Ultraviolet Photosimulated Thermoluminescence of Lithium Flouride

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ULTRAVIOLET PHOTOSTIMULATED THERMOLUMINESCENCE
OF LITHIUM FLUORIDE

A Thesis
Presented to
the Faculty of the Department of Physics and Astronomy
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Martin R. Payne
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ULTRAVIOLET PHOTOSTIMULATED THERMOLUMINESCENCE OF LITHIUM FLUORIDE

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ULTRAVIOLET PHOTOSTIMULATED THERMOLUMINESCENCE OF LITHIUM FLUORIDE

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J:ly 1974

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TLD-100 (lithium fluoride) thermoluminescence dosimeters are widely employed for the detection of ionizing radiations. This paper shows that these dosimeters may also serve as practical germicidal ultraviolet radiation dosimeters. To measure ultraviolet radiation, the TLD-100 dosimeters are first exposed to 500,000 roentgens of gamma radiation and then annealed at 300°C. Subsequent dosage of ultraviolet radiation may be determined by observation of photostimulated thermoluminescence of the crystal. The presented data indicate that the thermoluminescence response is linear for exposures up to 6,000 μjoule/cm² and independent of exposure rate from 0.1 μwatt/cm² to above 50 μwatt/cm². Optical absorption, emission spectra, and sensitivity as a function of temperature of the dosimeters during ultraviolet exposure are presented. Also, a partial model of the photostimulated thermoluminescence process is presented.
INTRODUCTION

Ultraviolet (UV) radiation is emitted from a variety of industrial processes, various kinds of lamps specifically designed for ultraviolet emission, and natural sources such as sunlight. In addition to its numerous technical applications in medical therapy, there is an increasing application of UV radiation for disinfecting and sterilizing materials in industrial and public health areas.\(^1\) UV radiation also produces injurious effects on man, such as erythema (sunburn is a common example), painful inflammation of the membrane of the eye called conjunctivitis, and possibly skin cancer.\(^2\) These injurious effects of UV radiation appear to be related to the absorption of UV radiation by nucleic acid.\(^3\)

Recognizing UV radiation as a potential hazard, the Council on Physical Medicine and Rehabilitation of the American Medical Association has set limits of exposure tolerance to be 0.1 \(\mu\)watt/cm\(^2\) for continuous radiation exposures from germicidal lamps.\(^2\) There are several techniques now existing that are used for monitoring UV radiation. One commercial instrument using a photoelectric cell measures from as low as 10 \(\mu\)watt/cm\(^2\) up to 5,000 \(\mu\) watts/cm\(^2\).\(^4\) Photo-multiplier tubes are also commonly used, and the use of chemical photolysis is increasing.\(^5\)

An ultraviolet detector that measures UV radiation from below 0.1 \(\mu\)watt/cm\(^2\) up to high levels of exposure is needed. This detector should be small.
portable, stable, and unaffected by normal room lights. A number of phosphors utilizing the thermoluminescent phenomenon have been studied as possible dosimeters for the ultraviolet region. The low cost per phosphor, the absence of any associated electronics at the site of the measurement, and the fact that the thermoluminescent phosphor can operate unattended, are some of the advantages in using thermoluminescence. So far none of these phosphors have found widespread application for the detection of ultraviolet radiation.

TLD-100 (lithium fluoride) thermoluminescence dosimeters are widely employed for the detection of ionizing radiations. It has been noted that after use as an ionizing radiation detector, if the dosimeters are then exposed to UV, the thermoluminescence is restimulated.

The purpose of this investigation was to determine the suitability of using gamma irradiated lithium fluoride as a UV detector and to gain insight into the mechanisms of thermoluminescence in lithium fluoride.
REVIEW OF LITERATURE

In some materials, a small portion of the absorbed energy of ionizing radiation is not converted into heat nor used to break chemical bonds. Instead, this energy is stored in metastable energy states, often referred to as traps. Thermoluminescence (TL) is the energy that is released from these traps in the form of visible photons when the material is heated. This energy is over and above black body radiation.

TL can be quantitatively explained in terms of the properties of defects in solids, but the detailed mechanisms are not well understood. Ionizing radiation excites an electron from the valence band to the conduction band, leaving a hole in the valence band. The electron and the hole move through the crystal until they recombine or until they are trapped in metastable states at defects in the material. After the material has been exposed to ionizing radiation, the material is then heated. As the temperature is raised, electrons and holes escape from their traps at an increasing rate. The freed charges recombine with each other or with other defects, and often give out luminescence by this recombination. The site at which luminescence takes place is called a luminescence center. This resulting thermoluminescence reaches a maximum and then decreases to zero as the supply of trapped electrons or holes becomes exhausted. The plot of photomultiplier tube (PMT) current versus temperature or time taken at a constant heating rate is called a glow curve. The shape of a glow curve for a single trap can be predicted theoretically for linear heating. From the glow curve, one can determine the trap depth; the higher the temperature of the glow peak, the deeper the trap.
In most phosphors there are a number of traps, and the glow curve may consist of a number of glow peaks. Thus, thermoluminescence is a very complex process since it involves a trap or traps, a luminescent center or centers, and the transfer during heating of an electron or hole from the trap to the luminescent center.

