 77 K and the number of $[\mathrm{A}\ell_{e^+}]^0$ centers was monitored. The greatest rate of decrease in the production of $[\mathrm{A}\ell_{e^+}]^0$ centers by the 77 K irradiation occurred after the anneals in the 575 K to 675 K temperature range as shown in Fig. 14. In order to insure that isolated aluminum impurity ions were present in the lattice before each high-temperature anneal, the sample was always re-examined at 77 K after being warmed to room temperature. These additional steps in the sample treatment sequence confirmed that the 90-130 K thermal anneal stages of the $[\mathrm{A}\ell_{e^+}]^0$ centers, as shown in Figs. 6 and 9, had occurred.

E. DISCUSSION

Our experimental studies of the radiation response of high-quality synthetic quartz have provided a number of useful results. These can be grouped into the following four general categories: (1) previously unreported radiation-induced defects have been observed; (2) detailed thermal annealing behavior of defects in the 77-300 K range has been determined; (3) the phenomenon of radiation-induced mobility of interstitial ions in quartz has been established; and (4) a sensitive testing procedure to evaluate completeness of the sweeping process has been found.

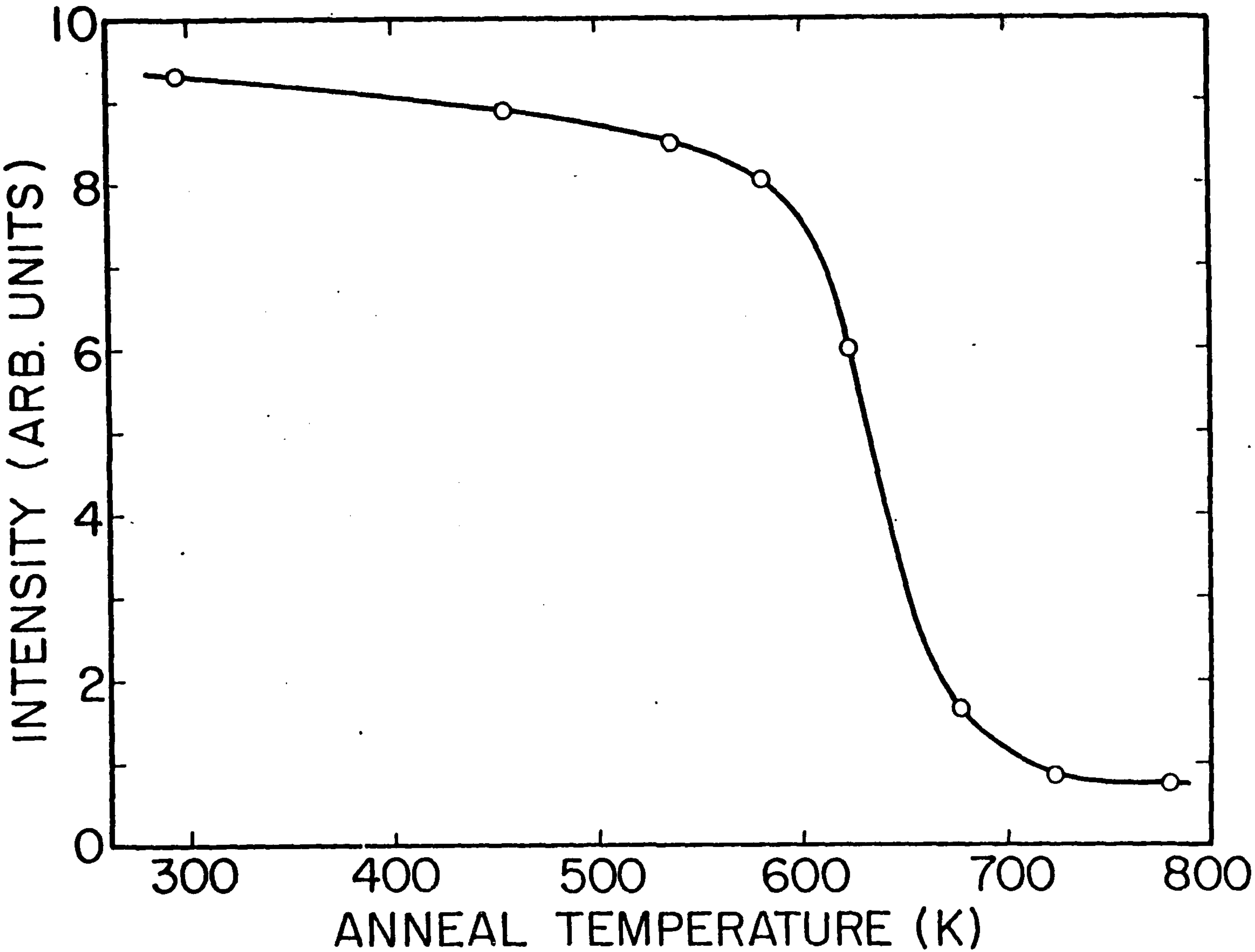


Fig. 14. Effect of high-temperature annealing on production of $[A\ell_e+]^o$ centers by 77 K irradiation for the unswept Electronic Grade sample EG-E38.

Four previously unreported centers, labeled U-1, U-2, U-3, and U-4, are shown in Fig. 5 and their g_c values are given in Table IV. The U-1 center has a hole-like g value and is one of the major defects produced by 77 K irradiations in both Electronic Grade and Premium Q quartz. Preliminary angular studies indicate that the U-1 center is an S = 1/2 spin system; but there are no easily-observable hyperfine lines to help establish a detailed model for the defect. The U-2 and U-3 centers have electron-like g values and their doublet nature suggests a hyperfine interaction with a 100% abundant I = 1/2 nucleus. Hydrogen is a good candidate for this nucleus, especially when one considers the existence of the hydrogen-related E_2' and E_4' spectra having very similar g values. In a more general sense, it is tempting to speculate that the U-2, U-3, and U-4 centers are all oxygen-vacancy-related defects in direct analogy with the E' family of oxygen-vacancy defects.

There are three temperature regions of interest in the thermal anneal results shown in Figs. 6 and 9 90 K to 110 K, 120 K to 130 K, and 140 K to 160 K. The slight growth of the H^o center (atomic hydrogen) in the 90-110 K range has been observed in a number of Sawyer samples. In this same temperature range the U-2 centers decrease and the U-3 centers increase, suggestive of a conversion of one center into the other. The $[A\ell_{e^+}]^o$ and U-1 centers, both hole-like, also decrease in the 90-110 K range with a further decrease of the $[A\ell_{e^+}]^o$ center in the 120-130 K range. In the 120-130 K range, the atomic hydrogen centers completely decay while both the U-2 and U-3 centers increase. This suggests that mobile hydrogen can be trapped at already-existent defects and, thereby, convert them into either U-2 or U-3 centers. This supports our earlier contention that the U-2 and U-3 centers are hydrogen-related.

