A STUDY OF THERMALLY STIMULATED LUMINESCENCE IN

SYNTHETIC QUARTZ (IN THE REGION 96K - 273K)

By

DOST MUHAMMAD MALIK

Bachelor of Science
University of the Punjab
Lahore, Pakistan
1965

Master of Science
University of the Punjab
Lahore, Pakistan
1968

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of the Oklahoma State University
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Thesis Approved:

W. A. Sibley
Thesis Adviser

Larry E. Halliburton

Joel J. Martin

E. E. Kohnke

Wm. L. Hughes

Norman N. Durham
Dean of the Graduate College

1064668

ii

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TABLE OF CONTENTS

LIST OF TABLES

v

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Quartz, crystalline SiO_2, has a wide range of practical applications, because of its mechanical, electrical and optical properties. Studies of its behavior are useful even in such fields as archaelogy and geology (1-3). It is also used in a variety of electronic and optical instruments. Because of its use in precision oscillators in satellites and research instruments and the finding (4) that its performance is adversely affected when subjected to radiation, more information in this area is necessary. Consequently, research being done locally is motivated by the desire for a better understanding of the important mechanisms of radiation damage.

A high energy (1.5 - 2.0 Mev) beam of electrons from a Van de Graaff generator has been used to produce defect centers. These defects change the properties of quartz and open a number of avenues of investigation which can aid in understanding the basic nature of the defect centers. This knowledge can ultimately be applied to developing the useful properties of this material. One approach toward this end is to study the various aspects of the luminescence process. Specifically, the present study involves the detection of thermally stimulated luminescence (Thermoluminescence) in irradiated quartz. For simplicity this process will henceforth be denoted by "TSL". The experimental procedure for TSL consists of irradiating a specimen at a fixed temperature and

observing both the intensity and spectral distribution of the glow while heating.

TSL is one of several contemporary tools such as optical absorption (OA), electron spin resonance (ESR), etc., which can be very effective in determining the nature of defects in materials. The desirable features of TSL studies are based on the fact that although the experimental apparatus and procedure are relatively simple, the technique itself can be extremely sensitive to the presence of defect centres and changes in their charge state.

Survey of Defect Studies in Quartz

Defects in quartz have been investigated by a number of conventional techniques including optical absorption (OA), electron spin resonance (ESR) and thermally stimulated luminescence (TSL). Radiation Effects in Quartz, Silica and Glasses, edited by J. E. Burke (5) and references therein provide a sequential summary of developments in OA and ESR studies in quartz up to the mid-sixties. Ditchburn et al. (6) were among the first to start systematic studies in OA and suggested correlation of 460 nm and 620 nm absorption bands with Al^{3+} impurities. Later Cohen (7) found that Al or other impurities should be substitutional. This idea was pursued by Kats, Weeks and Nelson and others (8,9). ESR work was systematically started by Griffiths, Owne and Wards (10), interpreted by O'Brien (11) and continued by others (12). Yokota (13) initiated TSL investigations with Batrak, Arnold, Schlesinger and others following suit. Arnold (14) has given a brief summary of TSL investigations in quartz up to 1960. Certain radiation-induced defect centers as reported and described during some of the earlier studies of

quartz are listed in Table I. Information contained in the table has been abstracted from reference (5) and the references listed therein.

The long list of references in the reviews referred to provide evidence of the considerable effort to understand and explore all mechanisms at work at defect sites in quartz. As mentioned above, the problem has mostly been investigated by OA and ESR. TSL has also been investigated but to a lesser extent. No clear understanding has been established at this time. Many of the past inconsistencies in experimental results appear to be due to the large variation in the sources of the specimens investigated and the lack of knowledge about the amounts and kinds of impurities present. Thus it has been difficult to compare results. Nonetheless, a number of details have gradually emerged and been developed over a period of time.

In the description of the experimental results, which have been important in identifying and describing the defect centres one must mention the OA studies pursued by Arnold (14). He observed 240 nm and 260 nm absorption bands in natural smoky quartz and the 240 nm band in synthetic quartz, and concluded that oxygen vacancy-interstitial pairs are the effective absorption centers in smoky quartz. Nelson and Weeks (9) observed absorption bands at 200 nm and 230 nm and attributed them to E_1' and E_2' centers respectively. They correlated their OA data with ESR data obtained from the same samples. Later, Weeks (16) studied the ESR of E_2' centres in crystalline quartz and concluded that this centre consists of an electron trapped at an Si-O vacancy which is compensated by interstitial impurities, especially hydrogen. More recently E-centres have been investigated by Yip and Fowler (17). They have shown that the Nelson-Weeks' (9) model of E_1' fails to explain hyperfine

TABLE I

BRIEF DESCRIPTION OF DEFECT CENTERS BELIEVED TO EXIST IN QUARTZ

Defect Name and/or Notation	Description	OA	ESR
Ge-Centers (Ge(I), Ge(II)	Electron trapped at Ge site assisted by + alkali ion	296 nm 3-fold symm.	$g_1 = 1.994$ $g_2 = 2.0021$ $g_3 = 2.0023$
		260 nm 6-fold symm.	$g_1 = 1.993$ $g_2 = 2.0010$ $g_3 = 2.0015$
Al-hole centers $[Al_{e+}]^o$	Hole trapped at Al site	460 nm; 620 nm	$g_1 = 2.00$ $g_2 = 2.00$ $g_3 = 2.06$
$[Al_{e+}/M^+]^+$	Combination of inter-ion and hole trapped at Al site	540 nm	$g = 2.0194$ for Na^+ $g = 2.0251$ for H^+
E_1'-Centers	Electron trapped at oxygen vacancy	200 nm	$g = 2.0006$
E_2'-Centers	Electron trapped at Si-O vacancy and charge compensated by interstitial ion	230 nm	$g = 2.0009$ for H^+
Atomic hydrogen center H^o	Electron trapped by proton		$g = 2.0021$

4

interactions. They presented a model of Si-O$_{vacancy}$-Si molecule in a

different symmetry with silicon atoms constrained to move along

Si-O$_{vacancy}$ directions.

ESR results related to Al-hole centres were reported by Griffiths, Owen and Ward (10) and were interpreted by O'Brien (11). Mackey (12) studied ESR spectra of impurity related colour centers in Ge-doped quartz and produced a table of possible defect centers. He found two types of electron traps at Ge sites (differing in symmetry) with no interstitial impurity at low temperature and two similar types of traps with alkali interstitials which were neutral and stable at room temperature. In addition, at low temperature he observed hole traps at Al^{3+} sites with H$^+$, Li$^+$ or Na$^+$ ions at interstitial positions. At high temperature these (ions) migrate to Ge sites, leaving $[Al_{e+}]^O$ stable centers. Mackey, Boss and Woods (18) reinvestigated Al-related hole centers in synthetic quartz in 1970 and found similar results.

Since the subject of the current study is TSL, a summary of previous experimental TSL results is particularly pertinent. A detailed summary of early work on colour in quartz which includes references on TSL is given by Arnold (14). His own TSL investigations included both natural and artificial quartz and reported TSL peaks at 518K and 553K for smoky Brazilian specimens using x and γ-irradiation. In a clear artificial sample he found a TSL peak at 518K and another reduced one at 603K. He also studied doped samples (Al,Ge), noting that only the presence of Ge alters peak positions and therefore its effect could be distinguished. He concluded that centers in smoky quartz were oxygen vacancy-interstitial pairs and for doped samples suggested that Al and Ge can replace each other in the lattice with observed emissions re-

sulting from transitions of an electron bound to an Al or Ge ion neighboring an oxygen vacancy.

Batrak (19,20) investigated TSL of alkali-doped natural quartz. He conceded that TSL of natural quartz, obtained from different localities, was different depending on inherent impurities. He observed a TSL peak at 578K in an x-irradiated and Na-doped sample and two peaks in an undoped specimen but gave no peak temperatures. He also showed that the data conformed to first order kinetics and estimated a trap depth average of 1.27 eV for the Na-doped sample. Medlin (21) studied a variety of natural and synthetic specimens and reported glow peaks at 165K, 250-270K, 350K, 500K and 600K in most of them. He also noted peaks between 90K and 150K in some cases and in these cases the 165K peak was either missing or very weak. Peaks were observed at 190K and 210K in almost all single crystals. He added a large number of cation impurities (Al^{3+}, Bi^{3+}, Li^+, Fe^{2+}, Ge^{4+}, Ti^{4+},...) during crystallization while all samples had 100 ppm of Na^+ ions, and concluded that of these only Ti^{4+} affected the glow curves of synthetic samples. The 165K peak was identified with Ti^{4+}, since it changed with Ti^{4+} concentration. He further associated the 140K, 210K, 260K and 330K peaks in synthetic material with nonimpurity lattice defects. He made a spectral analysis and observed that 390 nm output light was emitted for the 260K, 280K and 330K peaks and 520 nm light for the 165K peak (Ti). He studied decay curves of the 300K peak and concluded it obeyed first order kinetics with a narrow distribution of trapping levels. McMorris (22) reported peaks around 450K and 570K in natural quartz but gave no conclusive explanation.

Schlesinger (23) investigated the TSL of artificial samples either

doped with Ge or Ge-free while Al was present in all of them. He observed that the Ge-free material showed a peak at 570K and the Ge-doped at 460K and 600K. He also found that all peaks had a spectral distribution around 485 nm leading him to conclude that the recombination process is the same in each case.

A year later Schlesinger (24) repeated TSL observations in all temperature ranges and found glow peaks at 190K, 257K, 368K, 395K and 460K in Ge-doped samples containing 105 ppm Al and at 130K, 190K, 220K, 395K, 440K, 575K in Ge-free specimens with 225 ppm Al. He concluded from OA reexcitation experiments that peaks of either electron-release or hole-release origin existed between liquid nitrogen and room temperature. The re-excitation wavelengths used for electrons and holes were 280 nm and 440 nm, respectively. He remarked that in Ge-doped material all peaks were due to electrons released except that at 257K, which was due to hole release.

Later Zimmermann (25) reported TSL peaks at 250K, 370K and 620K from natural quartz. He found a spectral output around 390 nm for TSL in the 370K peak and observed a similar response in radioluminescence. TSL of natural and fused quartz has also been studied by R. I. Sheklmametev (26) and others with reported glow peaks at 473K and 573K.

Anderson, Feigl and Schlesinger (27) agreed that since the spectral distribution is independent of the presence of Ge (23), radiative recombination can be presumed to occur at Al sites. Fuller and Levy (28) investigated TSL in many natural crystalline quartz samples by using gamma-ray irradiation. They reported wide variation in glow curves and suggested they were dependent on both sample origin and radiation treatment. They observed glow peaks around 450, 570 and 603K. An

TABLE II

A BRIEF SUMMARY OF TSL PHENOMENON IN QUARTZ

Investigator	Type of Quartz	TSL Peaks Observed Below Room Temperature				Above Room Temperature		
Arnold	Nat.					330	553	603
	Art.					330	520	610
Batrak	Nat. Na$^+$ doped						578	
Medlin	Nat.	125	165	210	250-70	350	500	600
	Art.	140	165	210	260	330		
McMorris	Nat.						570	
Schlesinger	Art. Ge-doped			190	257	368	460	600
	Art. Ge-free	130		190,220			570	
Zimmermann	Nat.				250	370		620
Levy	Nat.						570	603
	Art.			182				
Durani	Nat.					350		620
Present Investigation	Art.	125		155,165,175	210,225			

emission spectrum peak around 500 nm was observed in all cases. From these observations they concluded that the luminescence centers responsible for emission were universal but that the charge trapping-centers were impurity-dependent.

Recently Durani, Groom and Ghazal (29) have investigated intensity dependence on the temperature of irradiation and have reported glow peaks at 350K and 620K in natural quartz along with a spectral distribution of 370-520 nm without further remarks. They attribute the 620K peak to an Al-alkali center capturing a hole.

A survey of the TSL investigations indicates that TSL peaks appear in quartz around 125, 165, 200, 230-250, 330, 570 and 600K in most cases (14,19,20,21-25,28,29). The spectral output, although much less frequently quoted, is generally detected around 380-390 nm (21,25,29), 485 nm (23,24,28) and 520 nm (21,29).

Current Studies at Oklahoma State University

A great deal of work is in progress on OA, acoustic loss factor and ESR studies at Oklahoma State University. This research has been concentrated on high quality synthetic quartz and certain important contributions have provided new insights into the defect properties. A Van de Graaff generator providing a beam of 1.5 to 2.0 MeV electrons has been used as the primary radiation source.

Optical absorption (OA) has been investigated in the ultraviolet, visible and infrared regions, but infrared (IR) region studies done by W. A. Sibley, et al. (30) have been more extensive and conclusive. Prominent bands have been found at 3581 cm^{-1}, 3437 cm^{-1}, 3400 cm^{-1}, 3348 cm^{-1}, 3367 cm^{-1} and 3306 cm^{-1}. It has been established that IR

bands associated with OH$^-$ impurities in SiO$_2$ are strongly temperature dependent and therefore must be studied at low temperature. In unirradiated samples containing alkali-compensated Al centers only the first four of the above-mentioned bands are observed. If a specimen is irradiated at 300K and the OA in the IR region is observed at 77K, it is found that the intensity of the four bands decreases but two new bands appear at 3367 cm^{-1} and 3306 cm^{-1}. However, these bands are initially present in unirradiated alkali-free material. Returning to the first case, the relative absorption intensity of these two bands is found to depend upon the dose and temperature of irradiation. It has further been established that prolonged electron irradiation at low temperature suppresses all of the OH$^-$ bands. These bands partially recover if the sample is annealed to room temperature and fully recover if annealed to 740K. From these OA studies the concentration of hydrogen impurity participating in OH$^-$ vibrational modes has been estimated for the two types of quartz (alkali-compensating and alkali-free) investigated. It has been concluded that the defect center responsible for each of the 3367 cm^{-1} and 3306 cm^{-1} IR bands is an Al-OH$^-$ complex.

Markes and Halliburton have used electron spin resonance (ESR) to investigate the defect formation, annealing, and migration effects in quartz (31). They have investigated both unswept (alkali-containing) and swept (alkali-free) samples. In the latter case, alkali ions have presumably been replaced by hydrogen ions during an electrodiffusion ("sweeping") process. They observed the previously reported defect centers of atomic hydrogen and a few of the Al-hole type in addition to some new defect centers by studying the ESR spectrum of unswept samples irradiated at 77K only. No ESR spectrum from unirradiated samples of

any type was observed. A subsequent irradiation of this sample at room temperature enhanced markedly the Al-hole center spectrum and spectra corresponding to E_2' centers and E_4' centers. These last three defect centers were also observed in other similar samples, which had not been subjected to a prior low temperature (77K) irradiation. A third low temperature irradiation of this sample, which had already received a sequence of irradiations at 77K and 300K, further increased the number of Al-hole centers. A strikingly different behavior was observed in a swept sample of the same quality. The initial 77K irradiation produced an Al-hole concentration some 25 times higher while the concentrations observed following subsequent room temperature and 77K irradiations were very similar to those in the unswept specimen.

Detailed studies of the thermal stability of all defects in the 77K to 300K region following a single irradiation at 77K were made using a pulse-anneal technique. It was observed that the few Al-holes originally present thermally decayed between 90 and 110K, the hydrogen atom signal was destroyed between 115 and 135K and two unidentified electron centers finally disappeared over the 135 to 170K temperature range. Similar results were obtained following a triple irradiation (77K - 300K - 77K) except that many more Al-holes were produced and although strong decay steps exist below 125K, a significant number of the centers did not disappear, at higher temperatures. Furthermore, E_2' and E_4' centers appeared above 120K.

A series of measurements involving irradiations at successively higher temperatures in an unswept sample revealed 200K as the critical irradiation temperature for the onset of enhanced Al-hole production by a second 77K irradiation. As suggested by the IR studies, annealing to

740K returned this specimen to its as-received condition. The acoustic loss factor (Q^{-1}) of quartz resonators fabricated from high-quality material has been measured by the logarithmic decrement method by J. J. Martin, et al. (32). The specimens were 5 MHz 5th overtone AT cut plano-convex resonators. In this study the acoustic loss factor for a Na-enriched resonator was measured as a function of temperature before and after irradiation at various temperatures. The Na-related loss peak at 50K was found to be unaffected by irradiation at 77K, significantly reduced by irradiation at 215K and finally removed by 300K irradiation.

Correlation of the local IR, ESR and Q^{-1} experiments described above has led to the conclusion that radiation-induced mobility of interstitial ions is the principal factor governing the radiation response of high quality quartz and has suggested the nature of the mechanisms involved. The TSL results of the current study will be discussed in the light of this picture.

CHAPTER II

THEORETICAL BACKGROUND OF TSL

Since this investigation is based on a study of TSL, it is appro-
priate to review the theoretical background of the process. Lumines-
cence is a process, characteristic of certain materials, in which
energy is absorbed by a lattice ion or a defect and is subsequently
released as the emission of photons (33). The radiation emitted during
this process is customarily called 'luminescence'. If the release of
energy is activated by thermal excitation, then the process is called
thermally stimulated luminescence (TSL).

After some empirical calculations on TSL by Urbach in 1936, the
first general attempt at TSL theory was put forward by J. T. Randall
and M. H. F. Wilkins (34) in 1945. Although it was soon recognized
that the processes are not as simple as theory assumed. The solutions
become more and more complicated as the theory is generalized.