Thermoluminescence has been observed for many years and the relation of TL to x-rays and gamma rays has been observed, but it was not until 1950 that Daniels first proposed that the phenomenon of TL could be used as a radiation dosimeter. Since that time many thermoluminescence dosimeters (TLD) have been developed. Vacuum-ultraviolet grade LiF crystals produced before 1955 by the Harshaw Chemical Company in Cleveland, Ohio, accidentally exhibited the useful TL. Harshaw, in collaboration with J. R. Cameron, developed thermoluminescent-grade LiF, available as TLD-100. Spectrographic analysis of TLD-100 has shown that it contains 100 ppm Mg impurity, 6 ppm Ti impurity, and Al and Si impurities in 10-20 ppm amounts. The Si may be the result of contamination in grinding crystals for analysis. Most investigators agree that Mg is an activating impurity essential to the TL, largely because LiF with small amounts of Mg (about 1 ppm) displays little of the useful TL.

Figure 1 shows a typical glow curve from TLD-100. After irradiation peaks 1 through 5 decay at room temperature with the approximate half-lives of 5 minutes, 10 hours, 0.5 year, 7 years, and 80 years, respectively. Thus, because of their long half-lives and because they occur at a low enough temperature that the competing effects of black body radiation
Figure 1. Typical glow curve of LiF (TLD-100) read soon after irradiation to 100R
are minimal, peaks 4 and 5 are the most suitable for dosimetry. There are pre-irradiation and post-irradiation annealing procedures for the elimination of peaks, 1, 2, and 3 in the glow curve. Five more glow peaks occur below room temperature at 14°C, -6°C, -8°C, -10°C, and -12°C for a heating rate of 35°C/min. These peaks are labeled 0 through -4 respectively in the literature.

The emission spectrum for peaks 3-5 consists of a broad band extending from below 320 nm to 400 nm. Peak 1 has several weak maxima at 310, 250, and 210 nm and a strong maximum at 400 nm. Peak -4 has two strong maxima occurring at 210 and 250 nm.

COLOR CENTERS IN LiF

F Center

Traps or defects produce optical absorption bands in normally transparent crystals and some of these defects or color centers have been identified.

The best understood of the color centers is the F center which is an electron trapped in an anion vacancy. The number of F centers giving rise to the F band absorption, which peaks at 250 nanometer (nm), can be calculated from Smakula's equation:

\[ \text{FN}_0 = \frac{9mc}{2e^2} \left( n/\left[n^2+2\right]^2 \right) a_{\text{max}} W_1/2 \]

\[ = 1.29 \times 10^{17} a_{\text{max}} W_1/2 \]

where:

- \( m \) = the mass of an electron
- \( c \) = the velocity of light
- \( e \) = the charge of an electron
n = the refractive index of the crystal for the wavelength at the peak of absorption band; for LiF, n = 1.416

\( \alpha_{\text{max}} \) = the absorption coefficient in cm\(^{-1}\) at the peak of the absorption band

\( w_{1/2} \) = the half width of the absorption band in electron volts; for LiF, \( w_{1/2} = 0.58 \) ev

\( N_0 \) = the number of F centers per cm\(^3\)

f = the "oscillator strength", a factor that is related to the probability of the optical transition producing the absorption; for the F band, f is near unity.

In his treatment, Smakula assumed a Lorentzian shape for the absorption band and treated the absorbing centers as damped oscillators according to classical dispersion theory. Arguments exist for assuming a Gaussian shape for the absorption band. Another treatment assumes a Gaussian shape and the width of the absorption band arises from interaction of the center with the lattice vibrations rather than from classical dispersion considerations. From this viewpoint, the numerical factor should be 0.87\( \times 10^{17} \) rather than 1.29\( \times 10^{17} \).