Quite striking effects were discovered while monitoring the ESR spectrum of the $[A\ell_{e^+}]^o$ centers during the sequence of irradiations and thermal anneals described in Sec. D. The relative concentration of the $[A\ell_{e^+}]^o$ centers following each step of the sequence is given in Table V for six Sawyer samples, four Electronic Grade and two Premium Q. From the table, it is easy to distinguish between swept and unswept samples by simply noting the $[A\ell_{e^+}]^0$ center concentration after STEP 1 (77 K irradiation of a previously unirradiated sample). The three unswept samples had very few $[A\ell_{e^+}]^0$ centers. After STEP 4 in the sequence, the six samples were similar in that they all contained large numbers of $[A\ell_{e^+}]^0$ centers.

We offer the following simplified interpretation of the data summarized in Table V. In the as-received unswept Sawyer samples (EG-E37, EG-C4, and PQ-E5), the majority of substitutional aluminum ions were charge-compensated by an adjacent interstitial Na^+ ion. The initial 77 K irradiation (STEP 1) of the unswept samples failed to produce many $[A\ell_{e^+}]^0$ centers because of the presence of the interstitial Na^+ ion near the aluminum.

However, the intermediate room temperature irradiation (STEP 3) caused the interstitial Na^+ ions to become mobile and migrate far away from the aluminum ions. Since the aluminum ions no longer had a neighboring Na^+ ion during the second 77 K irradiation (STEP 4), they each easily trapped a hole and gave rise to a large $[A\ell_{e^+}]^0$ center ESR spectrum. On the other hand, in the as-received Sawyer-swept samples (EG-F12, EG-D2, and PQ-F10), the sweeping process had already removed the interstitial alkali ions from the aluminum sites and replaced them with hydrogen ions. Infrared results on OH^- molecules[23] and ESR results on hydrogen atoms both demonstrate that hydrogen is mobile under irradiation at 77 K. Thus, the initial 77 K irradiation (STEP 1) of the swept samples removed the hydrogen from the aluminum sites and allowed large numbers of $[A\ell_{e^+}]^0$ centers to be immediately formed without the need for an intermediate room temperature irradiation.

The data in Fig. 14 show that the interstitial Na^+ ions can be returned to the aluminum sites by simply heating the samples to the 575-675 K temperature region. At these high temperatures, the $[\mathrm{A}\ell_{e^+}]^0$ centers have been thermally destroyed, thus leaving isolated $\mathrm{A}\ell^{3+}$ ions in the lattice, and the Na^+ ions have been released from possible trapping sites. The resulting electrostatic attraction of the $\mathrm{A}\ell^{3+}$ and Na^+ ions within the lattice when combined with the increased diffusion rate of the interstitials at higher temperatures leads to a rapid recombination of the two ions (i.e., restoration of the sample to its as-received condition). In contrast to the unswept behavior characterized in Fig. 14 Sawyer-swept samples did not show the decrease in $[\mathrm{A}\ell_{e^+}]^0$ center production (for 77 K irradiations) when heated to 773 K, and this agrees with the lack of alkali ions in such material.

A most important feature of the present investigation was the failure to observe the $[\mathrm{A}\ell_{e^+}/\mathrm{M}^+]^+$ centers described by Mackey.[11] For example, in our as-received unswept quartz, a large concentration of $\mathrm{A}\ell^{3+}$-Na^+ centers are present but the initial 77 K irradiation produced no observable $[\mathrm{A}\ell_{e^+}/\mathrm{Na}^+]^+$ centers. Also, in our swept samples, large numbers of $\mathrm{A}\ell^{3+}$-OH^- centers are present but 77 K irradiations produced no $[\mathrm{A}\ell_{e^+}/\mathrm{H}^+]^+$ centers. These results support the contention of Mackey[11] that the germanium-doped quartz, in which he observed the $[\mathrm{A}\ell_{e^+}/\mathrm{M}^+]^+$ centers, behaves differently than the undoped quartz. Also, as was the case with the undoped samples studied by Mackey, we have been unable to identify the major electron traps in the Sawyer quartz. Although large numbers of hole centers are easily created in our samples, a corresponding number of electron centers cannot be observed. The only clearly identified electron trap is the hydrogen atom, but it thermally decays near 125 K while many of the hole centers are stable above room temperature. The remaining possibilities in our spectra are the E' centers. However, it is not clear whether E' centers are electron or hole traps since it is not known whether the oxygen vacancies normally trap two electrons or no electrons and, at any rate, our samples contained far to few E' centers to account for all the trapped electrons created by the radiation.

Besides providing a more fundamental understanding of the radiation response of synthetic quartz, the present investigation also has practical application with regard to sweeping. The onset of the radiation-induced mobility of interstitial Na^+ ions above approximately 200 K provides a method for evaluating the extent to which these alkali ions have been removed from a crystal by the sweeping process. This evaluation procedure would consist of examining the $[A\ell_{e^+}]^o$ center ESR spectrum after each step of the following sequence of three irradiations; initial 77 K irradiation, room temperature irradiation, and re-irradiation at 77 K. For a sample in which the sweeping process is complete (i.e., all the alkalis have been replaced by hydrogen), the $[A\ell_{e^+}]^o$ center ESR spectrum will have the same intensity after the first 77 K irradiation as after the second 77 K irradiation. In the case of a partially-swept sample, the ratio of the $[A\ell_{e^+}]^o$ center ESR spectrum intensity after the first 77 K irradiation to that after the second 77 K irradiation is a sensitive indicator of what fraction of interstitial Na^+ ions have been replaced by hydrogen ions. In this sweeping evaluation procedure, the intermediate room temperature irradiation is, of course, a crucial step. This technique for evaluation of completeness of sweeping has given consistent results for every Sawyer-grown quartz sample we have investigated and we believe it to be valid for any synthetic quartz grown using sodium carbonate as the mineralizer. We cannot yet generalize the result to all quartz since it is not known whether interstitial Li^+ ions will become mobile at the same temperature as the Na^+ ions when the sample is subjected to a radiation field.