The basis of a phosphor, according to simple TSL theory, is a pure
insulating crystal, which luminesces due to the presence of impurity
atoms, present naturally or added deliberately, which may occupy normal
or interstitial sites. Impurity atoms or lattice irregularities create
localized electron/hole states which may occur between the conduction
and valence bands. In a semiconductor, the upper of these levels is
close to the conduction band and from some of these levels electrons
may be excited to this band, resulting in limited electrical conduction.

In insulators this energy gap is usually large and conduction is generally below measurable level. The higher of these energy levels are usually empty and are called 'traps'. When electrons are excited to the traps directly or indirectly (first to the conduction band and after losing some energy are trapped) they leave behind holes (called luminescent or recombination centers). If this process is continued for sufficient time, most of the traps may be filled. Later on when the material is thermally excited, electrons are either raised to unstable levels between the bands and can recombine with luminescence centers. If the energy level of a tra-ped electron is E(ev) below the conduction band/unstable level, it should absorb energy at least equal to E in order to escape from the trap. The probability of escaping from the trap, for an electron at temperature T is given by Boltzmann factor,

$$P = S e^{-E/kT},$$

where k is Boltzmann constant and S is another constant ($\sim 10^{8 \pm 1}$ s^{-1}) which may vary slightly with temperature and is usually referred to as 'attempt to escape frequency' or 'frequency factor'. The theory makes the following assumptions:

    i)   E is single valued.

    ii)   Heating rate is constant.

    iii)   There is no retrapping.

The second of these conditions can be fixed, but the other two may or may not be valid in a particular situation and hence limit the scope of the theory. Under these assumptions, if n is the number of electrons in the traps at any time t and temperature T, then

$$\frac{dn}{dt} = -n\,P = -nSe^{-E/kT}$$

The intensity of glow 'I' is proportional to the supply of electrons to the luminescence centers:

$$I \propto \frac{dn}{dt}, \text{ or } I = -cnSe^{-E/kT}$$

where c is a proportionality constant. If the heating rate 'β' is constant, then $dT = \beta dt$ and the solution of (2) becomes:

$$I = c\,n_o \exp\left(-\int_{T_o}^{T} \frac{S}{\beta} e^{-E/kT}\,dT\right) Se^{-E/kT}$$

where n_o is the number of traps filled initially at T_o. To estimate the trap depth 'E', the theory relates the temperature T_m at which the maximum glow occurs to the temperature at which probability of escaping is one, by the relation:

$$S \exp\{-E/k\,T_m[1+f(S,\beta)]\} = 1 \text{ where } f(S,\beta) < 1 \ .$$

The authors argue that E can be reasonably approximated by

$$E \approx 25\,kT_m \text{ eV}$$

A TSL process, in which retrapping is not prevalent is called first order or monomolecular and second order or bimolecular when retrapping is present. Retrapping is favourable at high temperature and at low temperature at the beginning of excitation when most of the traps are empty. The Mean-Life-Time (τ) of traps can be estimated from the relation:
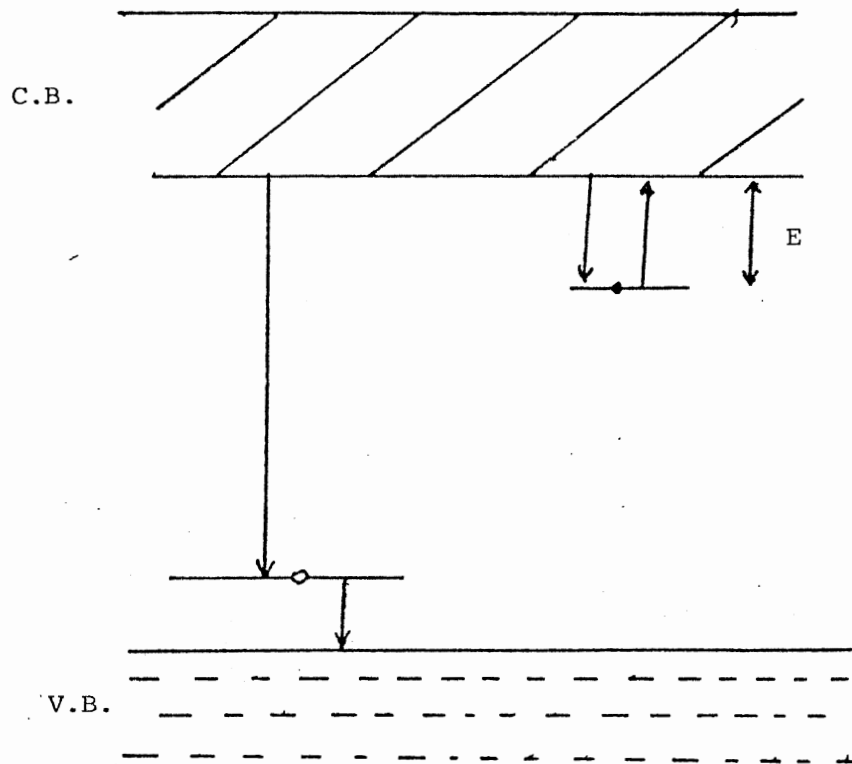
Figure 1. Energy Level Diagram. This energy level
diagram represents one model, which
is described here and explains the
thermoluminescence. In the second
model all energy levels are believed
to be strictly within the band gap
and electrons are not raised to the
conduction band by the stimulation
process

$$\therefore \ \tau = \frac{1}{P}; \ \ln \tau = \frac{E}{kT} - \ln S$$

Thus the mean life time of the trapping level depends upon the trap depth, the temperature and the frequency factor. It can range from seconds to days. In the case of optically stimulated luminescence if the optical transition is allowed then the mean life time in the excited state is found to be of the order of 10^{-8} second. But in the case of forbidden transitions a much longer life time of the order of 10^{-3} second has been observed. Thus there are considerable differences in the nature of TSL and OSL.

Garlick and Gibson (35) have studied the chance of retrapping and estimated the trap depth from the initial exponential rise of the glow curve which is popularly described as the 'initial rise method'. They have proposed that the initial rise follows the exponential relation:

$$I = n_o S \exp(- E/kT)$$

where E can be estimated from experimental curves. Later researchers have suggested that this is not a preferable method since good agreement lasts only up to about 25% of the maximum emission (36). Garlick and Gibson have studied the effects of retrapping under equal probability of retrapping and recombination with luminescence centers theoretically and experimentally in many sulphide and silicate phosphors. They concluded on the basis of the experimental investigation that retrapping is negligible and the TSL can be explained if it is assumed that the traps are spatially associated with the immediate neighboring luminescence centers formed by the activating impurities.

Booth (37) has used the condition of a maxima on the glow curve to

derive a relation for trap depth, namely:

$$E = \frac{k\, T_1^*\, T_0^*}{T_0^* - T_1^*} \ln\left[\left(\frac{T_1^*}{T_0^*}\right)^2 \frac{\beta_0}{\beta_1} \right.$$

where β_0, β_1 are different heating rates and T_0^*, T_1^* are corresponding temperatures at which maxima occurs. He also confesses that it is only few per cent better than the original result (34). Hoogenstraaten (38) has extended this idea by using a number of different heating rates and T_m (or T^*, the temperature corresponding to maximum) is determined as a function of heating rate β. From the slope of the plot of

$$\ln(T_m^2/\beta) \quad vs \quad \frac{1}{T_m}$$

the trap depth E can be found.

Grossweiner (39) and Luschik (40) have derived a relation for E on the basis of peak-shape-analysis which is of the form:

$$E = \frac{c\, k\, T_m\, T'}{T_m - T'} \cdot$$

The constant c has different values for different kinetics and T' is the temperature corresponding to 50% of the maximum output. Grossweiner evaluates the rising part of the peak, whereas Luschik uses the falling part.

The subject of TSL was reviewed in 1964 by Nicholas and Woods (41) and they discussed different methods for different types of kinetics, giving a caution note against the methods using peak shapes unless 'thermal cleaning' has been done. 'Thermal cleaning' means the removal

of small partially overlapping peaks from the rising part of the major

peak by heating up to the small peak, cooling, and rehating. They have

recommended the method of Hoogenstraaten.

Kelley and Laubitz (42) have deduced expressions for trap depth

using non-linear heating rates ($\beta \, \alpha \, T^2$) which are similar to that of

Grossweiner and Luschik. They have given no reason for using a non-

linear heating rate except saying that it is reproducible and calcula-

tions are simplified. Land (36) used a point of inflection condition

in addition to the maximum condition and derived results similar to

those of Booth.

R. Chen (43) used both rising and falling parts of the glow curve.

He approximated the integral of TSL theory by an asymptotic series,

retaining the first two terms and, using the maximum condition. He

found $E = 2k \, T_m \, (\dfrac{1.25 \, T_m}{T_2 - T_1} - 1)$ for 1st. order kinetics and

$E = 2k \, T_m \, (\dfrac{2 \, C_w \, T_m}{T_2 - T_1} - 1)$ for 2nd. order kinetics. In both cases S is

assumed independent of T. T_1 and T_2 are the temperatures at half maxi-

mum and the value of the constant C_w depends upon slow or fast retrap-

ping. Chen also discussed cases when the frequency factor 'S' is de-

pendent on temperature. He criticized the 'initial rise' method on

theoretical as well as experimental grounds. He suggested corrections

in lower-half-peak (Grossweiner) and upper-half peak (Luschik) methods

and made them agree with that of his own.

In summary, there are several different techniques for estimating

the trap depth (E). All techniques have arguments for and against

their applicability. The 'initial rise' method even with all the pre-

viously mentioned criticism has the advantage of being applicable to all sorts of kinetics. The second method of using different heating rates seems to have a better theoretical foundation, but suffers from the uncertainty of filling the same number of traps under repeated experiments. Methods using half-widths of peaks are said to be very sensitive to measurement of the temperatures of the corresponding half-widths. The method of Chen (43) should be somewhat better (at least for clean peaks) as it uses the whole glow curve and hence should reduce errors to some extent.

It does not seem fruitful to investigate the minute details of the methods for evaluating trap parameters on the basis of a theory, the model of whichseems to be inadequate. The assumption of a single trap level and a single recombination level is an oversimplification of a real situation in the complex network of solids. It is usually assumed that the density change of free carriers is small compared with that of trapped carriers during stimulation. Under these circumstances after working on the subject for some years Kelly, Laubitz and Bräunlich (44) have concluded that "Even on the basis of such a simple and naive model, any analysis of the thermally-stimulated process is very complicated. All the observable properties depend on several parameters, and it is virtually impossible to interpret the experimental results uniquely. It will be meaningful only if the defect structure of the solid is known."

The processes in solids being very complex, it may be not only useful but imperative to consult results obtained by other means of investigation (OA, ESR, etc.) and correlate them with TSL information to draw conclusions and develop models for the defect structures, their effect on material properties, and the mechanisms of their production and change.

CHAPTER III

EXPERIMENTAL DETAILS

Specimen

All the samples investigated during this study were cut from
quartz single crystal bars, grown by Sawyer Research Products, Inc.,
of Ohio. These were grown by a hydrothermal process and were z-growth
materials (grown along the z-axis of the seed crystal). Two main types
of samples were investigated. The first type included as-grown, alkali-
containing 'Electronic Grade' and higher quality 'Premium Q', specimens
as named by the manufacturer. The second type was swept 'Electronic
Grade', with the alkali impurities believed to be swept out by an
electrodiffusion process and replaced by hydrogen. They were cut by a
diamond saw and then polished for optical measurements. The dimensions
and other specific information is given in the following Table III. All
the samples were cleaned by dipping in acetone for a short time and then
rinsed in warm distilled water for a few minutes each time before mount-
ing in the sample holder for experimentation. They were handled care-
fully and none showed visual evidence of damage during the experimental
investigation.

Description of Apparatus

The sample fixture apparatus was originally designed for optical
absorption measurements. It consisted of a cryostat, capable of hold-

TABLE III

DESCRIPTION OF THE SPECIMENS

| Type | Sample No. | Dimensions | Estimate of Impurity Concentration | | |
			H*	Na**	Al***
Electronic-	EGE-9	$1.5 \times 1.3 \times .23$ cm^3			
Grade	EGE-10	$1.5 \times 1.3 \times .25$ cm^3			
"	EGE-11	$1.5 \times 1.3 \times .28$ cm^3	30×10^{16} cm^{-3}	50×10^{16} cm^{-3}	20×10^{16} cm^{-3}
"	EGE-12	$1.5 \times 1.3 \times .2$ cm^3			
"	EGE-13	$1.5 \times 1.3 \times .3$ cm^3			
Premium Q	PQA-10	$1.8 \times 1.6 \times .3$ cm^3	3×10^{16} cm^{-3}		3.9×10^{16} cm^{-3}
Swept Electronic-	EGF-14	$1.8 \times 1.25 \times .3$ cm^3			
Grade	EGF-15	$1.8 \times 1.3 \times .38$ cm^3			

*From IR absorption studies (30).

**Analyzed by Analytical Chemistry Division at Oak Ridge National Laboratory.

***Local ESR analysis.

ing a good vacuum and sufficient liquid nitrogen and having a copper "coldfinger" plate attached to its bottom. The cryostat was about 30 cm long with an inner diameter of 7.2 cms. The copper plate was 11.5 cm x 2.0 cm x 0.3 cm and contained a rectangular hole of 1.2 cm x 0.6 cm close to its lower end. The samples were bigger than this hole and mounted symmetrically across it. Thus they could be irradiated from either side and observed from both sides while being warmed. This is significant because total luminescence output can be observed and recorded simultaneously along with the spectral distribution. Later a second small copper plate (3.3 cm x 2.0 cm x 0.3 cm) having a rectangular hole of exactly the same size was attached by long brass screws to the larger plate in such a way that both holes coincided. This was done to achieve a better and more uniform thermal contact for the sample which was held sandwiched between the two plates. A drawing of the sample fixture apparatus is shown in Figure 2. The upper 9.0 cm of the main copper plate was covered by a small copper cylindrical tube with optical cutouts fixed to the lower part of the main body of the cryostat. This provided a radiation shield for the plate and thermocouple leads. One end of a copper-constantan thermocouple was soldered to the cold finger, close to the bottom of the sample and the other junction was outside the cryostat, maintained at room temperature. The sample-holding copper plate was placed in a rotatable-sealed brass cylindrical vessel with a cubical base. It had four windows at 90 degrees, each of which could be turned in front of the sample position. Three windows were of quartz, through which optical observations were carried out and the fourth was a thin (0.005 inch) aluminum window through which the sample could be irradiated. A rubber ring seal
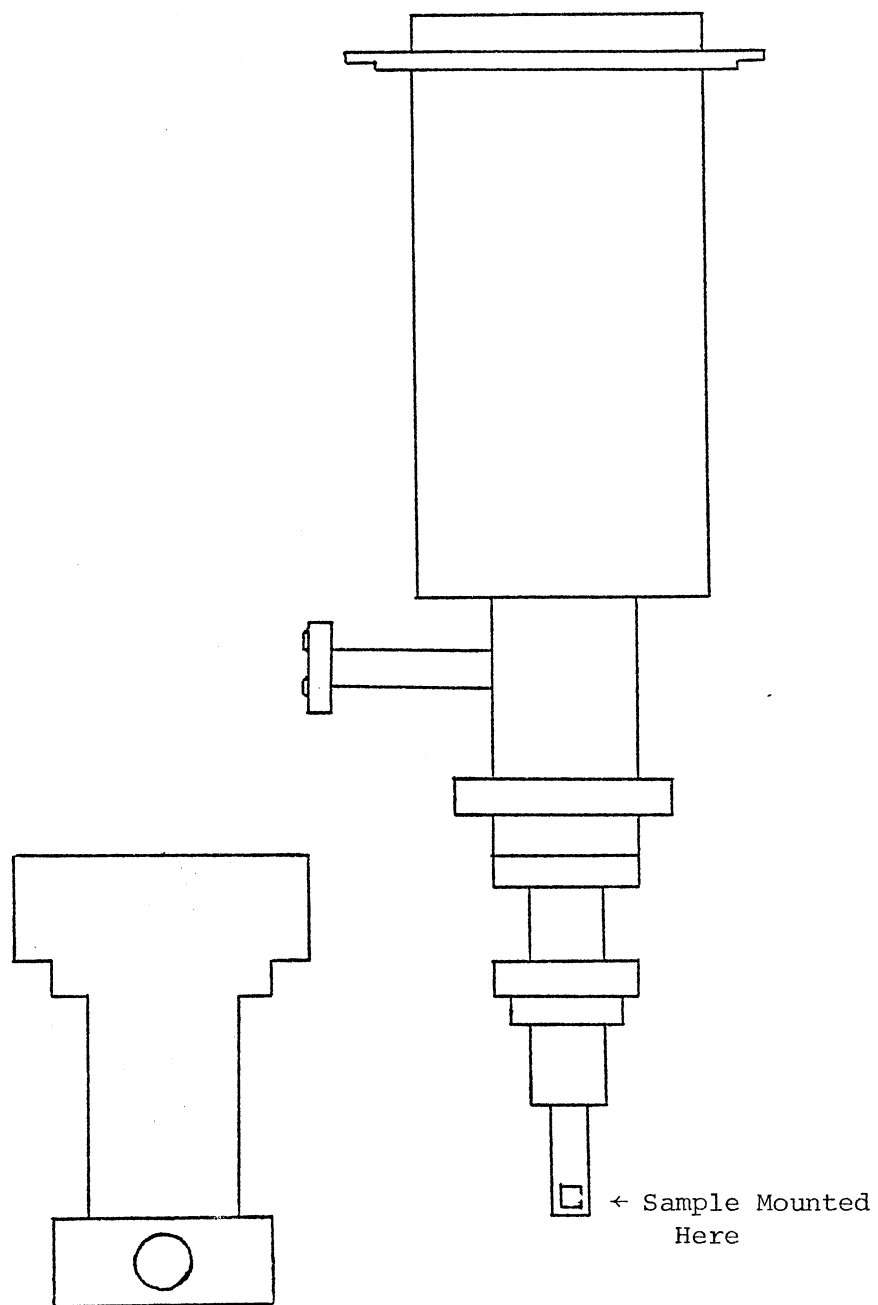
← Sample Mounted
Here

Figure 2. Cryostat and Sample Holder

between the brass sample chamber and the lower part of the cryostat sufficed to maintain a good vacuum around the sample. A pumping stand providing a combination of mechanical and diffusion pumping system could reduce the sample chamber pressure to the order of 10^{-5} torr in about half an hour.