**Other Electron Centers in Pure LiF**

Two adjacent F centers form the M or F\(_2\) center. In LiF, the M center gives rise to the M band absorption with maximum absorption occurring at 444 nm. Three F centers joined together form the R or F\(_3\) center. The R center gives rise to three absorption bands: R\(_1\) and R\(_2\) are found between the absorption of the F and M bands. R\(_3\), however, is hidden under the F band. In LiF, the R\(_1\) and R\(_2\) bands have maxima occurring at 313 nm and 380 nm respectively. It has been suggested that there is an additional band at the position of the M band in LiF and that it arises from the F\(_3^+\) center, an R center that has lost an electron. The F\(_3^+\) center with an absorption band at 645 nm has also been identified in LiF.
Electron Center Modified by Presence of Impurity

Bleaching of the F center in LiF: Mg with F band light or thermally annealing the crystal was shown to reduce the F band with a subsequent formation of a weaker band at 222 nm. 25, 26, 37, 38

Another investigation determined that the 222 nm absorption band was associated with Mg impurity. This investigation failed to produce the 222 nm band by bleaching with the F band light, although there appears to be a shift of the F band absorption toward shorter wavelengths. 39 The 222 nm band was produced when the temperature of the crystals during radiation exposure was 350°C, in agreement with a previous investigation that the production of the 222 nm band was enhanced when the temperature of the crystals during radiation exposure was above room temperature. 38 The 222 nm band was suggested to represent an F2 or Z band which are electron traps that are associated with divalent foreign cations. 39

The 222 nm band has been identified as a Z3 center. 40, 41 The Z3 center in LiF: Mg is a perturbed F center with one of the nearest lithium ions being replaced by a divalent magnesium ion. 42

Hole Centers

In addition to centers involving trapped electrons, centers can be produced with trapped holes. The best understood of these centers is the VK center for which both electron paramagnetic resonance and optical absorption data are available for LiF. 43, 44 The center consists of a hole that is localized between two halide ions. When this happens, the halide ions are pulled together and
the hole is bound to them. The $V_K$ center gives rise to an absorption band at 348 nm in LiF but bleaches above -148°C.

Other Optical Absorption Bands

In addition to the previously mentioned bands, gamma irradiation of LiF:Mg, Ti produces bands at 380 nm, 310 nm, and 232 nm. Also bands occur at 205 nm, 195 nm, and 200 nm. The 232 nm absorption band has been suggested to be the K band which is the optical transition of the F center electron from the ground state to the second excited state. The 195 nm and 200 nm are probably the same absorption bands since they occur in the crystal before irradiation and are associated with the Ti impurity. The 380 nm and 310 nm bands have been identified as electron traps associated with the Mg impurity. The 205 nm band is produced in a virgin crystal before irradiation when irradiation is preceded by a 400°C anneal and rapidly quenched to room temperature. Also a small band, occurring after irradiation, has been suggested to occur at 270 nm.

Two bands located at 110 nm and 130 nm LiF have been interpreted to be the $\beta$ and $\alpha$ bands respectively. The $\beta$ band arises from the perturbation of the fundamental lattice absorption of the crystal by the presence of the F center. The $\alpha$ band arises from the perturbation of the lattice absorption of the crystal by the presence of a negative ion vacancy.

It has been alternately suggested that the 110 nm band is the $V_3$ band which is a molecular halogen band.
MODELS FOR THE TL PROCESS IN LiF: Mg, Ti

The basic facts which one wishes to know about a particular thermoluminescent process are the atomic nature of the trap, the atomic nature of the luminescent center, and whether an electron or hole is transferred between them.

A correlation has been established between the 310 nm absorption band and peaks 4 and 5 of the glow curve, and also between the 380 nm absorption band and peaks 2 and 3 of the glow curve.\textsuperscript{24-26} It has been further reported that the 310 nm absorption band consists of two components that correspond to peaks 4 and 5 respectively.\textsuperscript{24,45,52} The 380 nm band consists of two components corresponding to peaks 2 and 3.\textsuperscript{24,52}

On the basis of these experiments, it is concluded that peaks 2-5 are types of electron traps associated with the Mg impurity.

On the basis of optical repopulation studies, it is concluded that peaks -4 and -1 are types of hole traps while peaks -3, -2, and 0 are electron traps.\textsuperscript{28}

The luminescent center has been identified as being associated with the Ti impurity.\textsuperscript{46,47,53}

There are no commonly accepted models for the transfer mechanism occurring between the trapping centers and the luminescent centers, but it is generally thought that electrons are ionized from the trapping centers during the thermoluminescence process.\textsuperscript{28,54}
EXPERIMENTAL MATERIALS, INSTRUMENTATION, AND PROCEDURES

Commercial thermoluminescence radiation dosimeters (TLD-100) used for ionizing radiation measurements were obtained from the Harshaw Chemical Company. These dosimeters have dimensions of 0.32 cm x 0.32 cm x 0.09 cm. Four optical grade TLD-100 crystals with dimensions of 1 cm x 1 cm x 0.32 cm, were also obtained from Harshaw.