F. SUMMARY

Interstitial ions, both sodium and hydrogen, have been shown to play a crucial role in the radiation response of synthetic quartz. By using the electron spin resonance (ESR) technique, we have determined that the number and nature of irradiation-induced defects depend strongly on the irradiation temperature and previous "sweeping" treatments. In unswept Sawyer Electronic Grade and Premium Q samples, interstitial Na^+ ions originally trapped adjacent to substitutional $A\ell^{3+}$ ions become mobile if the irradiation temperature is above 200 K. Sawyer-swept samples have the interstitial Na^+ ions replaced with hydrogen, in the form of OH^- molecules, and irradiation at temperatures as low as 77 K causes the hydrogen to become mobile. The mobility of the interstitial ions is deduced, in both cases, by monitoring the intensity of the $[A\ell_{e^+}]^0$ centers as a function of irradiation temperature. The sodium and hydrogen interstitial ions have substantially different temperatures for onset of their radiation-induced mobility and this forms the basis of a sensitive method for testing completeness of the sweeping process, at least in quartz grown using sodium carbonate as the mineralizer.

In addition to the radiation-induced mobility of the interstitial ions, a number of previously unreported paramagnetic defects have been observed during the present investigation, and their production and decay properties have been described. Finally, insight into the transient and steady-state radiation response of quartz-containing devices has been obtained from detailed thermal annealing experiments in the 77-300 K range.

G. REFERENCES

1 J. C. King and H. H. Sander, IEEE Trans. on Nuc. Sci. NS-19, 23 (1972).

2. T. M. Flanagan, IEEE Trans. on Nuc. Sci. NS-21, 390 (1974).

3. F. Euler, P. Ligor, A. Kahan, P. Pellegrini, T. M. Flanagan, and T. F. Wrobel, IEEE Trans. on Nuc. Sci. NS-25, 1267 (1978).

4. R. A. Weeks, J. Appl. Phys. 27, 1376 (1956).

5. J. H. E. Griffiths, J. Owen, and I. M. Ward, Defects in Crystalline Solids (London, 1955), Bristol Conference, p. 88, Physical Soc.

6. R. H. Silsbee, J. Appl. Phys. 32, 1459 (1961).

7. F. J. Feigl, W. B. Fowler, and K. L. Yip, Solid State Commun. 14, 225 (1974); K. L. Yip and W. B. Fowler, Phys. Rev. B 11, 2327 (1975).

8. M. C. M. O'Brien, Proc. Roy. Soc. (London) A231, 404 (1955).

9. J. A. Weil, Rad. Effects 26, 261 (1975).

10. J. H. Anderson and J. A. Weil, J. Chem. Phys. 31, 427 (1959).

11. J. H. Mackey, J. Chem. Phys. 39, 74 (1963).

12. J. A. Weil, J. Chem. Phys. 55, 4685 (1971).

13. F. C. Laman and J. A. Weil, Physics of SiO_2 and Its Interfaces (Yorktown Heights, New York, 1978), Conference Proceedings, p. 253 (Pergamon Press).

14. J. H. Mackey, J. W. Boss, and D. E. Wood, J. Magn. Res. 3, 44 (1970).

15. P. L. Mattern, K. Lengweiler, and P. W. Levy, Proceedings of the 27th Annual Frequency Control Symposium, June, (1973).

16. A. Kats, Phillips Res. Repts. 17, 133 (1962).

17. Sawyer Research Products, Inc., 35400 Lakeland Blvd., Eastlake, Ohio 44094.

18. R. A. Weeks and M. Abraham, J. Chem. Phys. 42, 68 (1965).

19. R. A. Weeks, Phys. Rev. 130, 570 (1963).

20. R. A. Weeks and C. M. Nelson, J. Am. Ceram. Soc. 43, 399 (1960).

21. L. E. Halliburton, B. D. Perlson, R. A. Weeks, J. A. Weil, and M. C. Wintersgill, Solid State Commun. 30, 575 (1979).

22. J. Isoya, J. A. Weil, and L. E. Halliburton, to be published.

23. W. A. Sibley, J. J. Martin, M. C. Wintersgill, and J. D. Brown, J. Appl. Phys. 50, 5449 (1979).

VI. ACOUSTIC LOSS

A. INTRODUCTION

The application of quartz in electronic devices such as oscillators and filters is growing steadily. Precision quartz devices are increasingly used in aerospace and other applications where they may be exposed to ionizing radiation.[1-3] These applications highlight the need for information on both transient and steady state radiation effects in quartz. In this study, we investigate the role of the Al-Na center (i.e., a substitutional Al^{3+} coupled with an adjacent interstitial Na^{+}) on the radiation response of the internal friction, Q^{-1}, in 5 MHz 5th overtone AT cut synthetic quartz resonators. The results will be compared with the parallel infrared (IR) studies by Sibley *et al.*[4] and electron paramagnetic resonance (ESR) studies by Markes and Halliburton.[5]

The principal defect in synthetic quartz which is grown hydrothermally is an aluminum atom substituting for a silicon atom. This substitutional Al ion leads to a charge imbalance which is compensated by either an interstitial alkali ion or by a proton on a non-bonding p orbital of an adjacent oxygen. The Al probably comes from the natural quartz nutrient while the charge compensators may come from either the nutrient or the Na_2CO_3 or NaOH mineralizer. The interstitial ions are usually in the relatively large Z-axis channels and at high temperatures can move along the channel under an applied electric field. King,[6] and later Kats[7] used this characteristic to "sweep" hydrogen and alkali ions into and out of quartz. Since charge neutrality must be maintained, if one species is removed, it must be replaced by another. This technique of changing the relative concentration of alkali and hydrogen ions has been used by many investigators and has proven extremely useful in defect identification studies. More recently, the removal of Na by sweeping prior to resonator fabrication, has been reported to increase the radiation hardness of quartz crystals used in precision oscillators.[8]

These interstitial ions have been shown to affect the performance of the 5 MHz 5th overtone AT cut resonators commonly used in precision oscillators. For example, King[6] and Fraser[10] have shown that the Al-Na center is responsible for the acoustic loss peak which occurs near 50 K. These interstitial ions also play a direct role in the response of quartz to ionizing radiation. Irradiation of a resonator at room temperature removes the 50 K Na loss peak[6,11] and causes a corresponding frequency shift. The Al-Na center also shows dielectric loss peaks.[12,1