The radiation source was a Van de Graaff Accelerator, capable of producing electrons with energies ranging up to 2.0 MeV. During TSL measurements the total TSL intensity was observed directly by an EMI-9558Q photomultiplier tube and light after passing through the Bauch & Lomb monochromator for spectral analysis was detected by an EMI-6256 photomultiplier tube. The output from EMI-9558Q was fed to a Keithley Instrument 'Model 602', electrometer. A block diagram of experimental set is shown in Figure 3.

The sample was warmed up in simple fashion by blowing room temperature compressed air at a consistently controlled rate through a rubber tube to the bottom of the cryostat. The heating rate was maintained quite consistent from run to run and averaged about 11 K/min except near room temperature. The wavelength of the TSL was detected by a Bauch & Lomb Grating Monochromator with a spectral range from 200 nm to 700 nm. The dispersion is 3.3 nm if the slit width is 1 mm in the first order. An electrometer, capable of detecting 10^{-14} amperes, for the output from the EMI-9558Q was used. The output from the Model 602 electrometer was fed to the Y-axis of a Houston Instrument X-Y recorder while the thermocouple voltage was fed directly to its X-axis for obtaining total TSL intensity versus temperature. The output from the Model 600B electrometer was originally fed to a Moseley Autograph X-Y recorder through an RC-stabilizer of time constant 0.5 seconds.
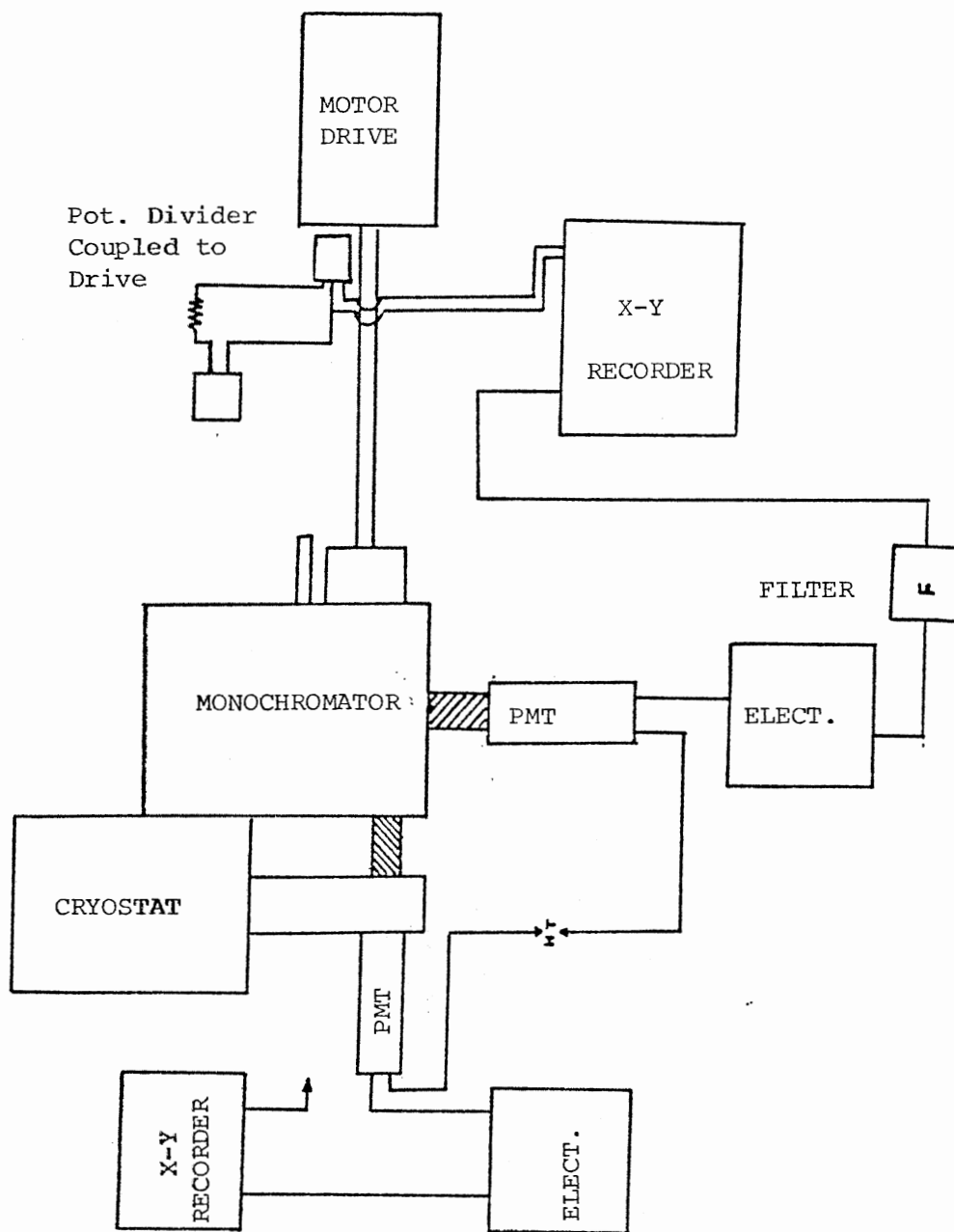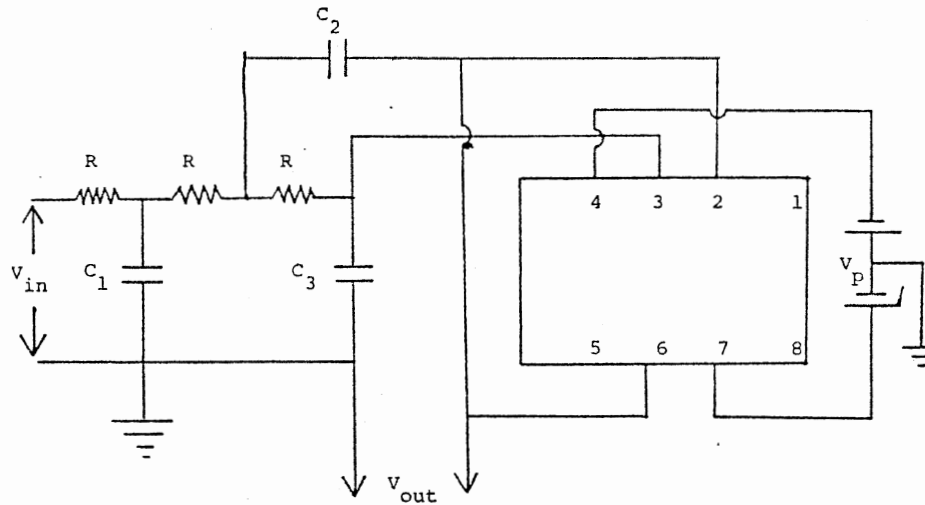
Figure 3. Block Diagram of Experimental Setup

Offset Null	1	8	NC
Inverting Input	2	7	V(+)
Non-Inverting	3	6	Output
V(−)	4	5	Offset Null

$R = 196K\Omega$ $C_2 = 10\ \mu F$ $V_p = 9$ volts
$C_1 = 3.3\ \mu F$ $C_3 = 180\ PF$

Figure 4. Filter Circuit Diagram. This design is suggested in 'Handbook of Operational Amplifier Circuit', designed by D. F. Stout (McGraw-Hill, 1976) and was constructed by Mr. Mike Shinn

For later experiments this was replaced by a second Houston Instruments X-Y recorder and a filter circuit, as shown. The monochromator scanning drive was coupled to a ten-turn potentiometer by means of a common drive, obtained from a motor through a system of gears, working at 2 revolutions per minute. Thus the whole monochromator range could be scanned in 2½ minutes. Voltage across the potential divider was supplied by a 15 V power supply, stabilized with Zener diodes. The schematic for the series resistance is shown in Figure 5. Each rotation of the ten-turn potential divider resulted in a 9 mV voltage variation across its output, which was applied to the X-axis of the X-Y recorder to provide a wavelength scan. The output of the EMI-6256 was applied across the Y-axis of this X-Y recorder through the 600B electrometer and the stabilizer/filter circuit.

Experimental Procedure

The specimens were cleaned each time before mounting for experimentation and were demounted generally after a few experiments. Initially the samples were attached to the copper cold finger by means of General Electric adhesive glue. However, it was soon discovered that because of poor thermal contact the specimen was heated enough during irradiation to destabilize the trapped charges at some defect centers. The thermal contact was improved by coating a small amount of Dow Corning 340 silicon Heat-Sink Compound between upper shoulder of the specimen and the copper plate. This compound was kept about 2 to 3 mm away from the window of the copper plate, through which the sample was irradiated to avoid its direct irradiation by the electrons beam. As a result of this improvement the total TSL output was increased by

R

Coupled to the Drive

R_1

P.S.

To X-Y Recorder
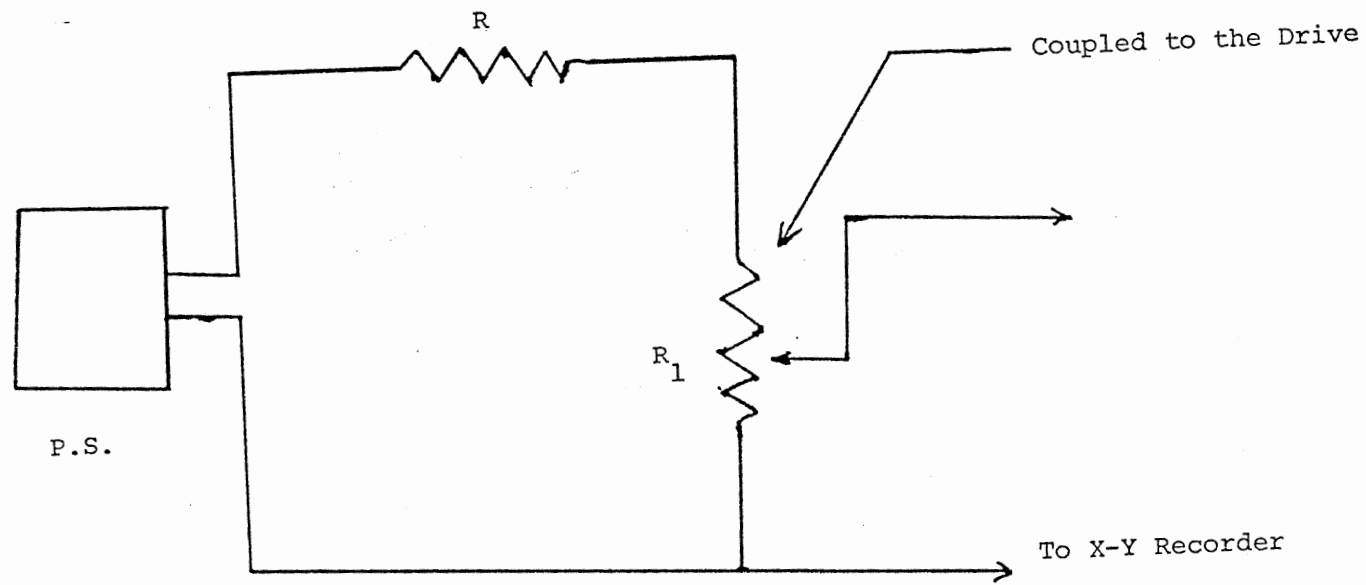
P.S. = Power Supply (15V)

R = 1.5 MΩ R_1 = 10KΩ

Figure 5.   Potential Divider Coupled to Monochromator Drive

roughly five times and the peaks were well defined as compared to the previous results. However, it was found that <u>directly</u> <u>irradiated</u> Silicon Heat-Sink material itself produced at least two TSL peaks at about the same temperatures as ones observed in crystalline SiO_2. To insure that no contribution from the silicon heat-sink material was present in the observed TSL of the quartz, this material was finally totally abandoned. Subsequently, a mounting using soft indium foil was stuck to the copper plate by General Electric adhesive at only a few remote points from the window and pressed against the copper plate and the boundary of the sample was used. However, the thermal contact was not reliably improved. The best results were achieved by using the additional small rectangular copper plate having a window at the center of the size of the one in main copper plate. It was fixed to the main plate by screws through its corners and the sample was sandwiched between the plates. All adhesives were abandoned and small pieces of indium foil were wrapped around the boundary of the sample and the plates to improve the thermal contact. An additional purpose of this setup was to maintain the whole specimen at uniform temperature during the irradiation and subsequent warming. A surface of the sample equivalent to the size of the windows in the copper plates was always kept completely uncovered. This was the part of the sample irradiated directly and the source of the TSL observed. Generally the side of the sample towards the small additional copper plate was irradiated and the total TSL observed from the same side. The opposite side was exposed to the monochromator for TSL spectral analysis. It was observed that the data obtained by this system was consistent in an overall sense with the data obtained using the Silicon Heat-Sink

material about 2 to 3 mm away from the window through which the specimen was irradiated and physically shielded from the direct electron beam. The thermocouple cold junction was placed in several different positions on and around the specimen to check temperature uniformity and reliability and differences of several degrees were observed. The implications will be discussed later.

After mounting the virgin sample, the whole assembly of the sample holder and the cryostat was fixed to the vacuum pumping stand and pumped until the pressure was of the order of 10^{-5} torr. Then the cryostat was cooled with liquid nitrogen, but since the sample was mounted some distance away from the liquid nitrogen with a stainless steel thermal resistor between the cold finger plate and the cryostat, the lowest temperature the sample attained was near 96K. After about half an hour of cooling, the sample was irradiated through the aluminum window by 1.5 MeV electrons from the Van de Graaff accelerator. It was irradiated for 100 seconds at a time followed by a 200 second interval for allowing the heat generated during the process to dissipate. The total irradiation time was 300 seconds with 1.5 MeV electrons and a beam current of 10 μA. The intensity of the electron beam at the sample surface was of the order of 0.20 $\mu A/cm^2$. After completion of the irradiation the cryostat/sample holder was taken to the laboratory and the base rotated 90 degrees to allow sample viewing. It was positioned at the entrance slit of the monochromator and the phototubes and associated electronic were attached. The EMI-9558Q photomultiplier tube was placed to detect the total TSL. Its output was applied across Y-axis of the X-Y recorder through the Keithley 602 electrometer. The voltage across the thermocouple was applied to the

X-axis of one X-Y recorder, thus plotting arbitrary units of total TSL versus the temperature voltage. The other side of the sample was exposed to the monochromator with each slit opened to 3 mm because of the low total luminescence output. The scanned output from the mono- chromator was observed by EMI-6256 photomultiplier tube. Its output was applied to the Y-axis of the second recorder through the Keithley 600B electrometer and the filter circuit. The voltage corresponding to the spectral range of the monochromator, obtained from the 10-turn potential divider coupled to the scale of the monochromator by means of a common drive, was applied to X-axis of the other X-Y recorder. This plotted arbitrary units of the intensity of scanned luminescence against the wavelength. The optical alignment on this side was always done by physically adjusting the position of the phototube to provide a maximum response to room light passing through the sample and monochromator at a setting of 500 nm.

The sample system was warmed by room temperature air blown into the cryostat for convenience and simplicity. After some practice, a con- sistent heating rate around 11 degrees Kelvin per minute could be easily maintained by adjusting the air jet and keeping watchful eye on time and temperature. The heating was relatively constant at this rate escept in the region near 273K where no TSL activity was observed. The specimen emitted luminescence during heating and its total intensity and spectral output were recorded as described earlier.

For reasons which will be discussed later, multiple irradiation studies were also carried out. The basic measurement sequence and tech- nique were the same as described above but this was preceded by another irradiation at elevated temperature (usually room temperature) using

similar beam energies, currents and total irradiation times. After this was completed, the cryostat was cooled and the 96K irradiation procedure initiated.

CHAPTER IV

GENERAL COMMENTS CONCERNING THE

EXPERIMENTAL RESULTS

The purpose of this chapter is to present the results of the TSL experiments on rather well-characterized quartz. It should be emphasized that the measurements taken on these high quality single crystals of both swept and unswept quartz under similar conditions despite some variations are found to be relatively consistent. Thus, the respective data presented here, although chosen selectively, represent characteristic behavior for each type of crystal. Remarks that refer to quartz specimens without specifying a particular type or treatment are meant to be true for all types.

The following description of irradiation procedures is presented because certain difficulties encountered in the early stages of the investigation and subsequently overcome could be of help to others and are now recognized to be important in interpreting the data. The present investigation started with the basic approach of adopting some standard procedure of low temperature irradiation and detecting the TSL, if any, present in synthetic quartz. It was observed that whenever the specimen was not maintained near its lowest achievable temperature during irradiation, the lowest temperature TSL peak was either absent or reduced to a great extent pointing to the fact that this peak was very sensitive to the temperature at which the specimen was irradiated. It

may be mentioned here again that the lowest temperature the specimen could attain in this apparatus using liquid nitrogen in the cryostat was about 96K, the reason being that the cryostat was separated from the copper sample holder by a piece of stainless steel which caused a built-in temperature gradient. Thus in this thesis the term "liquid nitrogen temperature" (LNT) refers to 96K.