Pre-gamma annealing of the crystals used for the linearity of response to UV and for dose rate independence studies consisted of baking the dosimeters in air for one hour at 400°C and then heating them on a hot plate at 800°C for 24 hours. Pre-gamma annealing of all other crystals consisted of baking the crystals in air for one hour at 400°C and then for one hour at 100°C.

The crystals that were used for the linearity of response to UV and for dose rate independence studies were irradiated in a cobalt gamma cell at an exposure rate of $10^6$ roentgens (R) per hour to a total exposure of $4.83 \times 10^5$R. All other crystals were irradiated at an exposure rate of $1.69 \times 10^6$R/hr to a total exposure of $5 \times 10^5$R.

All of the small dosimeters (0.32 cm x 0.32 cm x 0.09 cm), after the gamma exposure, were then placed in a Harshaw Model 2000 thermoluminescence unit employing an EMI 9635 QA photomultiplier tube (PMT) and heated to 300°C and kept at 300°C for one minute. The thermoluminescence unit was adjusted for a linear heating rate of 3°C/sec. During the previous run, a neutral density filter with an optical density of three was placed over the dosimeter to protect the photomultiplier tube of the thermoluminescence unit.
A Hewlett-Packard Model 7000 X-Y Recorder was connected to the thermoluminescence unit to allow recording of the glow curve. After recording the glow curve to 300°C, the crystals, without further preparation or gamma irradiation, could then be used to repeatedly measure ultraviolet radiation. Ultraviolet exposures were made at various intensities and TL glow curve was recorded to 230°C after each exposure. Immediately after the glow curve was recorded for the small crystals, the crystals were allowed to cool down and were again heated to 230°C to record the shoulder of a TL peak occurring above 230°C. This shoulder was then subtracted from the UV stimulated glow curve.

The optical grade crystals (1 cm x 1 cm x 0.32 cm), after gamma exposure, were placed on an aluminum block attached to a soldering iron and heated to 300°C at a linear heating rate of 90°C/min. The linear heating rate was accomplished by attaching a Variac to the soldering iron and varying the settings during the heating cycle at periodic intervals. The temperature was monitored using a chromel-alumel thermocouple attached to the aluminum block and to a Hewlett-Packard Model 7000 X-Y recorder. The temperature readings on the X-Y recorder were checked with a Honeywell Model 2745 Potentiometer and were found to be within ±1°C. An RCA 1P21 PMT was employed to detect the TL. The PMT current was measured with a Keithley Model 610B, the output of which was applied to the X-Y recorder. After recording the glow curve to 300°C, the crystal could then be exposed to UV and the glow curve recorded to 225°C.
UV exposures of various levels were supplied by a fifteen-watt germicidal lamp (General Electric G15T8). This radiation consists primarily of the 253.7 nanometer line of mercury, which coincides with the F center absorption of the lithium fluoride (TLD-100) dosimeter. Lines occurring at 310 nm, 362 nm, 402 nm, 433 nm, 503 nm, and 539 nm were also present in the emission of the lamp, but were lower in intensity by a factor of 10 than the 253.7 nm line. The emission spectrum of the lamp is shown in Figure 2.

Radiation levels were determined by using a short wave Blak-Ray Ultraviolet Intensity Meter and the inverse square law.

The emission spectra were observed with a Bausch and Lomb No. 45, 500 mm Monochromator that had a grating with 1200 lines/nm. An EMI 9558QA PMT was employed at the exit lens of the monochromator. The PMT current was measured with a Keithley Model 610C electrometer, the output of which was applied to a Moseley Model 7000A X-Y Recorder. The voltage drop across a ten-turn precision variable resistor connected to the wavelength drive of the monochromator was applied to the other axis of the X-Y recorder.

Optical absorption measurements of the optical grade TLD-100 crystals were made with a Cary-14 spectrophotometer. One optical grade crystal was not gamma irradiated and was placed in the reference beam of the spectrophotometer to compensate for scattered light and non-radiation induced absorption.