Recent infrared studies by Sibley et al.[4] and ESR studies by Markes and Halliburton[5] on well characterized synthetic quartz show that in the presence of an ionizing radiation field hydrogen is mobile at all temperatures; but that sodium and, probably, the other alkalis are mobile only at temperatures above 200 K. They found that irradiation of unswept quartz at temperatures above 200 K produced infrared bands at 3367 cm^{-1} and 3306 cm^{-1} which can be attributed[7] to an unperturbed center formed from an Al^{3+} charge compensated by a H^{+} ion associated with a non-bonding orbital on a neighboring oxygen. This Al-OH center, which can also be produced by sweeping,is thought to be formed by replacing an interstitial alkali with the hydrogen. Following an initial irradiation at 77 K and a subsequent irradiation above 200 K, a third irradiation of the sample at 77 K gave an enhanced production of the unperturbed aluminum hole center, $[\mathrm{Al}_e+]^o$, over that caused by the initial low temperature irradition in the case of unswept samples. Samples which have been swept to replace the alkalis by hydrogen show the enhanced $[\mathrm{Al}_e+]^o$ centers production upon the first low temperature irradiation. An initial low temperature irradiation of unswept quartz usually produces a small $[\mathrm{Al}_e+]^o$ concentration because the Al-alkali center is stable in the presence of the radiation. Above 200 K, the center is unstable and the alkali is replaced by a hydrogen to form the Al-OH center which is then readily broken up by a subsequent low temperature irradiation. We present here a parallel study of the effect of ionizing radiation on the 50 K Na loss peak in 5 MHz 5th overtone AT cut resonators fabricated from unswept and Na swept synthetic quartz. The results show that the Al-Na center is stable under irradiation at temperatures below 200 K. Between 200 K and 250 K, the Na interstitial becomes mobile in the presence of the radiation field as shown by the disappearance of the loss peak. This disappearance strongly correlates with the production of the Al-OH and $[Al_{e^+}]^o$ centers. We also present a technique for directly sweeping the AT cut resonators.

A. EXPERIMENTAL PROCEDURE

The resonators used in this study were fabricated from synthetic pure Z growth lumbered bars of both Electronic Grade and Premium Q quartz purchased from Sawyer Research Products. Circular plano-convex AT cut 5 MHz 5th overtone resonators were fabricated from the bars either by Kansas Crystals or by K-W Manufacturing according to the specifications given by Fraser.[9] Optical samples were also cut from the bars for infrared characterization.

The internal friction, Q^{-1}, and series resonant frequency of the resonators were measured as a function of temperature by the log decrement method.[9] The measurements were made in a variable temperature helium Dewar with the resonators initially mounted horizontally in a gap holder similar to the one described by Fraser. This system which had no mechanical attachments to the crystal gave very high Q values below 20 K. In order to perform irradiations *in situ* with a horizontal radiation source it was necessary to devise an angled mounting. Since this mounting often led to poor thermal contact, small tabs were epoxy cemented to the edge of the resonator and the tabs were then clamped in the holder. This mounting technique gives a fairly constant Q value below 20 K but did not significantly alter the resonator performance at the higher temperatures.

In the log decrement method the resonator is driven for 10 ms at its series resonant frequency and then allowed to freely decay. The decaying rf signal was detected with a superheterodyne detector and displayed on a variable persistence storage oscilloscope. The exponential decay times were measured using a window detector to gate a digital timer.

Irradiations were carried out with the resonators mounted in the Dewar with either 1.7 MeV electrons from a Van de Graaff accelerator or with 50 kV x-rays. Typical doses were approximately 2000 J/cm^3 ($\sim 10^8$ rads). This dose is not expected to produce significant amounts of knock-on damage, but it has been shown to saturate the impurity related defects[4,5] such as the Al-OH and $[Al_{e^+}]^o$ centers.

The two methods described below were used to sweep or electrodiffuse Na into and out of our samples. A Premium Q bar from Sawyer autoclave run D14-45 was first swept in an Ar atmosphere, then a layer of Na_2CO_3 was vapor deposited, and the sweeping run was repeated. Infrared studies at 77 K on an optical sample from this bar show the presence of the Al-OH center after Na sweeping as determined by the presence of the 3367 cm^{-1} and 3306 cm^{-1} bands.[4] However, these bands increased by approximately 20% when the sample was irradiated at room temperature. This result suggests that the bar contained approximately 1.7×10^{16} cm^{-3} Al-OH centers[7] and 3×10^{15} cm^{-3} Al-Na centers after the second sweeping run.

Sweeping was also carried out directly on AT cut resonators fabricated from Electronic Grade bar EG-S. In this process, NaCl was deposited on the flat side of the plano-convex resonator. The resonator was then mounted in a graphite holder with a platinum foil between the flat NaCl coated side and the positive electrode. The electrolysis was carried out in vacuum with an applied potential of 450 V for 24 hours. This potential gave an electric field resolved along the Z axis of approximately 2100 V/cm. The same procedure with the NaCl coating and the platinum foil omitted was used to sweep the alkalis out of the resonator. A room temperature irradiation of an optical sample cut from bar EG-S followed by an IR scan at 77 K indicated that the bar contained approximately $9 \times 10^{16} cm^{-3}$ Al-OH centers after the irradiation. If the Na sweeping was completely effective the resonator should then have $9 \times 10^{16} cm^{-3}$ Al-Na centers.

C. RESULTS AND DISCUSSION

Since the 50 K acoustic loss peak in 5 MHz 5th overtone AT cut resonators is known to be due to the presence of the Al-Na center,[8] it was decided directly to investigate the radiation induced mobility of the Na interstitial which had been suggested by the temperature dependence of the radiation production of Al-OH and $[Al_{e^+}]^o$ centers.

The as received Q^{-1} spectrum of a resonator fabricated from the Na swept Premium Q bar, D14-45DC is shown in Fig. 15 A Q^{-1} spectrum taken on a resonator fabricated from an unswept bar from the same autoclave run does not show the 50 K Na loss peak. The spectra for successive irradiations at 77 K, 215 K and 300 K are also shown. The loss peak is unchanged by the 77 K irradiation, significantly reduced by the 215 K irradiation and completely removed by the 300 K irradiation. This sequence of irradiations clearly shows the removal of the Al-Na center over the same temperature range where the IR[4] and EPR[5] results show the Al-OH and $[Al_{e^+}]^o$ centers grow in.

A more detailed variable temperature irradiation sequence was carried out on an unswept Electronic Grade resonator, EG-S7(1), which contained substantially more Na than the Na swept Premium Q resonator. The Q^{-1} spectrum was measured from 5 to 100 K in the as-received condition and after <u>in situ</u> irradiations with a 50 kV x-ray source at temperatures of 180 K, 200 K, 220 K and 250 K. The results show that the Na loss peak was only slightly