It was realized that the specimen temperature was raised by irradiation and some of the trapped charges ordinarily responsible for the TSL could also be released by heat during irradiation. Therefore in order to keep the sample cold, irradiation was done with alternating intervals of beam-on and beam-off. In the meantime, the contemporary group at Oklahoma State University, studying ESR effects in the same material reported some interesting results by using combinations of irradiations at different temperatures (31). To investigate similar effects it was decided to study TSL also by irradiating at room temperatures followed by irradiation at liquid nitrogen temperature (96K in this case). The following procedure for such double irradiations was observed through out the investigation. The specimen was irradiated at room temperature continuously for 300 seconds. This was followed by irradiation at 96K carried out in three steps each of 100 seconds duration and punctuated by 200 seconds of no irradiation. Later on it was actually verified that the specimen could regain its lowest temperature after interrupting irradiation for only 150 seconds.

At the beginning an attempt was made to detect TSL by using an RCA IP28 photomultiplier tube but the results were not encouraging. Subsequently this tube was replaced by a more sensitive EMI-6256 tube and ultimately by an EMI-9558Q. At this stage a total TSL output was de-

tectable but it was still too low to allow a spectral analysis. In the meantime it was learned that the thermal contact of the sample and cold finger was an important consideration in the irradiation heating and it too was improved. All these factors have their imprints on the data and offer a number of suggestions for interpretation of the improved results that followed.

The TSL was investigated over the temperature range from 96K to 273K and glow peak structures were detected in the region from 110K to about 245K. Furthermore, the results could be conveniently divided into three temperature regions of separate interest. The first region was between 115K and 140K, the second between 150K and 180K and the third from 210K to 240K. The behavior in the three regions of interest could be described in the following general terms:

Region I

This region was generally found similar in all types of samples investigated. A sharp TSL peak usually appeared between 125K and 135K. This region was the most sensitive to the temperature at which sample was irradiated. Whenever the thermal contact between the sample and copper cold finger was poor the peak was either greatly reduced or almost disappeared. It was, however, little affected by the double irradiation procedure. The spectral output of this region was always in a broad band centered at greater than 400 nm wavelength. For purposes of identification, this will be referred to as the "longer" wavelength region with more specific details to be provided later in the chapter.

Region II

This region of peaks was also observed in all types of samples investigated but showed greater variability between specimens. It even showed fluctuations in different consecutive runs on the same sample and will be described in more detail when discussing individual specimen categories. TSL peak positions were generally observed in the 150K to 180K region and often showed complex overlapping. This region was slightly sensitive to double irradiation. The spectral output of this region was usually detected in a broad band centered somewhat below 400 nm. For convenience it is referred to as the "shorter" wavelength region.

Region III

Peaks in this region were observed in the unswept samples only and essentially disappeared when samples were subjected to double irradiation. They reappeared after the samples were annealed to 725K for about 10 minutes. The TSL peak was broad and usually contained a shoulder which might appear either to the right or to the left of the peak. It was not sensitive to the low temperature at which sample was irradiated, like Region II, and its spectral output was observed at the shorter wavelength.

Specific Experimental Results

The following are specific observations and comments regarding the unswept Electronic Grade, Premium Q and the swept Electronic Grade samples investigated.

Unswept Electronic Grade Specimens

The investigation was started with unswept Electronic Grade samples and hence the most extensive experimentation was carried out on this type. It is found that the data obtained from all of them are generally comparable in basic character and relatively reproducible. The following are the regionwise observations as categorized earlier.

Region I: Irradiated at 96K Only

Generally one sharp major peak centered around 128K is observed and occasionally there is a hint of a shoulder on the right side. It is higher in peak intensity than the other regions. The spectral output is always observed in the longer wavelength region. This peak is sensitive to the temperature at which the sample is irradiated and apparently also to the length of time between the completion of irradiation and starting the TSL run.

Region II

Three distinctly separable peaks were observed during the first or up to the second run. Later on generally two peaks were left, and they were somewhat broadened. Peak positions generally occur around 155K, 167K and 175K. The peak intensity of the TSL is roughly three times lower than that in the first region and spectral output is observed in the lower wavelength region.

Region III

A broad TSL peak is observed with a shoulder indication to the left in some samples (EGE-12) or to the right in some cases (EGE-13),

probably indicative of two closely overlapping peaks. Peak positions are around 212K and 225K. The TSL intensity of the peaks is about one-half that of Region II. Spectral output is the same as in Region II.

Region I: Irradiated at Room Temperature Followed by Irradiation at 96K

The peak position does not change but a shoulder indication is never observed. In some cases the TSL intensity is slightly lower than that resulting from only low temperature irradiation but no systematic change is observed. The spectral analysis remains unchanged.

Region II

A slight shift of up to few degrees sometimes occurs in peak positions and the peak structure seems to be partially cleaned out. The TSL intensity is generally depreseed by as much as 30%. The spectral analysis remains unchanged.

Region III

The TSL in this region is either wiped out or only a slight indication is left. At a minimum it is at least reduced five times as compared to what is observed following a single low temperature irradiation. No spectral analysis is possible. It cannot be reproduced by another single low temperature irradiation unless the specimen is first thermally annealed at about 725K.

After Thermal Anneal Irradiated at 96K Only

After thermally annealing the specimen around 725K for about 10

minutes, it behaves as a fresh virgin sample. Every aspect mentioned so far is then basically reproducible. Even the shoulder indication in the first region peak, which is observed very rarely, is also observed at least once after annealing the sample.

Figures 6, 7, and 8 provide a graphical representation of typical behavior observed for this type of specimen.

Premium Q Specimen

The TSL behavior of this type of unswept synthetic quartz is roughly a reduced intensity copy of that of the previously described unswept Electronic Grade type. Sawyer bar 'E' provided the Electronic Grade specimens investigated and Sawyer bar 'A' the Premium Q. Figure 9 indicated the consistency of the results obtained from one specimen of this type. It is found that in general the TSL effect in the Premium Q is less than that in the Electronic Grade, at least for the bars investigated. The following details the TSL observed in the Premium Q specimen under different irradiation conditions.

Region I: Irradiated at 96K Only

There is a single clean peak in this region and no evidence of any shoulder whatsoever. The peak position was first measured around 130K but later shifted to around 125K when thermal contact of the specimen was improved. It is higher in peak intensity by about three times than the peaks of Region II and the spectral output lies in the longer wavelength region.
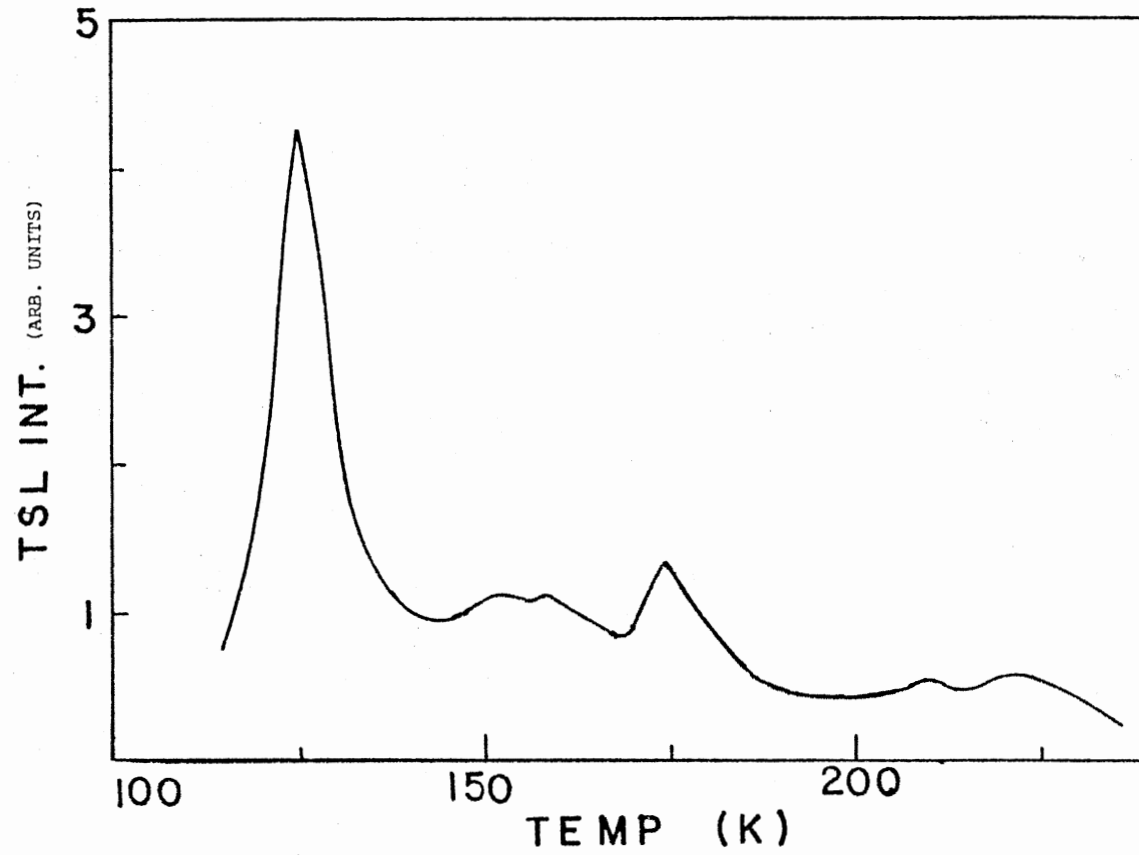
Figure 6. TSL Curve of an Unswept Electronic Grade Specimen
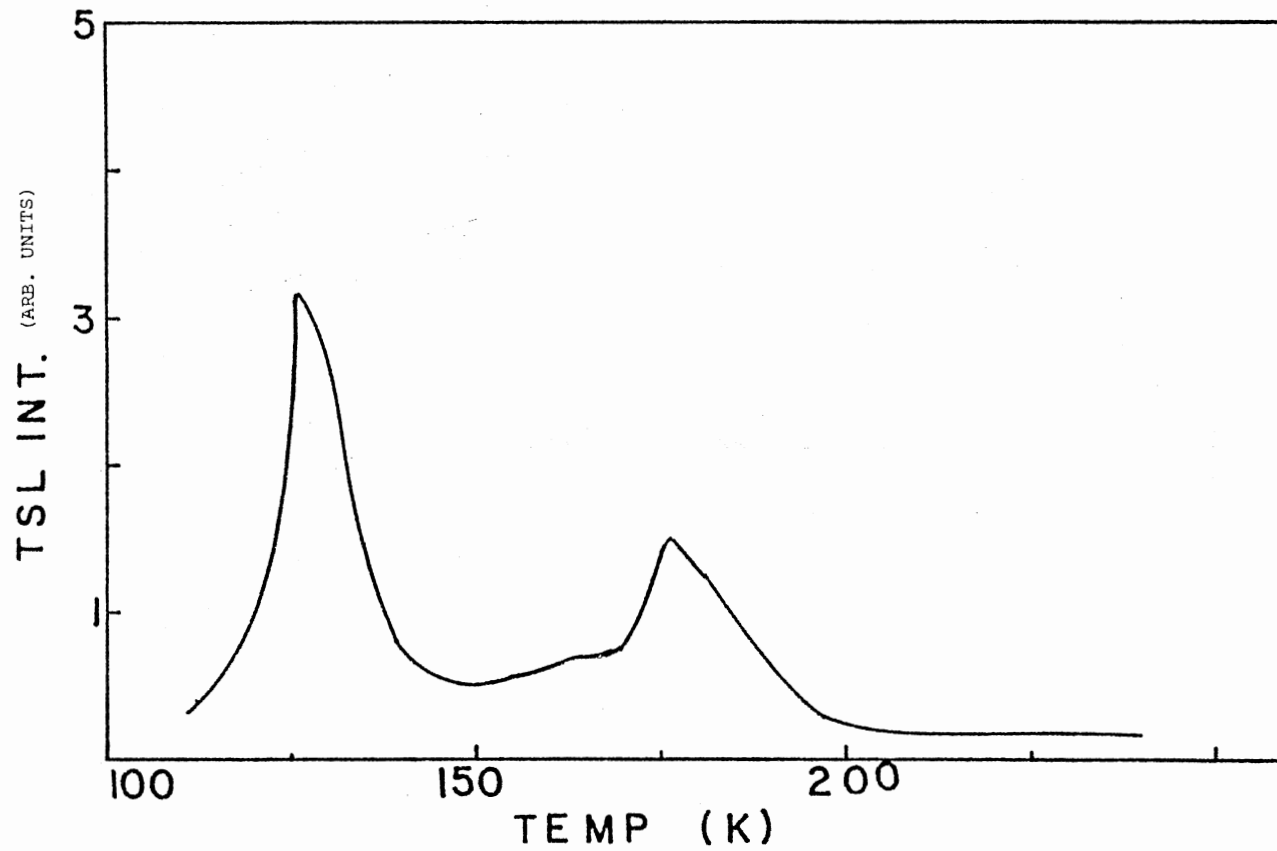(Irradiated at 96K Only)

Figure 7.   TSL Curve of an Unswept Electronic Grade Specimen (Irradiated at 300K and Then at 96K)
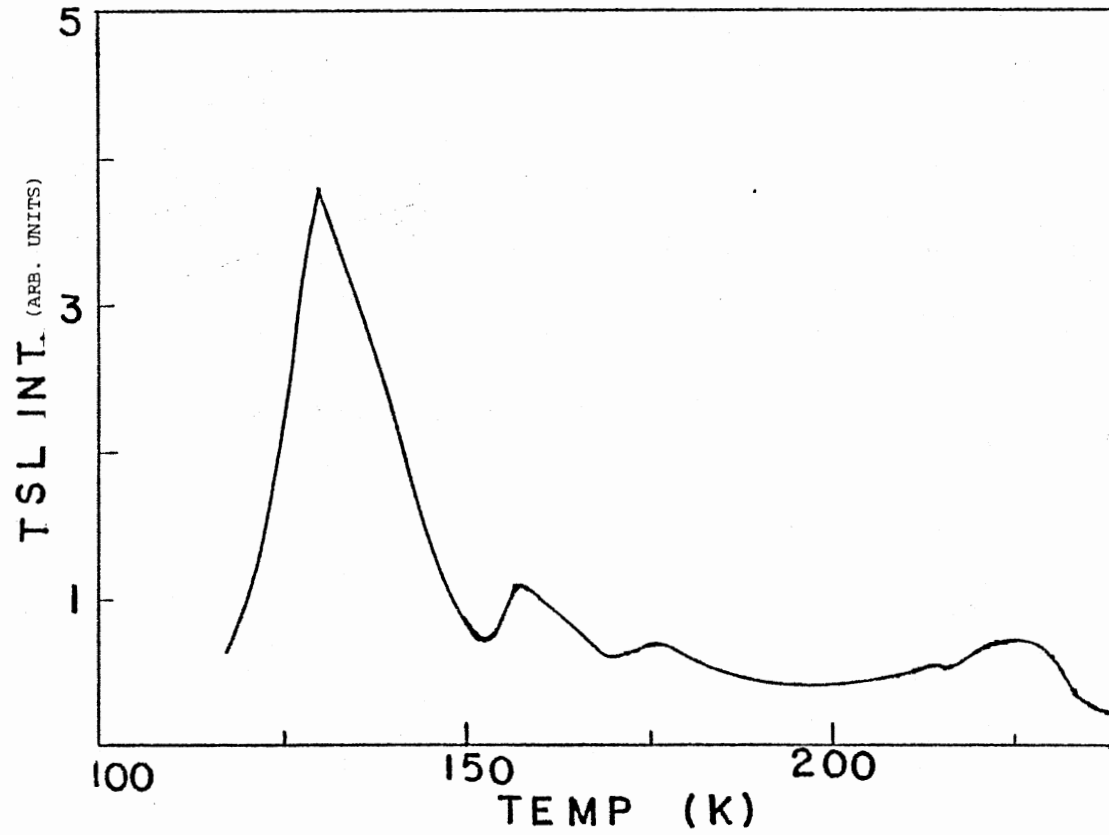
Figure 8. TSL Curve of an Unswept Electronic Grade Specimen
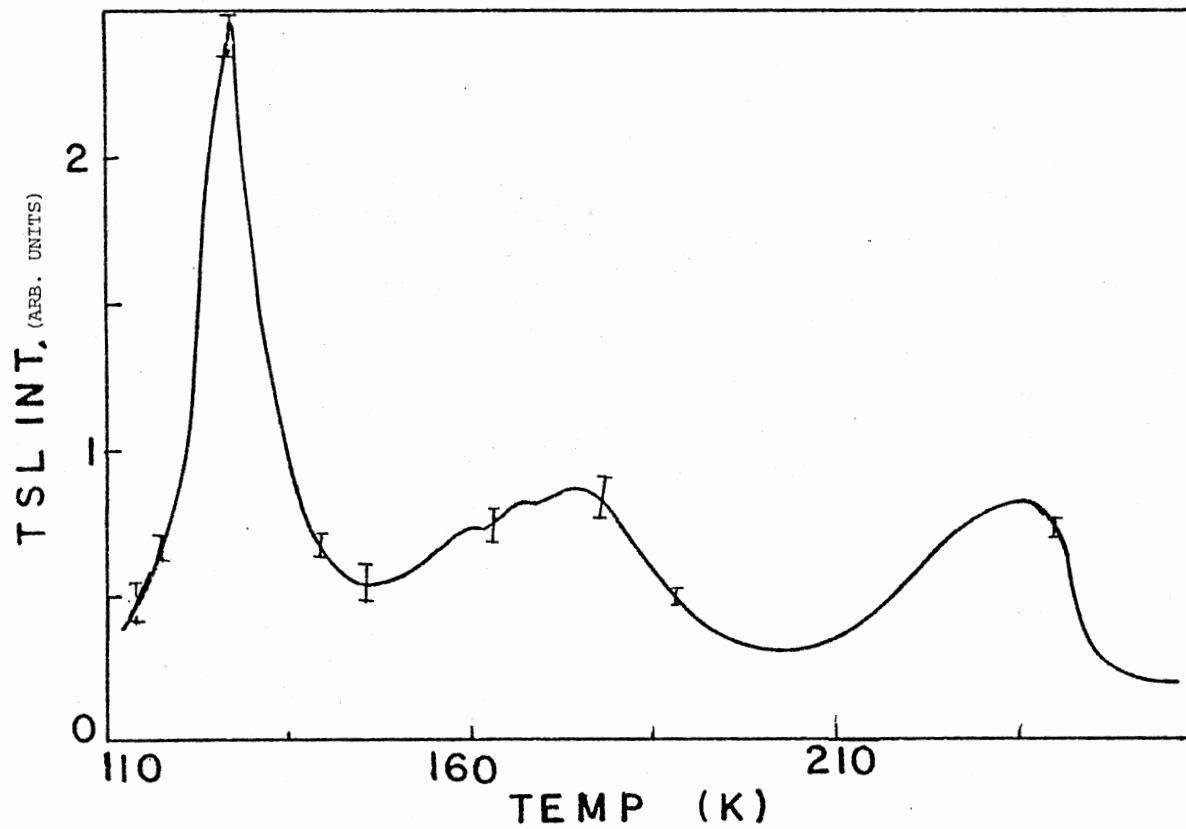(Irradiated at 96K (Annealed))

Figure 9. An Average TSL Curve for Three Runs of an Unswept Premium
Q Specimen (Irradiated at 96K Only)

Region II

The peak structure overlaps with sometimes an indication of three peaks. At other times one peak slightly broadens and only two are observable. The peak positions are generally located around 155K, 167K and 175K. Spectral output is not detected because the total output is too low.