The temperature of the dosimeter (below room temperature) during UV exposure was controlled by using a CRYO-TIP Joule-Thomson refrigerator with a WMX-1 cryostat. The temperature of the dosimeter during exposure
Figure 2. Emission spectra of GE G15T8 germicidal lamp
was monitored with a chromel-constantan thermocouple, located two centimeters from the crystal between the crystal holder and the cooling rod. The thermocouple was connected to the Honeywell Model 2745 Potentiometer. The error in the temperature of the crystal ranges from $+1^0K$ at $270^0K$ to $+5^0K$ at $217^0K$ was due to the distance at which the thermocouple was mounted from the crystal. The temperature of the crystals during UV exposure above room temperature was controlled by utilizing the glow curve apparatus for the optical grade crystals. However, the potentiometer, instead of the X-Y recorder, was used to measure the thermocouple voltage.
RESULTS AND DISCUSSION

RESULTS OF OPTICAL ABSORPTION MEASUREMENTS

The absorption curve of POG4, after a gamma exposure $5 \times 10^5 \text{R}$, is shown in Curve A of Figure 3. Before irradiation, the crystals normally display a band at 200 nm; but this band has been compensated for along with the scattering of light by the placement of an unirradiated crystal in the reference beam of the Cary 14. The three optical grade LiF crystals that were used are labeled POG4, POG3, and POG2. The maximum absorption band is the F band, while the band between 440 and 450 nm is the M band. Using Smakula's equation, the number of F centers formed by a $5 \times 10^5 \text{R}$ gamma irradiation is calculated to be $2 \times 10^{17}$ centers/cm$^3$. The absorption curves after various intervals of optical bleaching at 800 $\mu$ watts/cm$^2$ with germicidal radiation are shown in Curves B, C, and D. Note that after ten minutes of bleaching, the F band is decreased in height and the half width of the band has increased. After 20 minutes of bleaching, the F band height has increased to almost its original value while the half width has decreased. After 12 hours of exposure, the F band height has decreased and a band located around 305 nm is being resolved. Note also the bleaching of the M band.

The absorption curve of TLD-100 crystal POG3, after gamma exposure and repeated UV exposures of the crystal in the Cary 14, is shown in Curve A of Figure 4. The absorption curves, after various intervals of optical bleaching, are shown in Curves B, C, and D. Again, the F band first decreases in height and increases in half width and then increases close to its original height while the half width decreases. This time the effect was noted with
A. After $5 \times 10^5$ R gamma exposure
B. After 10 min UV exposure
C. After 20 min UV exposure
D. After 12 hrs UV exposure

The UV exposure rate was 800 μwatt/cm².

Figure 3. Absorption curve of TLD-100 crystal POG4 after various gamma and UV exposures.
Figure 4. Absorption curves of TLD-100 crystal POG3 after various gamma and UV exposures.
just UV exposure in the Cary 14. The first decrease in height of the F band is assumed since all three crystals were exposed to gamma radiation at the same time and both of the other two crystals exhibited the same optical density (OD - 15) for the peak of the F band after gamma irradiation. The absorption curve after gamma irradiation and before UV irradiation is not available due to attempts to measure the absorption curve while the Cary 14 was inoperative.

Note also after 26 hours of exposure, the bleaching of the M band, the resolving of the band at 305 nm, and the emergence of the Z₃ band at 225 nm.

To illustrate the changes in the absorption curves, the difference in the curves with respect to the curve after gamma irradiation is shown in Figure 5 for crystal POG4. A positive number indicates a decrease in absorption while a negative number indicates an increase in absorption. Curves A and B show first the decrease and then the increase of the F band. Curve A illustrates, that after bleaching for ten minutes, the Z₃ band has built up and the F band has been bleached. Curve B, after 20 minutes exposure, illustrates re-stimulation of the F band and the decreasing of the Z₃ band. Curve B also shows the bleaching of a band centered around ~ 270 nm. Figure 6 illustrates, under further UV exposure, a decrease in the F band and a subsequent increase in the Z₃ band. The bleaching of the M band is also shown to occur at 444 nm. There is a possibility of a slight build-up of bands in the 300-400 nm range, but these bands are bleached after long periods of UV exposure.

The difference in absorption, with respect to the absorption curve after repeated UV exposure in the Cary 14 for crystal POG3, is shown in Figure 7.
Figure 5. The difference in absorption of crystal POG4 after UV bleaching
The UV exposure rate is 800 uwatt/cm².

Figure 6. The difference in absorption of crystal POG4 after continued UV bleaching.
A. After 10 min UV exposure
B. After 20 min UV exposure
C. After 1 hr 50 min UV exposure
D. After 6 hr 50 min UV exposure
E. After 11 hr 50 min UV exposure

The UV exposure rate is 800 μwatt/cm².

Figure 7. The difference in absorption of crystal POG3 after UV bleaching.
These curves illustrate the same changes as observed for crystal POG4. However, the changes in the 300-400 nm range are more pronounced for crystal POG3.

The absorption curve for crystal POG2, after a gamma exposure, is shown in Curve A of Figure 8. The absorption curve for the crystal after heating to 300°C is shown in Curve B. Note the bleaching of the F band and the subsequent build up of the Z3 band.