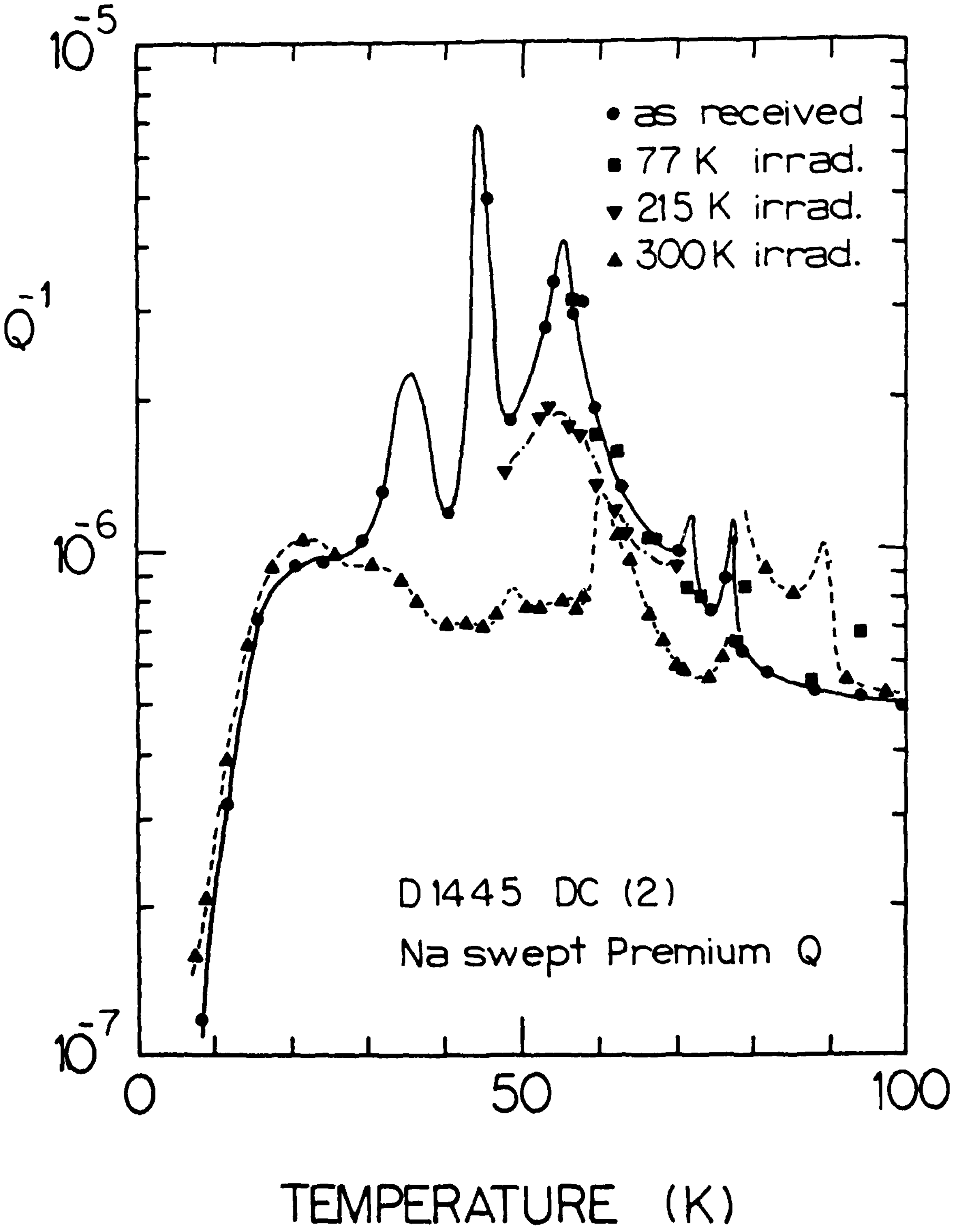


Fig. 15. The acoustic loss spectrum of a Na swept Premium Q resonator, D1445DC, is shown in the as received condition and following successive irradiations at 77 K, 215 K and 300 K. The Na loss peak near 50 K is not affected by the 77 K irradiation, but is reduced by the 215 irradiation, and is removed by the 300 K irradiation.

altered by irradiations at temperatures below 200 K. The 220 K irradiation reduced the loss peak to 20% of its original value, and the 250 K irradiation completely removed the loss peak. After the 250 K irradiation the resonator was removed from the cryostat and annealed for 10 minutes at 750 K. This annealing procedure has been shown to remove the Al-OH centers and to restore the sample to its unirradiated condition.[4,5] The 5 to 300 K Q^{-1} spectrum for this resonator after the 250 K irradiation and after the 750 K anneal are shown in Fig. 16. The annealing has completely restored the 50 K Na loss peak. The large loss peaks between 90 K and 180 K which appear to change under irradiation and annealing have not been identified. Similar loss peaks were observed by Capone et al.[8] who attributed them to coupled modes. The loss peak near 270 K may be caused by OH.[9] Table VI summarizes the Na loss peak height versus irradiation temperature for the various resonators and gives the estimated Na concentrations for these resonators.

The above results when combined with the IR studies of Sibley et al.[4] and the EPR studies of Markes and Halliburton[5] suggest the following model for the radiation response of the center formed by the substitutional Al and its Na charge compensators. In unswept quartz the Al-OH center is not present in appreciable quantities before irradiation. This center is produced from the Al-Na center by irradiation if the sample temperature is greater than 200 K. Apparently the Na interstitial becomes mobile under irradiation at these temperatures and moves away from the Al site. Subsequently, a hydrogen is trapped on an adjacent oxygen. Depending upon the number of deep electron traps available, some of the Al sites will trap holes to form $[\mathrm{Al}_{e^+}]^0$ centers rather than the Al-OH centers.[5] Since hydrogen is mobile under irradiation at all temperatures a subsequent low temperature irradiation will replace the Al-OH centers with $[\mathrm{Al}_{e^+}]^0$ centers. It should be noted that an initial low temperature irradiation does not affect the Al-Na centers so the initial