Region III

In this region either one broad peak is observed or two peaks of equal magnitude are closely superimposed. The peak position was observed close to 235K but it shifted to 225K after improving the thermal contact of the specimen. The TSL intensity more closely compares to that in Region II than is true for the Electronic Grade specimens and spectral output is not observable.

Region I: Irradiated at Room Temperature Followed by Irradiation at 96K

There is a single clean peak having the same magnitude as in the case of single low temperature irradiation. The peak position is around 125K. Spectral output is occasionally observed in the longer wavelength region.

Region II

The peak structure seems reduced as there is only an indication of two peaks instead of the three occasionally observed after a single irradiation. The TSL peak intensity is reduced about 20 to 30% as compared to the single irradiation result. The low temperature side peak

seems to be wiped out as peak positions appear around 168K and 178K. Spectral output is not observable.

Region III

There is nothing noticeable left in this region after double irradiation.

After Thermal Anneal Irradiated at 96K Only

After thermally annealing the specimen at 725K for 10 minutes, all of its previously described behavior reappears. The peak magnitudes are quite comparable to the runs before anneal, their positions with respect to temperature are almost the same and the overall TSL structure is almost a true copy of the original.

Characteristic TSL observations on this specimen are presented in Figures 10, 11 and 12.

Swept Electronic Grade Specimens

Two specimens of this type were thoroughly investigated but they were possibly from different bars or widely separated parts of the same bar. Their behaviors differed from the unswept samples in a similar manner, but they showed some difference from each other also and hence are described separately.

Speciemn EGF-15

This sample, when subjected to single low temperature irradiation, shows only one peak in Region I and it is of the same general magnitude as the comparable peak in unswept samples. In Region II it shows a two-
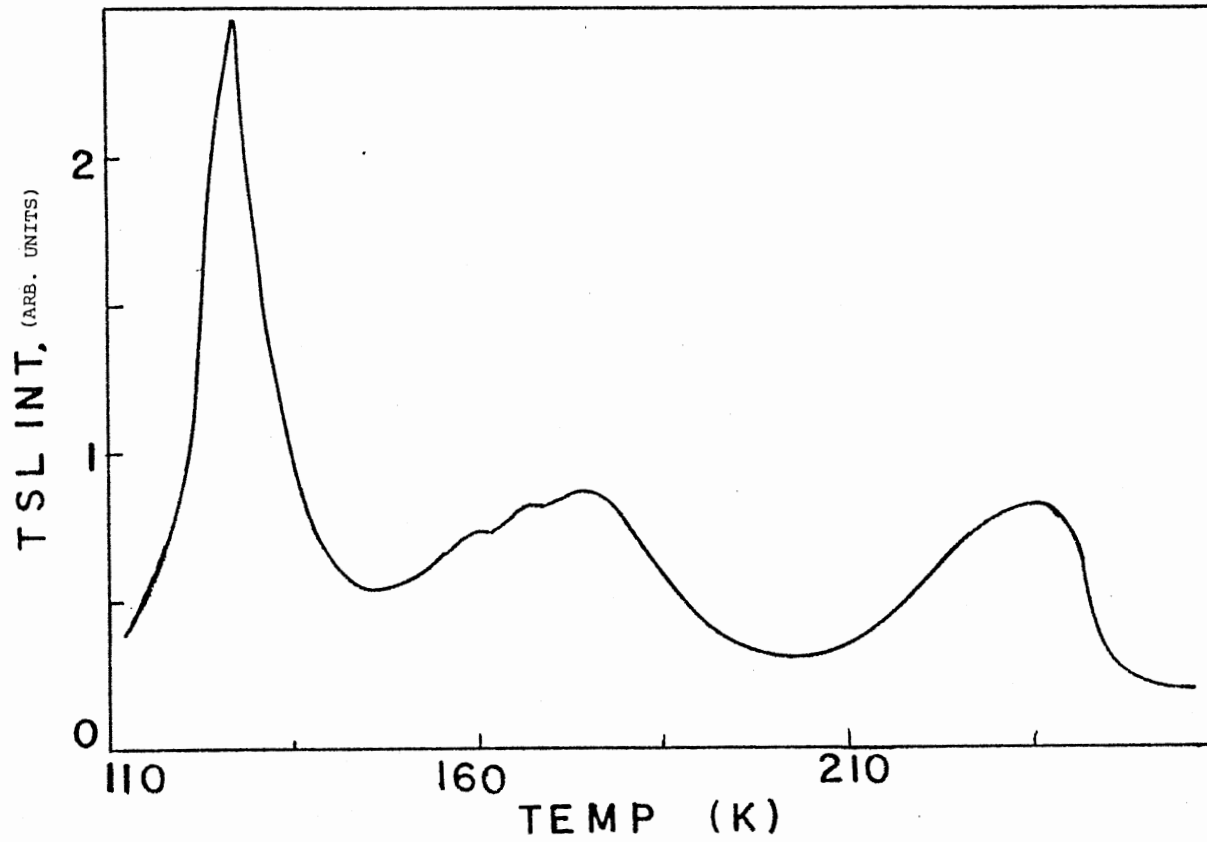
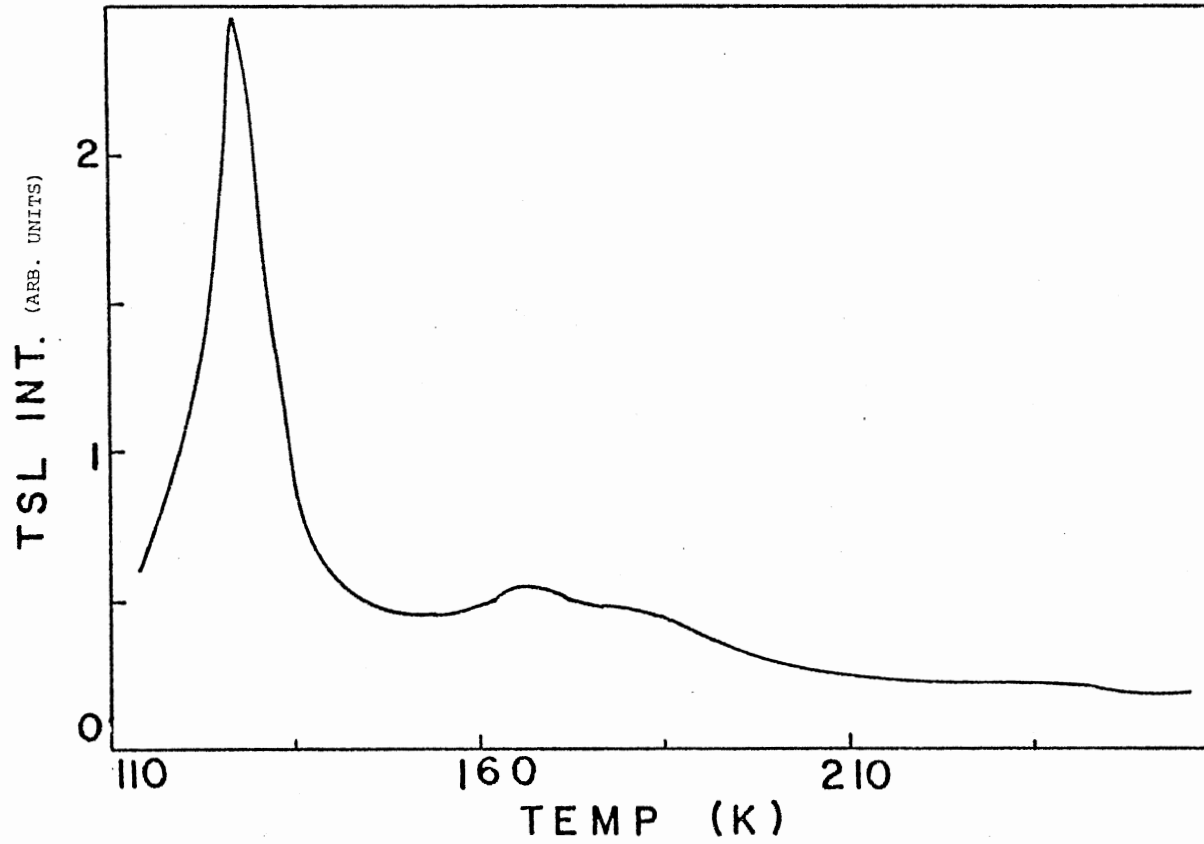Figure 10.   TSL Curve of an Unswept Premium Q Specimen (Irradiated at 96K)

Figure 11. TSL Curve of an Unswept Premium Q Specimen (Irradiated at 300K and Then at 96K
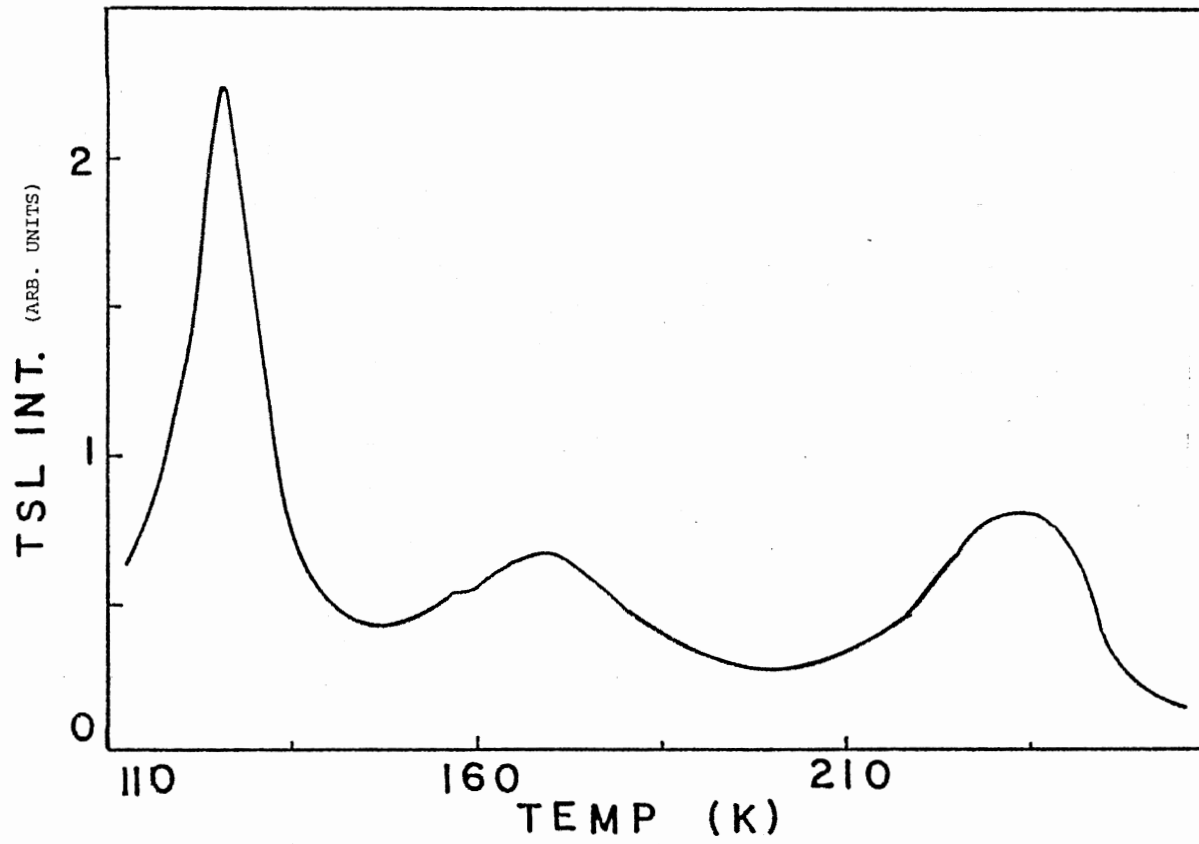
Figure 12. TSL Curve of an Unswept Premium Q Specimen (Irradiated at 96K After Anneal)

peak structure but the output is quite low as compared to that of the first peak and the unswept specimens. There is a very slight indication corresponding to Region III of the unswept samples. The peak positions generally match with unswept samples. Spectral output is only detectable in Region I and is in the longer wavelength region.

The double irradiation procedure basically produced no change in any respect as shown in Figure 13.

Specimen EGF-14

This sample showed only two clean sharp, peaks corresponding to Regions I and II of the unswept samples when subjected to single low temperature irradiation. The peak positions matched with peaks observed in unswept samples and there was almost no indication of a corresponding Region III. The peak intensity was relatively higher in both regions than observed in unswept samples but Region II output was greater than that of Region I and it kept increasing during first few runs. The spectral output in both regions was in the longer wavelength region.

Double irradiation produced no change in any respect. The Region II peak was lost when the specimen was remounted with indium foil backing on one side for better thermal contact.

After annealing at 725K the overall TSL output was low and almost exactly matched with that of the other swept sample. A slight indication of Region III was observable. Spectral output was only observable in Region I and was in the longer wavelength region.

Figures 14, 15 and 16 give relevant data for this sample.