Figure 9 illustrates the changes produced in the absorption curves after various stages of crystal POG2 use as a UV dosimeter. Note that after the first ten minutes of exposure to UV, the Z3 band is reduced in height. After a read-out of the glow curve and another ten minute exposure, there is an increase in the height of the Z3 band from the previous exposure. Curve D represents the changes produced in the absorption after four exposures to UV with subsequent read-out of the glow curve. The total time for the four exposures was five hours and fifty minutes. Note the decrease in both the F and Z3 bands.

Figure 10 represents the difference, with respect to Curve D of Figure 7, produced in crystal POG2 after five continuous hours of UV exposure. Note the large decrease in the F band and 270 nm band with a build up of the Z3 band and slight build up of the 290-380 nm region.

Curve A of Figure 11 represents the changes in the absorption of crystal POG2, three days after the five hour UV exposure. The crystal remained untreated in the dark during this period. Note the decrease of the Z3 band. Curves B, C, and D represent changes in absorption after heating through
Figure 8. Absorption curves of crystal POG2

Curve A. After $5 \times 10^5$ R gamma exposure

Curve B. After heating to $300^\circ$C
A. After heating to 300°C
B. After 10 min exposure to UV
C. After read out of glow curve and another 10 min exposure
D. After 4 exposures totaling 5 hr and 50 min with subsequent read out of glow curve after each exposure.

The UV exposure rate was 800 µwatt/cm².

Figure 9. Absorption curves for crystal POG2 after various stages of use as a dosimeter.
Figure 10. Difference in optical density produced in crystal POG2 after 5 hours of UV exposure to 800 µwatt/cm²
Figure 11. Differences produced in crystal PGC2 after UV exposure and subsequent read out of the glow curve

Curve A. Three days after exposure to 800 \( \mu \)watt/cm\(^2\) UV for 5 hours
Curve B. After heating through peak 2
Curve C. After heating through peak 3
Curve D. After heating through peak 5
peaks 2, 3, and 5. These changes are with respect to the absorption curve taken three days after exposure. Note the build up of the F band and Z$_3$ band as the crystal is heated through the three peaks in the glow curve. Further observe in Curve D, after heating through peak 5, a decrease in absorption occurs in the 280-340 nm range.

DISCUSSION OF OPTICAL ABSORPTION MEASUREMENTS

In the first few minutes of UV exposure, both the F band and the Z$_3$ band are reduced in height and appear to have increased in half width; but as UV stimulation continues, these bands increase in height and appear to decrease in half width. This change can be correlated with the 257 nm mercury line since the change is also noted in UV exposure in the Cary 14. After the first few minutes of UV exposure, both continued UV exposure and heating to 300°C decrease the F band and produce a subsequent build up of the Z$_3$ band.

The production of the Z$_3$ band is in agreement with most investigators, but is in disagreement with the work of F. Pl'cher, D. Schinke, and R. J. Friauf. They were unable to produce Z$_3$ centers by bleaching with F band light. They did produce Z$_3$ centers when the temperature of the crystal during neutron irradiation was elevated to 350°C and found a correlation between the presence of Mg impurity and the production of Z$_3$ centers. The crystals in the present investigation were gamma irradiated at 30°C; thus, a difference of crystal temperature during gamma irradiation does not account for the different results. One possible reason for the difference in results might be the presence of Ti in the crystals used in this investigation and the absence of Ti in the work of
Pilcher, et. al. Another possible reason might be a difference in pre-gamma annealing procedures.

No accurate data is available from the present investigation on the height of the $Z_3$ band immediately after formation by heating of crystal POG2 to 300°C. This is due to the faulty working condition of the Cary 14. However, no detectable decay (within 15 percent) of the $Z_3$ band occurred over a five month period; although a slight decrease in the $Z_3$ band height was detected over a two day period after a five hour UV stimulation.

Exposure to the UV lamp releases electrons from the F band and from a band around 270 nm. These electrons appear to be mobile electrons that can then be trapped at other defects in the crystals, i.e. $Z_3$ band, with a subsequent build up during UV exposure of the absorption band corresponding to these defects. Another explanation would be the tunneling of the F center electron to nearby defects with a subsequent decrease of the F band and increase of the absorption bands corresponding to these defects. There appears to be competing mechanisms occurring with the $Z_3$ band and the band at the 310 nm.