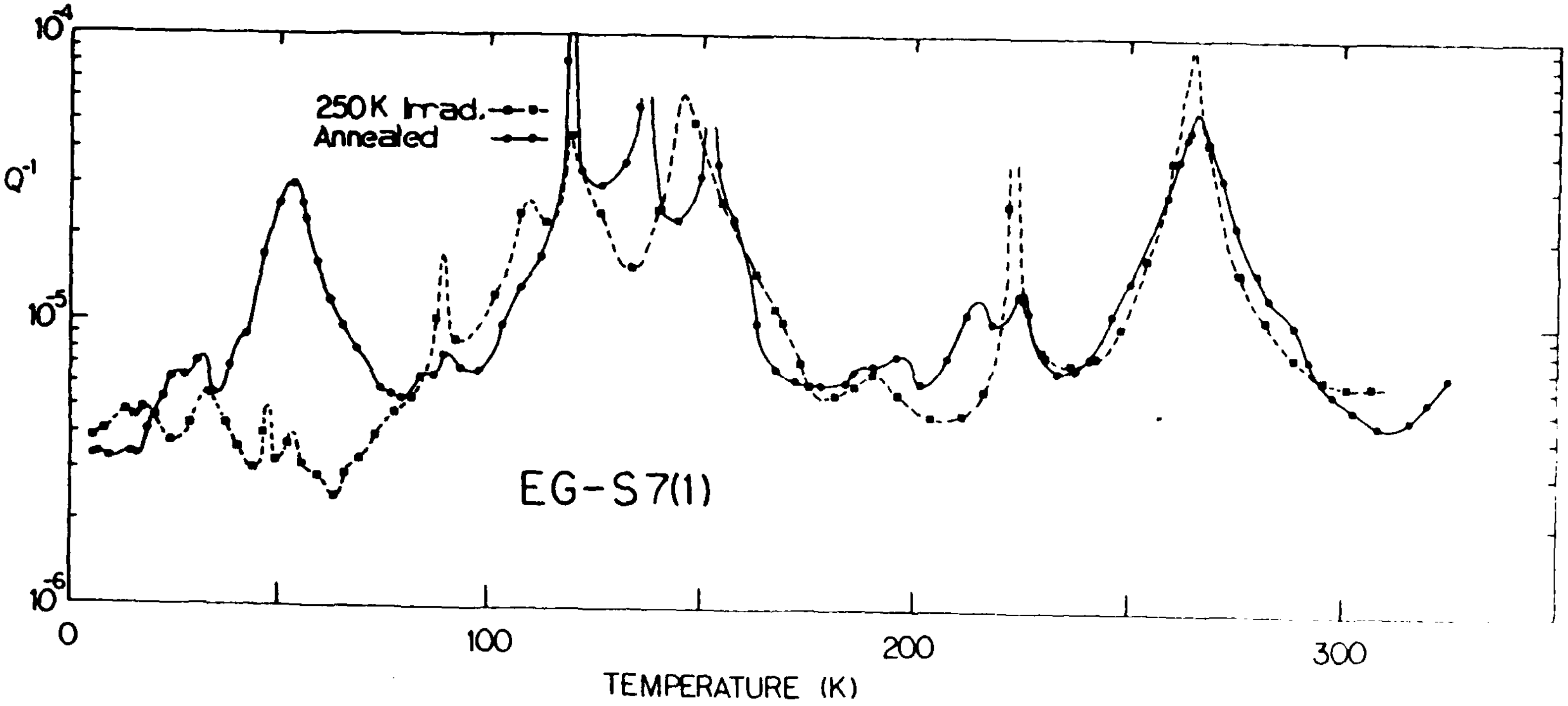


Fig. 16. The acoustic loss spectrum from 4 K to 300 K for Electronic Grade resonator EG-S7(1) following an irradiation at 250 K which removed the Na loss peak and after a subsequent 750 K anneal is shown. The anneal completely restored the Na loss peak.

TABLE VI 50 K Na loss peak versus irradiation temperature and sweeping.

Resonator	Irradiation T(K)	$\Delta Q^{-1} \times 10^6$	N_{Na} † (10^{16} cm^{-3})	N_{Al} † (10^{16} cm^{-3})	Comment
D1445DC	as received	2.7	0.3	2	Na swept
	77	2.7			
	215	1.0			
	300	0			
EG-S7(1)	as received	14	2	10	unswept
	180K	13			
	200K	11			
	220K	2.8			
	250K	< 1			
EG-S7(2)	----	70	9	9	Na swept in
EG-S7(2)	----	0			Na swept out

† These concentrations are estimated from the strength of the Al-OH infrared bands after a room temperature irradiation. Since some hole centers are also produced, they may be as much as 25% low. The height of the Na loss peak, ΔQ^{-1}, scales reasonably well with this estimate of the Na content.

$[Al_{e^+}]^o$ concentration is small. Figure 17 illustrates the decrease in the Al-Na center as determined by internal friction and the complimentary growth in the Al-OH center as measured by IR absorption as a function of sample temperature during irradiation. The growth of the $[Al_{e^+}]^o$ center following a subsequent irradiation at 77 K is also shown in Fig. 17.

In order to check the effectiveness of the sweeping process and to determine if it was possible to directly sweep a resonator, an AT cut Electronic Grade resonator, EG-S7(2) was Na swept according to the process described above. Fig. 18 compares the internal friction for this Na swept resonator with an otherwise identical unswept resonator, EG-S7(1) fabricated from the same bar. The 50 K Na loss peak shows a five fold increase in the Na swept resonator. The resonator was then swept to remove the sodium. The resulting Q^{-1} spectrum shown as the lower curve in Fig. 18 shows this second sweeping run completely removed the sodium. The corresponding frequency versus temperature curves for this resonator with Na swept in and with Na swept out are shown in Fig. 19. The measured frequency shift, 80 ppm, introduced by the Na loss mechanism is in good agreement with the measured height of the Na loss peak, 70×10^{-6}. It should be noted that if this Na swept resonator was irradiated at room temperature a 70-80 ppm frequency shift would take place. Table VI gives the Na loss peak height and estimated Na concentration for this resonator.

D. SUMMARY

The loss peak near 50 K in 5 MHz 5th overtone AT cut resonators has been used to determine the behavior of the Al-Na center during irradiation. The center was found to be stable for irradiations carried out at temperatures below 200 K. However, above 200 K the Na was found to be mobile in the radiation field and was replaced by a hydrogen to form the Al-OH center. The decrease in