Comments on Wavelength Analysis

Having only observed a very low TSL output in the early stages of
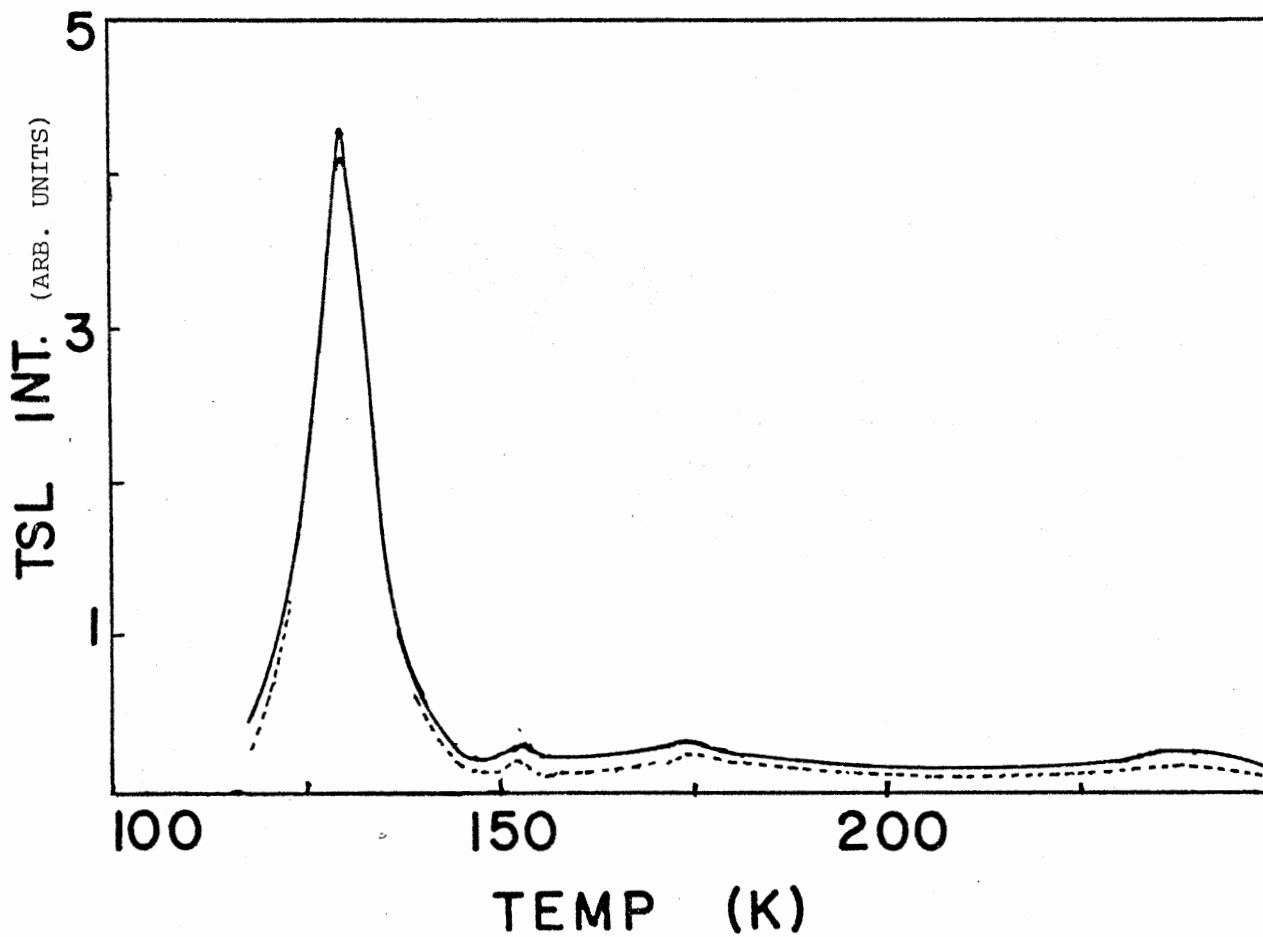
Figure 13. TSL Curves of a Swept Specimen (EGF-15) (Irradiated at 96K Only and Irradiated at (300K + 96K, Dotted Curve))
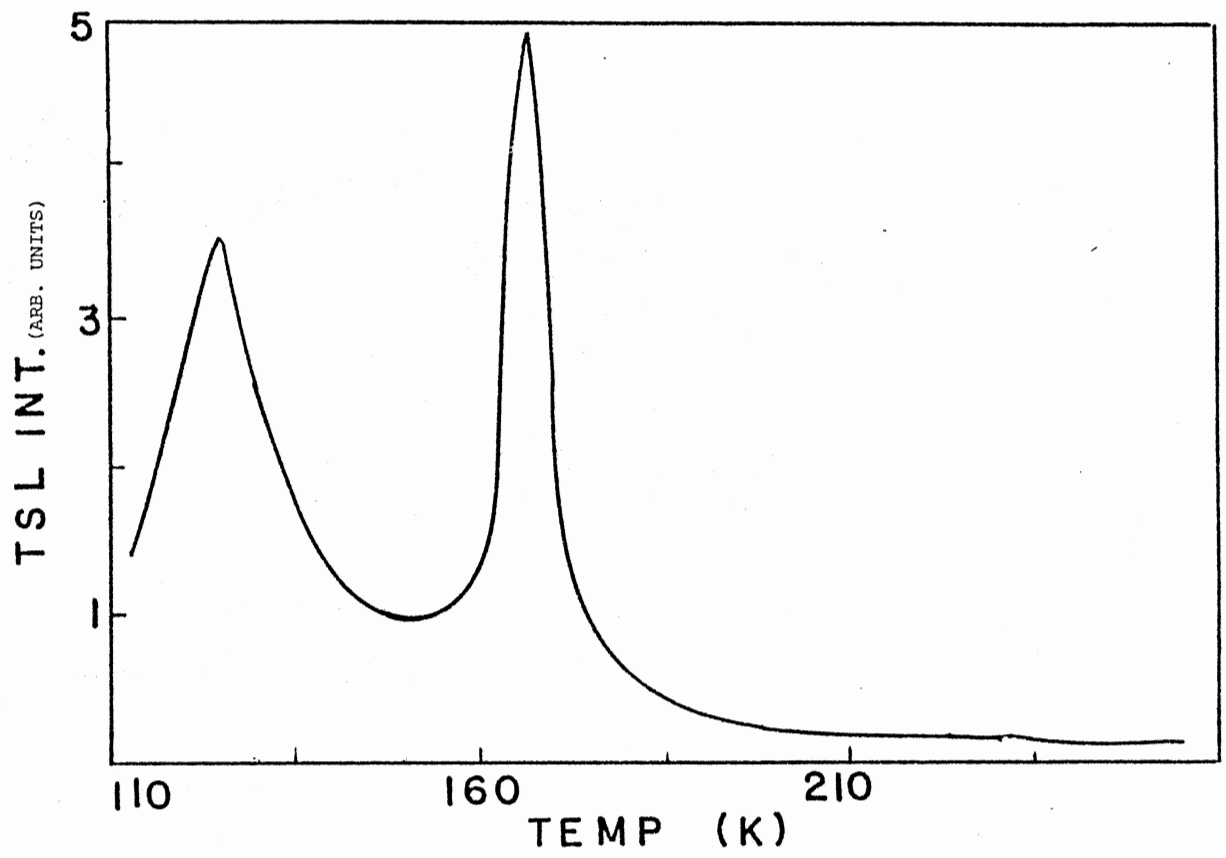
Figure 14. TSL Curve of a Swept Electronic Grade Specimen (EGF-14)
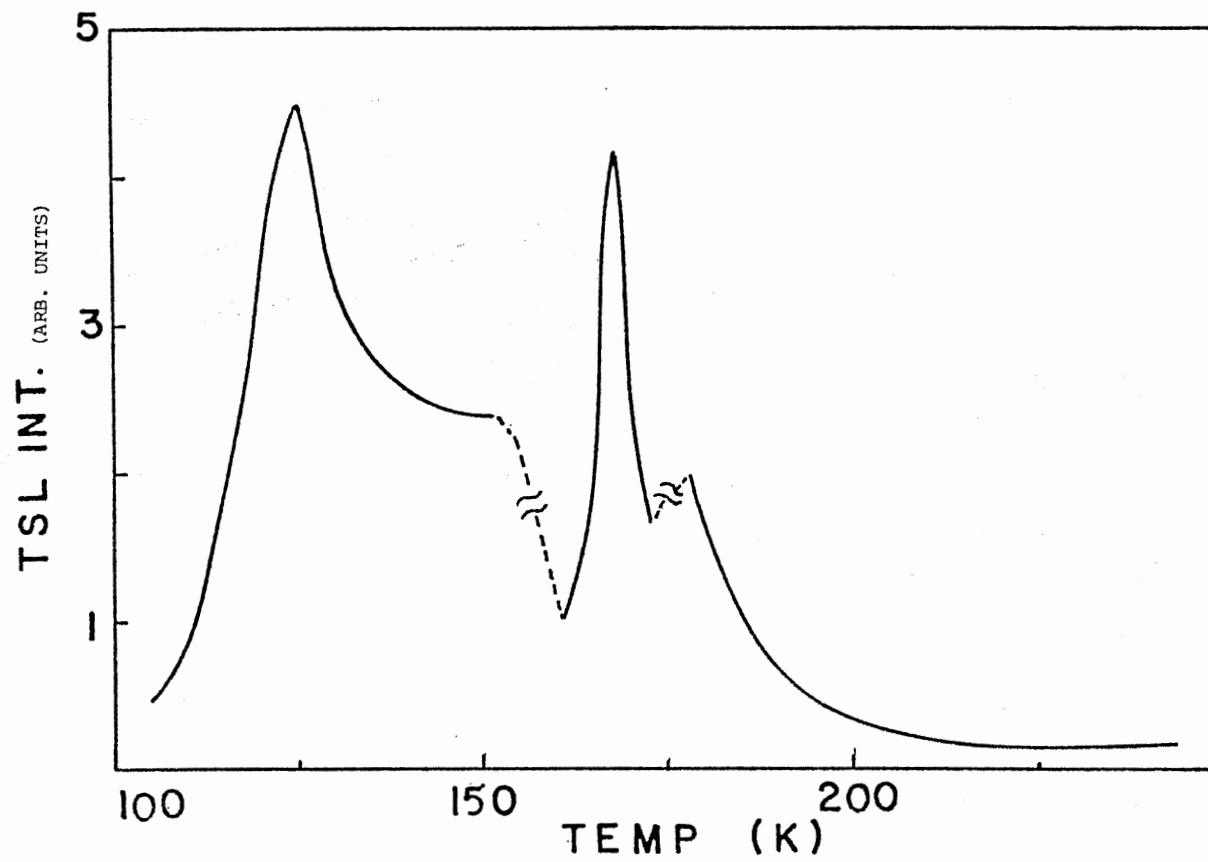(Irradiated at 96K Only)

Figure 15.   TSL Curve of a Swept Electronic Grade Specimen (Irradi-
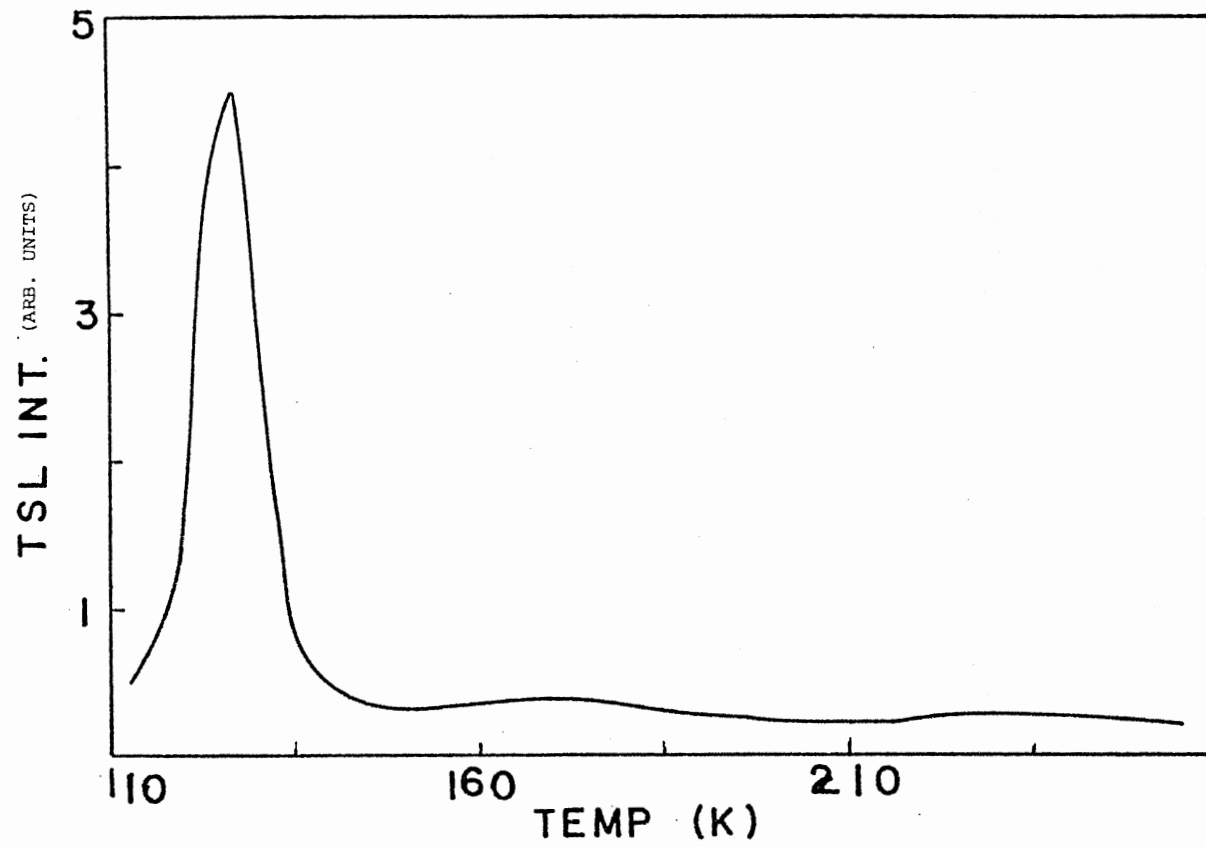ated at 300K and Then at 96K, Second Peak Reduced by
5)

Figure 16.   TSL Curve of a Swept Electronic Grade Specimen (EGF-14)
(Irradiated at 96K After Anneal)

the work, it seemed unlikely that the wavelengths of the TSL peaks in the high quality synthetic quartz would ever be satisfactorily determined. However, as time progressed the situaton somewhat improved after establishing a better thermal contact of the sample with the cold finger. Still the TSL was so low that the output from the monochromator could not easily be separated from the noise. An R-C stabilizer was first used to reduce the noise effects and finally a small filter circuit, described in Chapter III, was introduced. Even then the output was so low that the monochromator slits had to be opened to 3 mm in order to get measurable output. This obviously reduced the accuracy of the wavelength measurements.

In Region I the TSL peak was very sharp and its intensity could change very rapidly with time and temperature, meaning that on many occasions the spectral output curve was correspondingly shifted. This effect was however less prominent in Regions II and III where the TSL intensity was lower and did not change as rapidly.

Under the prevailing circumstances the best estimated results are considered to be the following: In Region I, the spectral output curve peaks around 450 nm and in Region II and Region III it peaks around 380 nm.

Figure 17 is characteristic of the best wavelength data in terms of peak height, shape and half-width.

The Correlation Experiment

As mentioned in Chapter I, during the ESR and infrared studies of this material some interesting changes occurred when unswept specimens were given a combination of irradiations--at liquid nitrogen temperature

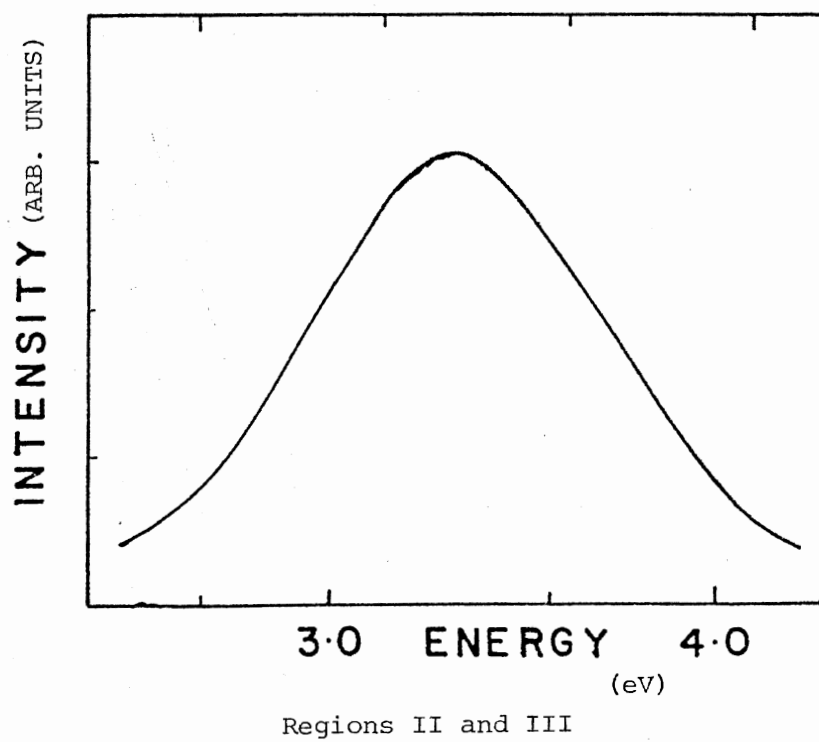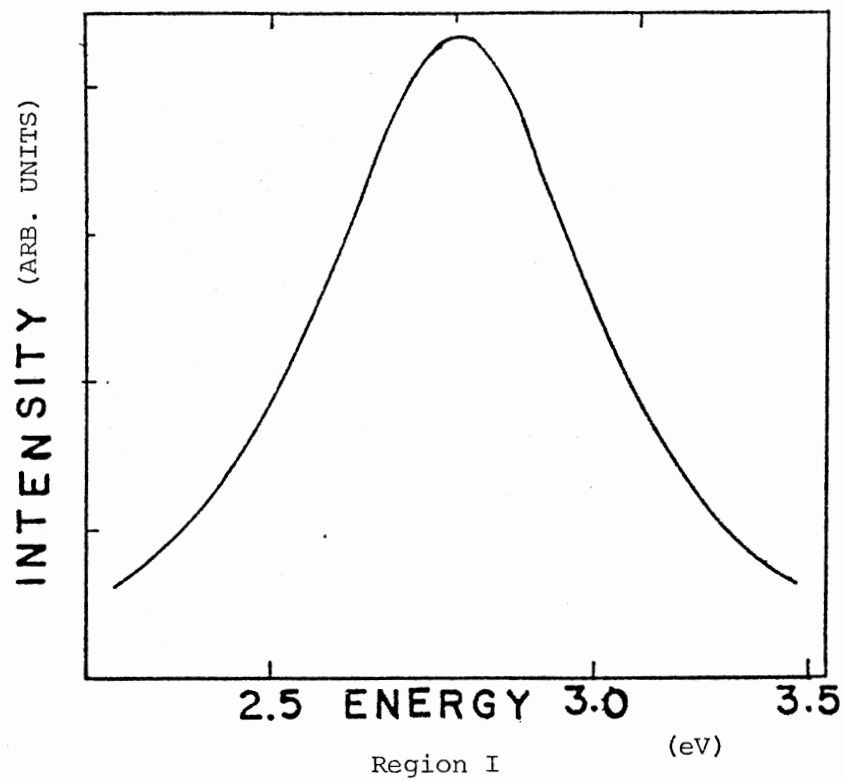Region I

Regions II and III

Figure 17. Spectral Analysis Results

followed by a second at room temperature and this followed by a third at liquid nitrogen temperature--were used. It was observed that certain changes had almost completely been introduced when irradiation at room temperature was used in these sequences of irradiations and these changes were not evident after low temperature irradiations alone. To study the phenomena more carefully it was decided to replace the room temperature irradiations in these sequences by a series of irradiations at successively increasing temperatures starting from the low temperature side. By this technique it was hoped that the temperature region around which these changes take place could be identified. The procedure was carried out both in the ESR and the OA investigations and a good correlation of results emerged (30,31).