With respect to the 310 nm band in the gamma irradiated TLD-100 crystal, one mechanism is trapping of free electrons by (or tunneling of the F center electron to) the defect giving rise to the absorption band; the other mechanism is the bleaching of this band by the 310 nm line of the lamp. With respect to the $Z_3$ band, one process is the trapping, or tunneling, of free electrons by the defect giving rise to the $Z_3$ band; the other process is the bleaching of this band by the 257 nm line of the lamp, since a small portion of the $Z_3$ absorption band extends to 257 nm. Furthermore, the 310 nm band can be
correlated with peak 5 of the glow curve as indicated in Curve D of Figure 10. This peak is associated with electron traps as reported in the literature.\textsuperscript{24-26,45,52} Recording the glow curve releases electrons from peaks 2, 3, and 5 as evidenced by the increase of the F and Z\textsubscript{3} bands during this process. The re-stimulation of peaks 1, 2, 3, and 5 of the glow curve by ultraviolet radiation is due to the de-trapping of electrons from the F and Z\textsubscript{3} bands and the subsequent capture of some of these electrons by traps corresponding to peaks 1, 2, 3, and 5 of the glow curve. Most of the free electrons are due to the de-trapping of electrons from the F centers; but as the number of F centers decrease, the de-trapping of electrons from the Z\textsubscript{3} centers by UV stimulation becomes the major source of free electrons.

LINEARITY OF RESPONSE

A thermoluminescence glow curve typical of gamma irradiated TLD-100 crystals that have been heated to 300\textdegree C and then photostimulated with ultraviolet radiation is shown in Figure 12. The glow curve is in agreement with that reported in the literature.\textsuperscript{28} An analysis of the glow curve produced two results.\textsuperscript{55} 1) The peaks are too narrow to fit the model of Randall and Wilkins.\textsuperscript{17} The narrow peaks above room temperature have already been noted for x-irradiated LiF.\textsuperscript{56} 2) Also, peak 4 is not re-stimulated as has already been suggested in a previous investigation.

The height of peak 5 for three different crystals versus germicidal radiation exposure is plotted in Figure 13. From this Figure, it appears that the peak height exhibits a linear response to ultraviolet exposure up to about 4800 \textmu
Figure 12. Typical glow curve of UV stimulated TLD-100
The exposure rate is 60 µwatt/cm².

Figure 13. The height of peak 5 versus UV exposure
joules/cm² (within - 20 percent at 4800 μjoules/cm²), and at higher exposures the rate of increase of peak height per increase in exposure gradually decreases.

If the assumption is made that most of the electrons trapped at the defect corresponding to peak 5 are transferred during germicidal irradiation from F centers, then an equation for TL response versus UV exposure may be derived.

Assume that there is a probability p₁ that a photon with a wavelength of 250 nm will de-trap a F center electron, then:

\[ \Delta F = -p_1 I_1 F \Delta t \]  

(2)

where:

- \( F \) = the total number of F centers
- \( \Delta F \) = the change in total number of F centers
- \( \Delta t \) = the change in time
- \( I_1 \) = the number of incident photons of wavelength 250 nm in time

Assume that there is a probability p₂ that the de-trapped F center electron will be subsequently trapped at the defect corresponding to peak 5, then:

\[ M = p_2 (F - F \exp(-p_1 I_1 t)) \]  

(3)

where:

- \( M \) = the number of trapped electrons responsible for peak 5
- \( F \) = the original number of F centers

Further assume that the 310 nm line of the germicidal lamp is bleaching the trapped electrons corresponding to peak 5 in the same manner as the 250 nm line of the germicidal lamp is bleaching F centers and that the height of peak 5 is directly proportional to the number of trapped electrons in peak 5 defects,
then:
\[ TL = p_2C[F - F \exp(-p_1I_1t)] \exp(-p_3I_3t) \]  \hspace{1cm} (4)

where:

- \( TL \) = the height of peak 5
- \( P_3 \) = the probability that a photon of wavelength 310 nm will de-trap an electron in a peak 5 defect
- \( I_3 \) = the number of incident photons of wavelength 310 nm in time \( t \)
- \( C \) = the proportionality constant relating \( M \) and \( TL \)

A least squares fit of Equation 5 was made to the average of the three crystals in Figure 13 and the results are shown in Figure 14. \( I_1 \) \( P_1 \) and \( I_3 \) \( P_3 \) were determined to be \( 0.00334 \pm 7 \times 10^{-5} \) and \( 0 \) respectively while \( p_2CF \) was determined to be \( 73.15 \pm 0.9 \). The inclusion of the \( \exp(-p_3I_3t) \) term in the derivation of Equation 4 is not justified by the data. However, it has been shown that 310 nm light bleaches peak 5. If the 310 nm emission line of the lamp does significantly bleach peak 5 at high UV exposures, then the utilization of filters to attenuate the 310 nm emission line should improve the linearity of response of the crystals.