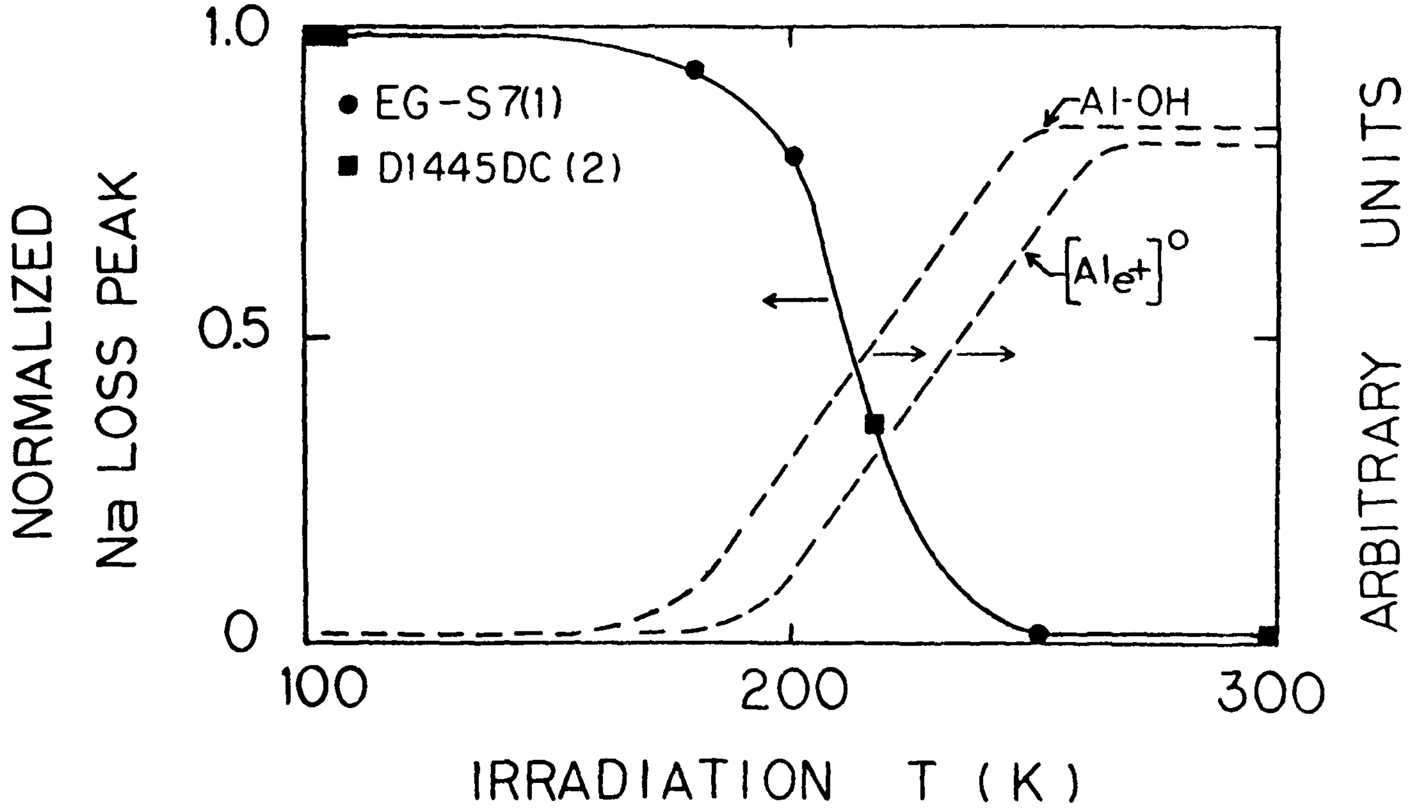


Fig. 17. The normalized Na loss peak, $\Delta Q^{-1}/\Delta Q_o^{-1}$, decreased for irradiations at temperature between 200 K and 250 K as the Na is displaced. The complementary increase in the Al-OH and $[Al_{e}+]^0$ centers as monitored by IR absorption and ESR is also shown.

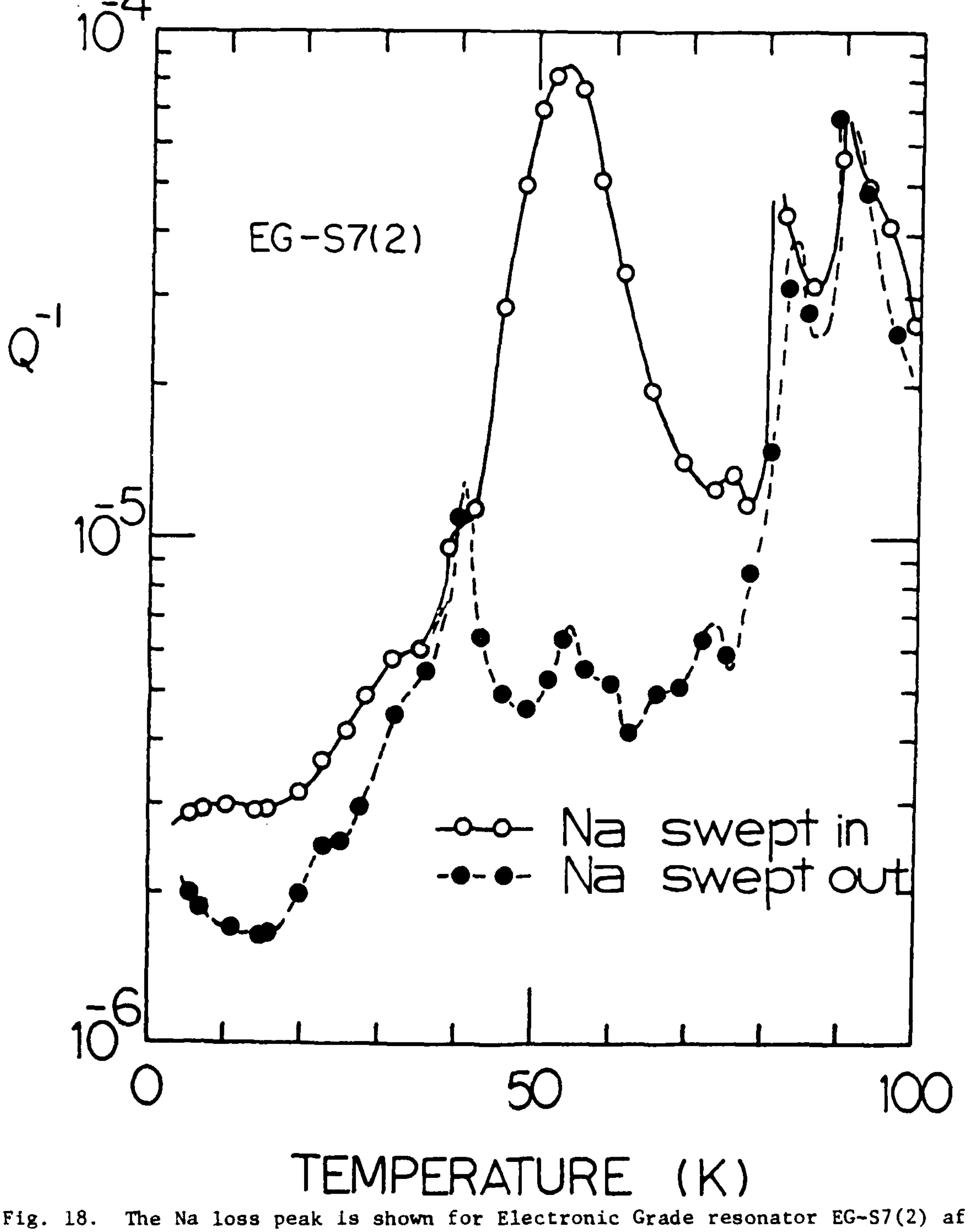


Fig. 18. The Na loss peak is shown for Electronic Grade resonator EG-S7(2) after it was directly swept with Na. The loss peak is five times the loss peak observed in the unswept resonator EG-S7(1) which was fabricated from the same bar. The lower curves shows the acoustic loss spectrum for resonator EG-S7(2) after the Na was swept out.