As described in the preceding section on results, it was also observed that 'Region III' of the TSL activity in the unswept samples was considerably reduced whenever these were subjected to a combination of irradiations at room temperature and then at low temperature (96K). It was decided to determine the intermediate temperature around which this change occurs and thus attempt to establish a correlation of the results with those from the other techniques. For this purpose unswept Electronic Grade specimen (EGE-13) was selected and the following experiment performed:

Step (1). The specimen was irradiated at 96K only and the TSL results were recorded.

Step (2). It was irradiated at 145K and then reirradiated at 96K and the TSL results were recorded.

Step (3). It was irradiated at 205K and then at 96K and the TSL results were recorded.

Step (4). It was irradiated at 253K and then at 96K and the TSL results recorded.

The results obtained are illustrated in Figure 18 and were as follows:

Step (1). TheTSL results were quite characteristic of those observed in the unswept Electronic Grade samples as expected and reported earlier. There was only one peak in Region I, two in Region II and one in Region III.

Step (2). All results were almost the same as in Step (1), except that there was a small but distinct shoulder located at 199K to the low temperature side of the Region III peak. The magnitude of the TSL peak in Region III was comparable to that of the previous run.

Step (3). There was no change in the Region I peak in any respect. Only one comparable TSL peak on the low temperature side was present in Region II.

A new peak of very high intensity appeared at 199K, where there had previously been only a shoulder or the beginning of a small peak in Step (2). The usual peak of Region III remained in tact and was basically comparable to the previous result.

Step (4). The peak in Region I remained unchanged. There were two peaks somewhat reduced compared to peaks of Region II in first two steps, around Region II at 172K and 197K. It was not absolutely certain whether one of them (at lower temperature) belonged to Region II and the second was a remainder of the new peak observed in Step (3) or whether both belonged to Region II and were shifted in temperature. However, the former seems more likely. The peak of Region III was roughly reduced by six times from its relative values in earlier steps. This
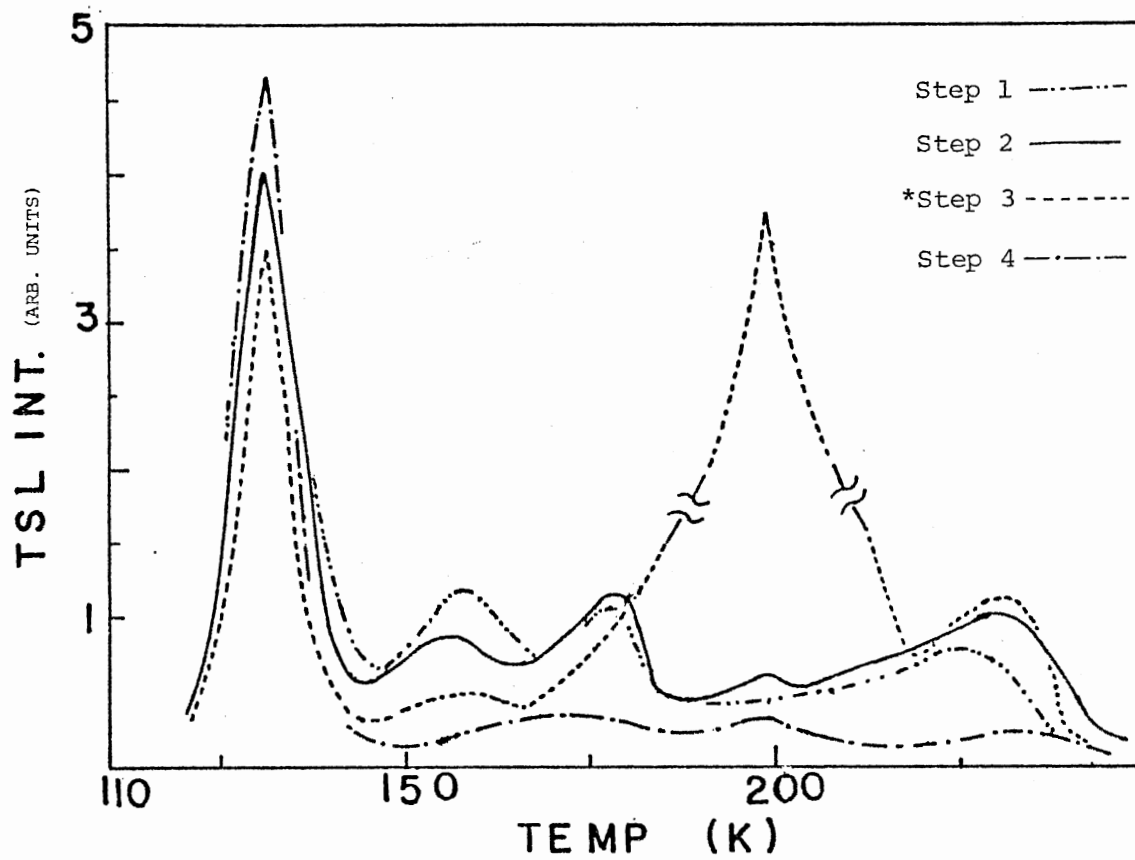
Figure 18.   TSL Curves of an Unswept Electronic Grade Specimen
Selected for Correlation Experiment (Peak at
~200K Reduced by 2)*

observation yields an anticorrelation between the formation of $Al^{3+}-OH^{-}$ and/or the $[Al_{e+}]^{O}$ centers as determined from infrared and ESR measurements and the TSL in Region III.

The spectral output of Region I belonged to the longer wavelength region in all steps and that of other Regions was not detected with the exception that the output of the new peak observed in Step (3) belonged to the shorter wavelength region.

CHAPTER V

DISCUSSION ON RESULTS AND SUGGESTED CONCLUSIONS

Crystalline SiO_2 has been investigated during the past few decades by a number of researchers using TSL. Although progress has been made in identifying some of the defects because the measurements were made by different investigators on a variety of types of specimens, there have been few generally agreed upon conclusions reached. Especially lacking are comprehensive studies carried out below room temperature. Thus it is necessary for quite a few investigators, using different techniques on the same type of material to colloborate. Otherwise, it is difficult to draw unified and acceptable conclusions regarding the details of defect centers and electronic processes responsible for the observed TSL. This has been the point of view adopted for all the radiation damage studies on quartz being done at Oklahoma State University.

It was mentioned earlier that at least in principle severla parameters of the defect centers and electronic processes can be estimated. Below I have attempted to analyze the data inso far as possible and subsequently to suggest ideas for further investigations.

The Activation Energy

Simply by inspecting the data presented in the previous chapter, it is obvious that the first TSL peak, occurring around 125K, is generally not overlapped by any other peak and is non-symmetric about the temper-

ature corresponding to the peak position. This implies that the luminescence process responsible for it is 'monomolecular' and hence there is little retrapping associated with this process. This seems quite likely and acceptable because it is the lowest temperature TSL process observed and most of the traps are full at the beginning.

As pointed out in second chapter a variety of approaches and respective formulas have been developed in the literature to find the activation energy of the corresponding traps and almost every approach has points for and against it. However, it is felt that the method due to R. Chen is the most appropriate choice for analysis. According to it, the activation energy 'E' for a monomolecular process is estimated by:

$$E = 2k\, T_m \left(\frac{1.25\, T_m}{T_2 - T_1} - 1 \right)$$

where T_1, T_m, T_2 are temperatures corresponding to the 50% point of TSL peak emission on the rising side of the peak, the peak maximum, and 50% of the peak emission on the falling side with k the Boltzmann constant. It is interesting to note that many mathematical procedures for determining E developed over the last three decades provide results comparable to those obtained from the estimate of activation energy first suggested by Randall and Wilkins along with their theoretical explanation of TSL process:

$$E \approx 25k\, T_m,\ eV$$

where k is Boltzmann constant and T_m is temperature corresponding to peak maximum. In the following table the activation energy correspond-

ing to the first TSL peak has been calculated using R. Chen's expression and compared to Randall and Wilkin's approximation on random data obtained from unswept Electronic Grade, Premium Q and swept Electronic Grade samples. The estimate of activation energy corresponding to this TSL peak is therefore of the order of 0.27 eV to 0.28 eV. It is observed that data analysis is more consistent with better thermal contact and there is evidence that an initial higher start on the intensity-- possibly due to some after-glow effect of irradiation--also adversely effects the estimate as suggested by the last entry in the table. It was not considered practical or worthwhile to make an estimate of activation energy corresponding to other TSL peaks in the data using Chen's method. The major reason is that the peaks overlap and the magnitude of the overlapping peaks is not firmly consistent from run to run. Uncertainties introduced by a "thermal cleaning" process would make it difficult, if not impossible to estimate what kind of kinetics is applicable.

To further check if this estimated value of activation energy is reasonable, an attempt-to-escape frequency 'S' has been calculated from this value of E. It can be found by applying the condition of maxima on TSL intensity, thus differentiating the intensity relation developed in Chapter II with respect to temperature is obtained the expression for S,

$$i.e., \quad \frac{dI}{dT} = 0, \quad \therefore \quad \left(\frac{E}{kT_m^2} - \frac{S}{\beta} e^{-E/kT_m}\right) = 0$$

$$\therefore \quad S = \frac{\beta E}{kT_m^2} e^{E/kT_m}$$

TABLE IV

COMPARISON OF TRAP DEPTH ENERGY 'E' FROM R. WILKINS
APPROXIMATION (E $\approx$ 25k T_m eV)

Run No.	Type and No. of Sample	E By R. Chen Method
1	Swept Electronic Grade EGF-15	E $\approx$ 23k T_m eV
5	Swept Electronic Grade EGF-15	E $\approx$ 27.3k T_m eV
4 (after anneal)	Unswept Electronic Grade EGE-12	E $\approx$ 27.5k T_m eV
6 (after anneal)	Unswept Electronic Grade EGE-12	E $\approx$ 27k T_m eV
3	Unswept Premium Q PQA-10	E $\approx$ 24.6k T_m eV
4	Unswept Premium Q PQA-10	E $\approx$ 29.7k T_m eV

on the basis of calculated value of E, the value of S is found to be approximately $3 \times 10^9 \text{ s}^{-1}$ (using $\beta \doteq 10$ deg./min.) which is within the range of generally accepted values of S.

To effectively calculate the impurity or other defect center strength it is necessary to estimate the base line of the dark current, the related TSL peaks should be free of overlapping and some standard specimen containing a known defect concentration should be available. Because of the obvious difficulties and the fact that some concentrations have already been estimated locally by OA and ESR methods which are generally accepted as better techniques for this purpose, TSL impurity strength estimates have not been carried out. From the OA and ESR intensity calculations mentioned in Chapter III one finds that impurity concentrations can differ by at least an order of magnitude from one bar of specimens to another in the material manufactured by the same company. In fact, there can also be significant differences between specimens from different parts of the same bar.

Charge Transfer

Charge transfer in this material has been found to occur around 125K, 165K and 225K. The latter two figures are only representative as it was suggested previously that these multiple glow-peaks indicate several trapping levels, which differ only slightly in energy from each other. This is consistent with earlier reports by Medlin, Schelsinger and Levy (21,24,45).

It has been observed occasionally that peak positions can fluctuate by a few degrees generally towards the higher temperature side. This effect was reduced by improving the thermal contact of the specimen.

The heating rate being fairly constant, other possible factors could be the quality of the vacuum around the specimen and the temperature of the second reference junction (at room temperature) of the thermocouple. Since window fogging was never observed the second reason seems more probable. This room temperature junction of thermocouple could be either affected by difference of temperatures in the irradiation room and the subsequent measurements room (difference observed up to 10K.) or by direct contact with some of the boiling nitrogen vapor from the cryostat. The fact that whenever shifts occurred all peaks were shifted in the same direction through almost the same amount, also supported this contention.

To improve the measurement of the peak position temperature, the sample thermocouple junction was placed between the sample and either of the two plates holding it but no significant difference was observed from the situation when it was soldered to the copper plate close to the bottom of the sample.

Since the copper plates maintain thermal contact with the specimen only around its boundary, there is undoubtedly a temperature gradient between the specimen center and its clamped boundary. Therefore the temperature values presented here may be greater than the real sample temperature by five or six degrees.

Spectral Analysis

Spectral analysis has provided basically two values for the emitted TSL wavelengths. The analyses are plagued with several difficulties: intensities are low and wavelength peaks are broad because of wide mono-chromator slits and probable temperature inhomogeneities within the

specimen itself. Furthermore two simultaneous but separate scanning process are involved--one through the thermal TSL peak and one through the wavelength range.

Returning to the data, one value corresponds to the first region (TSL peak around 125K). Over a number of runs its apparent peak has been recorded from a little over 400 nm to around 500 nm. Most frequently, the value has been measured between 440 nm and 480 nm. Since it is found that this TSL output rises and falls very sharply around its temperature peak position, its spectral analysis curve can shift considerably depending upon the direction of scan and the time of measurement. Out of the large number of attempts, a few times the peak maximum of the TSL curve and the spectral analysis curve maximum have been measured simultaneously and have given consistent values. The number resulting from these occasions is considered to be the best result. The central wavelength associated with the TSL emission band for the 125K peak is believed to be approximately 450 nm with a half width of about 80 nm.

The fluctuations observed in spectral analysis of the second and third TSL regions have been less, possibly because of the fact that the TSL peaks themselves do not rise and fall as sharply and partly because the luminescence output intensity is reduced by a factor of two to three times as compared to the first region. Whenever the overall output intensity was too low in these regions, a spectral analysis could not be obtained. Nevertheless, a number of times spectral outputs of these two regions have been measured and for both of them it was found to occur roughly between 370 nm and 390 nm. During the last few experiments studying effects of irradiation at different temperatures, a new

TSL peak of very high intensity was observed at 200K and the apparatus recorded a sharp spectral analysis curve, centered around 380 nm. This result supplemented with previous analysis strongly supports a contention that the spectral output of both of these higher temperature regions peaks near 380 nm with a half-width of about 90 nm.

In this regard, various results are reported in the literature, although most of the measurements were made at higher temperatures and may well be indicative of entirely different recombination processes. Durani and others have found bands at 370 - 520 nm, which would possibly agree with everybody. Zimmermann mentioned 380 nm and Medlin gave a value of 390 nm (21,25,45). In the higher wavelength region the results close to 450 nm were reported by a number of investigators (21,24,25, 28,45).

Recombination Processes

The results naturally raise questions as to what recombination processes can be associated with these wavelengths. A comprehensible and satisfactory answer requires much more information about the defect centers responsible for TSL and progress in this direction is far from satisfactory at this time. As weill be discussed shortly in detail, thus far, not as many electron-trapping centers have been discovered as hole-trapping centers. Thus with the information available at hand, it could be suggested that there is single recombination defect site in which two different radiative transitions are taking place. It is also possible that there are two different recombination processes, taking place at different sites and each process has its different spectral output. The latter case seems more likely. A major recombination

process might occur at an Al-hole site, but since this center has already annealed out in the temperature region where TSL activity is still observed (low temperature irradiation only), it is conceivable that the second-recombination process takes place at some defect site like an oxygen vacancy or $[O-H]^-$ complex.

General Considerations for TSL-Defect Relations

Earlier studies on TSL at least to some extent endorse the existence of TSL peaks in the temperature regions observed in this investigation, but none of these peaks have been firmly associated with a particular defect/impurity center, except the one at 165K, which Medlin related to the presence of Ti^{4+} by doping with different impurity strengths.

TSL by itself is generally not sufficient as a technique to identify all impurities/defects present. Therefore, the information provided by other techniques (OA, ESR, etc.) correlated with TSL observations should be of great help to speculate about the impurities/defects responsible for various TSL peaks. Especially, the OA and ESR studies conducted at Oklahoma State University on specimens of the same material as used for TSL measurements, should provide important guidance for this purpose. Unfortunately, it is well known that one technique may possibly not be sensitive to process/es detected by the others.

All effects contributing to the whole TSL process are observable in all types of specimens by using only low temperature irradiation with the single exception of the observation of a new peak, explained later. The effect of using a combination of irradiations at room temperature followed by the low temperature (96K) is the reduction of TSL phenomenon

in unswept specimens (no change in the swept). On the other hand, the results of similar procedures in the OA and the ESR are different. In the case of OA (IR), two new bands at 3306 cm^{-1} and 3367 cm^{-1} are created or at least become prominently detectable in unswept samples as a consequence of irradiation at 300K (30). The almost corresponding treatment in TSL results in prominent reduction of the Region III (defined earlier) peak.

In the case of ESR measurements, the incorporation of high temperature irradiation in the procedure causes a tremendous increase in the subsequent production of the ESR signal atributed to Al-hole centers in the unswept specimens and furthermore results in the production of E_2' and E_4' centers (31). Hence it seems that one of the effects of this high temperature irradiation of unswept specimens is to transfer some processes, detected in the TSL by low temperature irradiation only, to the domain of detection by ESR and OA, and these processes almost disappear from TSL records until the sample is annealed. This is one of the basic points in speculating about the impurities and other defect centers responsible for TSL in synthetic quartz.

Being more specific, the Al-hole and U-1 type of centers generally decay in the temperature region where TSL activity cannot be observed with the apparatus used in this investigation (31). The E_2' and E_4' centers are created by double irradiation and furthermore these centers do not decay or decrease significantly up to room temperature. The U-4 center, which can be produced by low temperature irradiation as well as by the combination of irradiations, also does not decrease significantly up to room temperature. Therefore, it appears that all of these centers do not play a major role in the TSL processes of the synthetic quartz.
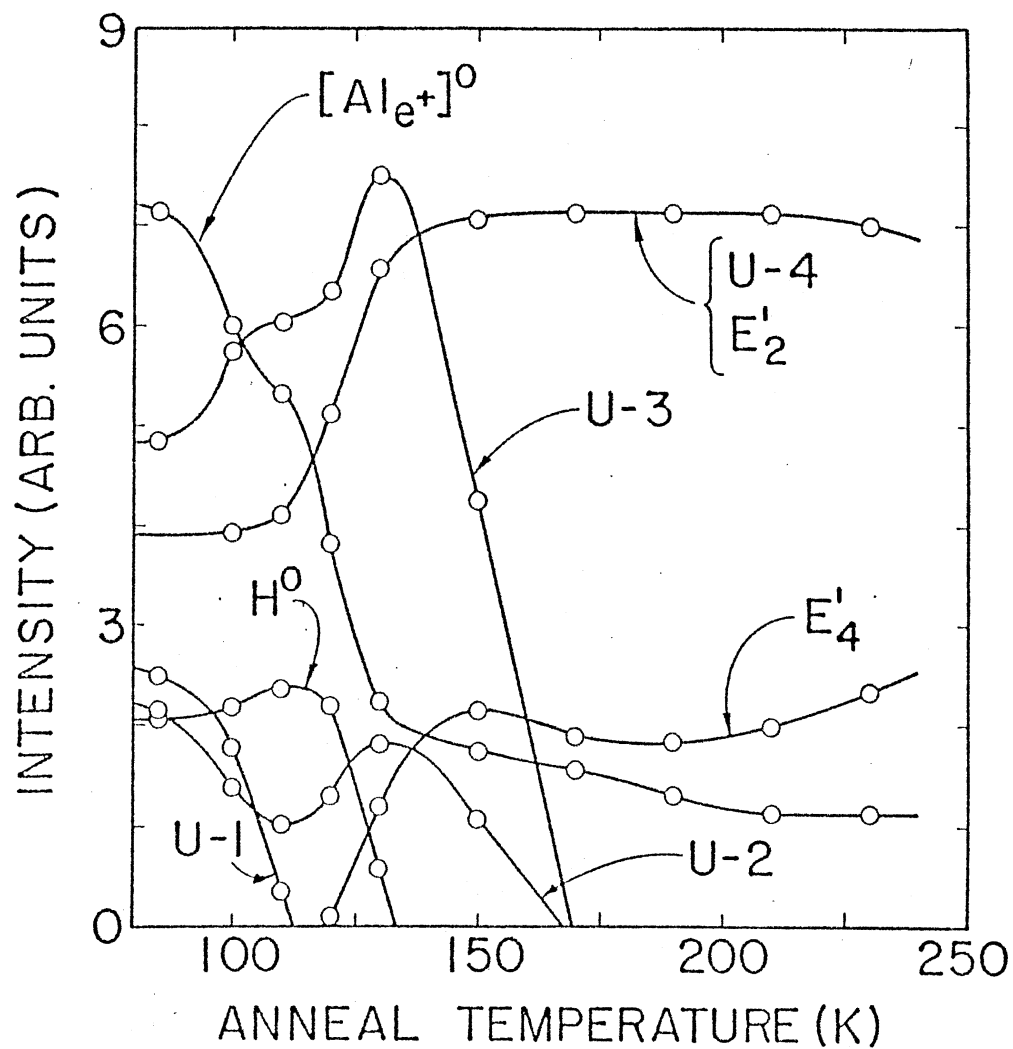
Figure 19. Thermal Anneal of Various ESR Signals
(Incorporated With the Permission of
Authors (31) Unswept)
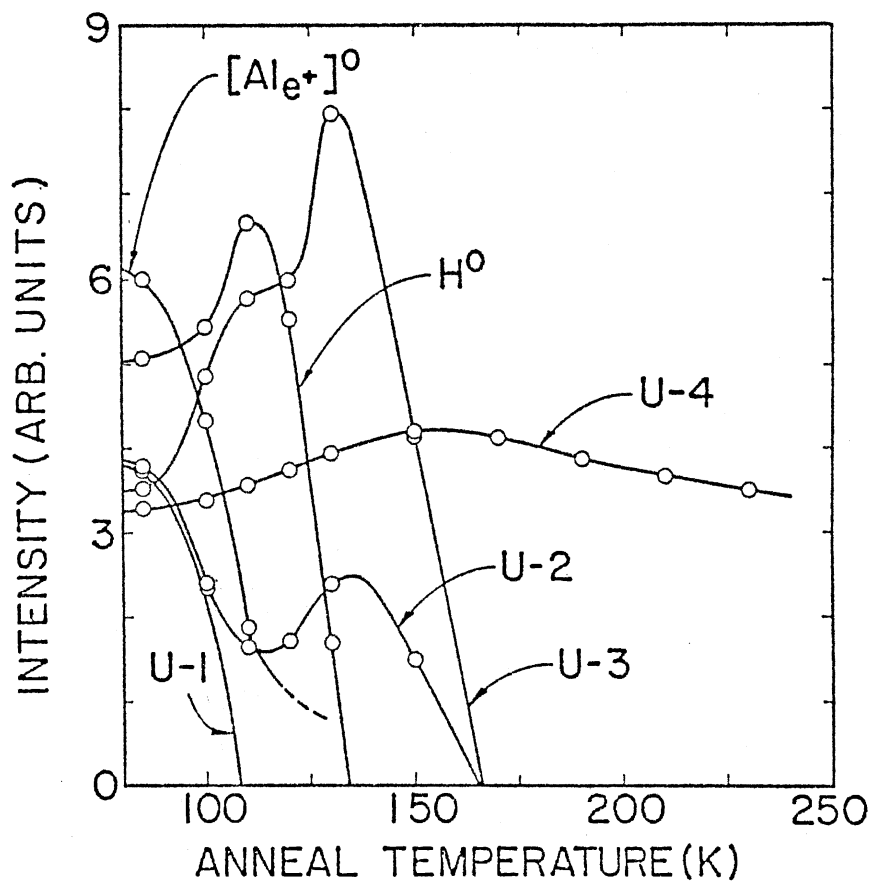
Figure 20.   Thermal Anneal of Various ESR
             Signals (Incorporated With
             the Permission of Authors
             (31) Unswept)

The remaining three centers, namely the H-atom center, U-2 center and the U-3 center, as reported in the same ESR studies are observable under all types of irradiation (single or combination) procedures and decay in temperature regions which seem relevant to TSL peaks and hence may be responsible for some of the TSL processes.

Specific Defect-TSL Relations for Various Regions

Region I

The following points are worthy of speculation about the defect center responsible for TSL in this region. The TSL intensity output in this region is found to be relatively higher in unswept Electronic Grade specimens than in the Premium Q. From the OA, it is found that the $\overline{OH}$ content in Electronic Grade unswept samples is also higher than the corresponding Premium Q (30). In at least one of the swept samples the TSL peak was relatively higher in intensity. This leads to the suggestion that the 125K TSL peak can be related to the amount of hydrogen present. The peak is also not appreciably affected by double irradiation in any type of specimen whereas alkali-related peaks are believed to be sensitive to double irradiation as discussed shortly.

It is also reported in ESR studies, that H-atom centers are producible in all kinds of samples under all combinations of irradiation and these signals thermally anneal out in the same temperature region in which this TSL peak is observed. It is also observed in TSL that this peak is sensitive to the low temperature at which the specimen is irradiated, i.e., it is not producible if irradiated above ~110K and this could possibly be indicative of the fact that this center is created by relatively more mobile ions.

Therefore, in the light of the said observations, it is believed that a change in the charge state of the H-atom centers is responsible for this peak.

Region II

This is a multiple-peak region, which contains at least three over-lapping peaks. The charge transfer takes place roughly around 155K, 165K and 175K. It is observed that the relative heights of individual peaks are not constant from run to run, especially in the case of un-swept samples, and occasionally one of these may be missing or not dis-tinguishable. Not always, but quite a few times in different unswept specimens of both Electronic Grade and Premium Q, this region is found to be depressed (~30%) by double irradiation (96K + 300K) and the number of peaks is reduced. This effect may be related to the irradiation-induced mobility of alkalis to be discussed in detail shortly. It is also observed that this region is relatively higher in total peak inten-sity in the unswept samples than in the swept.

Therefore, it appears that the presence of alkaline impurities may contribute to the emission in this region. These peaks are generally situated in the temperature region where U-2 and U-3 centers (reported by ESR) decay. It might be argued that this region may indicate the presence of some sort of complex centers like an $[E" - M^+]$ at different sites of oxygen-vacancies in the c-axis channel which differ slightly in symmetry. There might be some in which the interaction of M^+ is re-placed by H^+, which being relatively more mobile is not affected by high temperature irradiation. These centers might be created as precursors of E'_2 and E'_4 by low temperature irradiation only and the combination of

high temperature irradiation removing the alkali interaction and transforming them to E_2' and E_4' centers. It may be noted that the number of E_2' and E_4' centers created by high temperature irradiation is relatively small and so is the reduction in the peak heights of Region II.

Region III

This TSL peak is very significantly observed in unswept samples by using low temperature irradiation only and is either non-observable or shows only a slight indication in the swept samples. It is almost completely eliminated upon double irradiation and reappears approximately in its original form after anneal at 725K (the only anneal temperature used). It may be mentioned that the Al-hole center also decays around 650K. The double irradiation has no effect on swept samples. It seems quite plausible that the area under the TSL curve is a measure of the strength of alkalis present. Since the high temperature irradiation results in enhancement of Al-hole centers and creation of two new bands in the OA, the original orientation of this alkaline impurity is such that it does not allow the creation of significant numbers of Al-hole centers or the $Al-OH^-$ centers as long as it stays in the charge compensator position. When it is moved away by high temperature irradiation a hydrogen ion or a hole may be captured by the Al^{3+} for charge compensation.

In addition to these facts, the speculation that this region is association with the presence of alkalis is further supported by the results of the correlation experiment. From previous work an estimate was made of the temperature at which irradiation induced mobilization of alkalis occurs. Intermediate high temperature irradiations preceding

the low temperature irradiation were used in four experiments at 145K, 205K, 253K and 300K. The TSL signal and structure remained relatively the same when irradiated at 145K and 205K, except that a new intense peak is observed around 200K with the 205K irradiation. By using 253K irradiation, Region III emission is substantially reduced with no other prominent changes in the TSL structure. Irradiation at 300K basically eliminates the TSL signal in Region III.

These facts seem quite in agreement with the conclusions drawn by the other local studies about the irradiation-induced mobility of the alkalis in this material and the related reduction of this TSL region endorses the belief that the alkalis can be moved away from their initial sites by irradiations between 205K and 250K. Therefore it appears that this TSL region is related to the presence of alkalis in the synthetic quartz.

Suggestions for Further Studies

The following suggestions for further studies may be helpful in further understanding the TSL phenomenon in synthetic quartz.

1. A series of Al^{3+}-doped samples should be investigated to look for peaks which are sensitive to Al concentrations.

2. Iron is also reported to be present. Similar studies on Fe-doped samples should be carried out to look for comparable concentration effects.

3. Some investigation on reexcitation and bleaching should be done to see if these techniques can be of help in understanding and distinguishing between hole-occupied and electron-occupied charge centers and how they affect the recombination processes.

4. A most important project using all techniques (TSL, OA, ESR) would be to examine in more detail the effect of intermediate high temperature (205K) irradiation preceding the low temperature irradiation in all types of specimens.

As has been reported briefly, a new intense TSL peak has been observed by using irradiation at this temperature. Its investigation may be of considerable assistance in understanding a possible precursor process to the mobilization of alkalis by irradiation.

SELECTED REFERENCES

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

2. Aitken, M. J. and S. J. Fleming. "Topics in Radiation Dosimetry", Radiation dos suppl. I, edited by F. H. Attix (Ac. Press, N.Y.) 1972.

3. McDougall, D. J. (Ed.), TSL of Geological Materials, 1968.

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

5. Lell, E., N. J. Kreidl, and J. R. Hensler, "Radiation Effects in Quartz, Silica, and Glasses" in Progress in Ceramic Science, Vol. 4, edited by J. E. Burke (Perg. Press, N.Y., 1966).

6. Ditchburn, R. W., Page and others, Defects in Crys. Solids, Rep. Bristol Conf. (1954).

7. Cohen, A. J., J. Chem. Phys. 25, 908-914 (1956).

8. Kats, A., Y. Haven, J. M. Stevels, Phys. Chem. Glasses 3, 69-75 (1962).

9. Nelson, C. M. and R. A. Weeks, J. Am. Ceram. Soc. 43, 396-99 (1960).

10. Griffiths, J. H. E., J. Owen and I. M. Wards, "Report on Bristol Conference Defects in Solids", page 81 (Phys. Soc. Lond. 1955).

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

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

13. Yokota, R., Phys. Rev. 91, 1013 (1953).

14. Arnold, G. W., Jr., J. Phys. Chem. Solids 13, 306 (1960).

15. Levy, P. W., J. Chem. Phys. 23, 764 (1955).

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

17. Yip and Fowler, Phys. Rev. B11(6), 2327 (1975).

18. Mackey, and J. W. Boss, Jr., Mag. Res. 3, 44-54 (1970).

19. Batrak, E. N., Sov. Phys. Cryst. 3, 102 (1958).

20. Batrak and others. Optikai Spektroskopia 3, 619 (1957).

21. Medlin, W. L., J. Chem. Phys. 38, 1132-43 (1963).

22. McMorris, D. W., J. Geophys. Res. 1875 (1971).

23. Schlesinger, M., Phys. Letters 10, 49-50 (1964).

24. Schlesinger, M., J. Phys. Chem. Solids 26, 1761 (1965).

25. Zimmerman, J., J. Phys. C: Solid State 4, 3265-76 (1971).

26. Shekhmameter, R. J., Opt. Spektrosk, 34(3), 505-509 (1973).

27. Anderson, Feigl and Schlesginer, J. Phys. Chem. Solids 35, 1425
         (1974).

28. Fuller, G. E. and P. W. Levy, Conference on "Defects in Insulating
         Crystals", Oct. 1077, pp. 142-43.

29. Durani, S. A., P. J. Groom, and A. R. Ghazal, J. Phys. D: Appl.
         Phys. 10, 1351-61 (1977).

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

31. Markes and Halliburton, J. Appl. Phys. 50, 8172 (1979).

32. Sibley, W. A., L. E. Halliburton, and J. J. Martin, M. C. Winters-
         gill, A. Armington, and R. N. Brown. IEEE Trans. on Nuc. Sci.,
         NS-26,6 (1979).

33. Leverenz, H. W., "An Introduction to Luminescence of Solids".
         John Wiley and Sons, Inc., 1950.

34. Randall, J. T. and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184,
         366 (1945).

35. Garlick, G. F. J. and A. F. Gibson, Proc. Phys. Soc. (London) A60,
         574 (1948).

36. Land, P. L., J. Phys. Chem. Solids 30, 1681 (1969).

37. Booth, A. H., Can. J. Chem. 32, 214 (1954).

38. Hoogenstraaten, W., Philips, Res. Rep., 13, 515 (1958).

39. Grossweiner, L. I., J. Appl. Phys. 24, 1306 (1953).

40. Luschik, C. B., Dokl. Akad. Nauk., S.S.S.R., 101, 641 (1955).

41. Nicholas, K. H. and J. Woods, Brit. J. Appl. Phys., 15, 783 (1964).

42. Kelley, P. J. and M. J. Laubitz, Canad. J. Phys. <u>45</u>, 311 (1967).

43. Chen, R., J. Appl. Phys. <u>40(2)</u>, 570 (1969).

44. Kelley, P., M. J. Laubitz and P. Bräunlich, Phys. Rev. B, <u>4(6)</u>, 1960 (1971).

45. Mattern, P. L., K. Lengivaler, and P. W. Levy, Radiat. Eff. <u>26(4)</u>, 237-48 (1975).

VITA ^{2}

Dost Muhammad Malik

Candidate for the Degree of

Doctor of Philosophy

Thesis: A STUDY OF THERMALLY STIMULATED LUMINESCENCE IN SYNTHETIC
         QUARTZ (IN THE REGION 96K - 273K)

Major Field: Physics

Biographical:

    Personal Data: Born in Mardwal (Sargodha, Pakistan), October 13,
        1945, the son of Mr. and Mrs. Malik, Khan Muhammad.

    Education: Attended Govt. College Sargodha, from 1961-65 and
        earned the B.S. with a major in Physics under the auspices
        of Punjab University. Attended University of the Punjab,
        LAHORE (Pakistan) from 1965-67 and received the Master of
        Science in 1968 with a major in Physics; joined Oklahoma State
        University in 1976; completed the requirements for Doctor of
        Philosophy degree in May, 1980.

    Professional Experience: Lecturer in Physics Govt. M. A. O. Degree
        College, Lahore from 1969-1976. Graduate Teaching Assistant,
        Physics Department, Oklahoma State University, Stillwater,
        Oklahoma, 1977-1980.