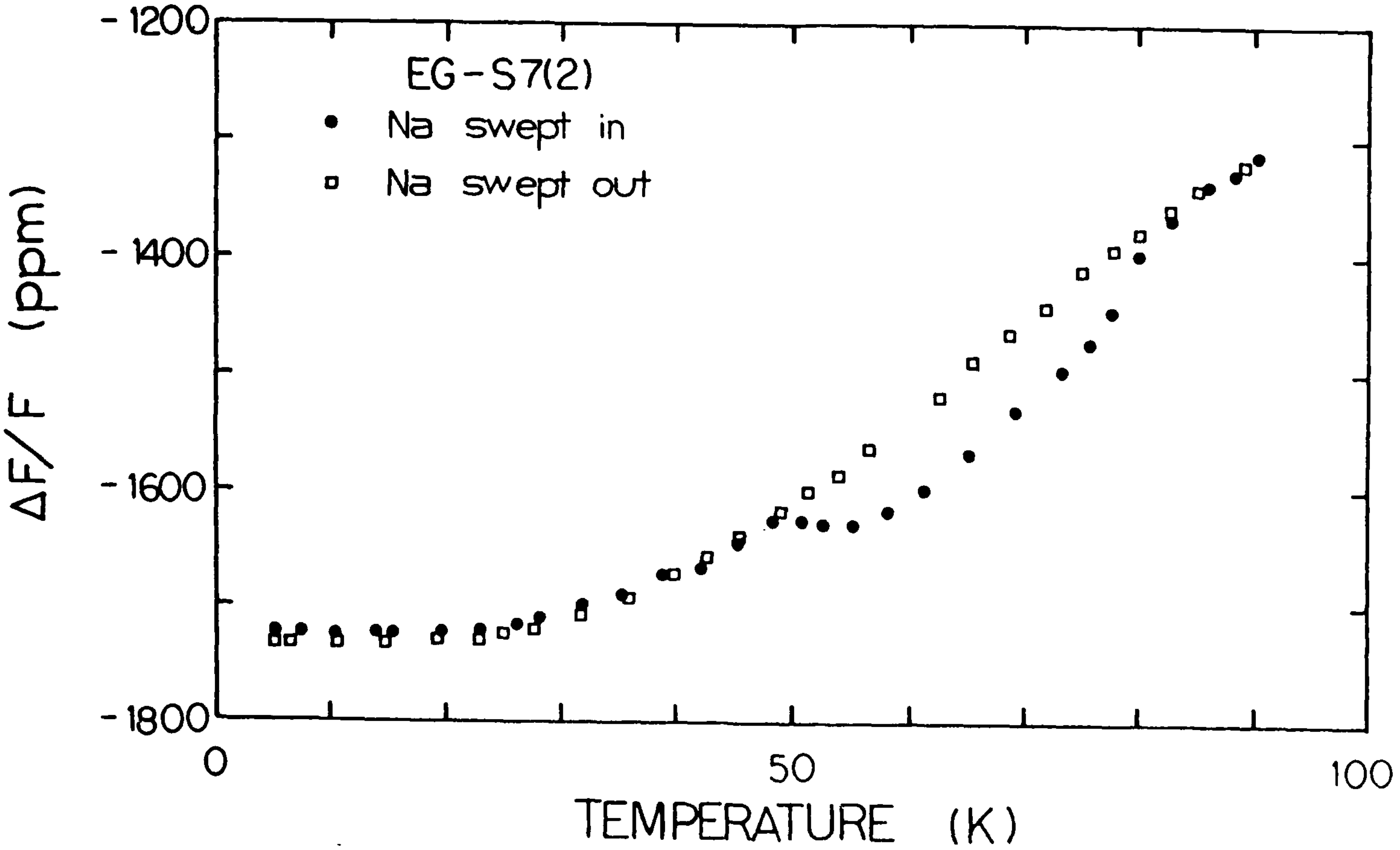


Fig. 19. The normalized frequency versus temperature curves are shown for the Electronic Grade resonator EG-S7(2) after the direct Na sweep and after the subsequent Na removal. The shift in the curve near 50 K is in good agreement with the height of the Na loss peak shown in Fig. 18.

the height of the Na loss peak during irradiation at temperatures between 200 K and 250 K correlates strongly with the growth of the Al - OH center[4] and of the $[Al_{e^+}]^o$ center[5] over this same temperature range.

Electrodiffusion (sweeping) has been carried out directly on plano convex AT cut resonators. Using this technique Na ions deposited on the flat resonator surface have been swept into the resonator as shown by a large increase in the 50 K Na loss peak. A subsequent sweeping of the resonator completely removed the Na loss peak. The direct sweeping of the resonator should reduce the number of steps needed in the fabrication of precision radiation-hardened resonators.

E. REFERENCES:

1. J. C. King and H. H. Sander, IEEE Trans. on Nuc. Sci. NS-19, 23 (1972).

2. T. M. Flanagan, IEEE Trans. on Nuc. Sci. NS-21, 390 (1974).

3. F. Euler, P. Ligor, A. Kahan, P. Pelligrini, T. M. Flanagan and T. F. Wrobel, IEEE Trans. on Nuc. Sci. NS-25, 1267 (1978).

4. W. A. Sibley, J. J. Martin, M. C. Wintersgill and J. D. Brown, J. Appl. Phys. 50, 5449 (1979).

5. M. E. Markes and L. E. Halliburton, J. Appl. Phys. (to be published).

6. J. C. King, Bell System Tech. J. 38, 573 (1959)

7. A. Kats, Phillips Research Reports 17, 133 (1962).

8. B. R. Capone, A. Kahan, R. N. Brown and J. R. Buckmelter, IEEE Trans. on Nuc. Sci. NS-17, 217 (1970).

9. D. B. Fraser, Physical Acoustics (W. P. Mason, ed.) Vol. III-Part A, pp. 1-42, Academic Press, New York (1966).

10. D. B. Fraser, J. Appl. Phys. 35, 2913 (1964).

11. C. K. Jones and C. S. Brown, Proc. Phys. Soc. 82, 375 (1963).

12. J. M. Stevels and J. Volger, Philips Res. Rep. 17, 283 (1962)

13. D. S. Park and A. S. Nowick, phys. stat. sol.(a), 26, 617 (1974)

MISSION
of
Rome Air Development Center

RADC plans and executes research, development, test and selected acquisition programs in support of Command, Control Communications and Intelligence (C^3I) activities. Technical and engineering support within areas of technical competence is provided to ESD Program Offices (POs) and other ESD elements. The principal technical mission areas are communications, electromagnetic guidance and control, surveillance of ground and aerospace objects, intelligence data collection and handling, information system technology, ionospheric propagation, solid state sciences, microwave physics and electronic reliability, maintainability and compatibility.

[illegible]