DOSE RATE INDEPENDENCE

A study of dose rate independence is shown in Table 1. From this data, it is concluded that gamma irradiated TLD-100 exhibits dose independence within \( \pm 25 \) percent. However, for any particular dose rate, variation of the time of exposure produced a response in peak 5 within \( \pm 10 \) percent of the original response, i.e., doubling the time of exposure doubles the height of peak 5. This result suggests that the crystals are more accurate in their response than the UV meter. These studies also suggest that the decrease in response of the crystals at higher exposures as noted in Figure 12 is due to the bleaching of peak 5 by the 310 nm line of the germicidal lamp.
Figure 14. Comparison of TL response of UV stimulated TLD-100 crystals with theoretical curve.
<table>
<thead>
<tr>
<th>TIME OF EXPOSURE</th>
<th>EXPOSURE RATE</th>
<th>PEAK 5 RESPONSE (RELATIVE UNITS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 minutes</td>
<td>25 μwatt/cm²</td>
<td>39.5</td>
</tr>
<tr>
<td>2 minutes</td>
<td>50 μwatt/cm²</td>
<td>44.0</td>
</tr>
<tr>
<td>1 minute</td>
<td>100 μwatt/cm²</td>
<td>38.5</td>
</tr>
<tr>
<td>30 seconds</td>
<td>200 μwatt/cm²</td>
<td>34.5</td>
</tr>
</tbody>
</table>
An attempt was made to vary the exposure rate by use of the UV meter and the inverse square law. The results are shown in Table 2. The data shows the use of the inverse square law as an approximation to be invalid for distances smaller than that used for the 0.5 \( \mu \text{watt/cm}^2 \) dose rate (- 8.5 meters). However, the data does demonstrate that the crystals can be used as a dosimeter for germicidal radiation levels below 0.1 \( \mu \text{watt/cm}^2 \).

**DECREASE IN RESPONSE AFTER USE AS A DOSIMETER**

A study of the decrease of peak 5 as a function of repeated ten minute, 800 \( \mu \text{watt/cm}^2 \) germicidal ultraviolet exposures yielded the following:

\[
TL_u = TL_0 \exp(-Ku)
\]

(5)

where:

- \( u \) = the UV exposure in joule/cm\(^2\)
- \( TL_0 \) = the initial peak 5 response
- \( TL_u \) = the height of peak 5 after germicidal UV exposure of \( U \)
- \( K = 0.19 \text{ cm}^2/\text{joule} \)

The above relation predicted the experimental results to within ten percent for a total exposure up to 8 joule/cm\(^2\) as shown in Figure 15. Note that after a total exposure of 10 joule/cm\(^2\) the curve appears to be approaching another straight line within a smaller slope. This suggests that the F centers are almost completely bleached from the crystal and the \( Z_3 \) centers are beginning to become the major source of electrons for the repopulation of the thermoluminescence centers.

**TEMPERATURE DEPENDENCE OF DOSIMETERS**

The temperature of the dosimeter during ultraviolet irradiation was found to affect the dosimeter’s sensitivity.
TABLE 2
DOSE RATE INDEPENDENCE STUDIES USING INVERSE SQUARE LAW

<table>
<thead>
<tr>
<th>TIME OF EXPOSURE</th>
<th>DOSE RATE</th>
<th>PEAK 5 RESPONSE (RELATIVE UNITS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 seconds</td>
<td>50 μwatt/cm²</td>
<td>28.5</td>
</tr>
<tr>
<td>1 minute</td>
<td>10 μwatt/cm²</td>
<td>38.5</td>
</tr>
<tr>
<td>2 minutes</td>
<td>5 μwatt/cm²</td>
<td>43.5</td>
</tr>
<tr>
<td>10 minutes</td>
<td>1 μwatt/cm²</td>
<td>45.0</td>
</tr>
<tr>
<td>20 minutes</td>
<td>0.5 μwatt/cm²</td>
<td>53.5</td>
</tr>
<tr>
<td>100 minutes</td>
<td>0.1 μwatt/cm²</td>
<td>53.0</td>
</tr>
</tbody>
</table>

The 50 μwatt/cm² exposure rate was determined with a UV meter. All other exposure rates were determined by the use of the inverse square law.
Figure 15. Decrease of peak 5 as a function of repeated exposures to UV
The average relative heights of peak 5 for two sets of crystals versus crystal temperature during UV exposure are shown in Table 3. Each crystal was irradiated at the same exposure rate and for the same period of time. Also the response of each crystal is adjusted to compensate for the decrease in response after repeated exposures, as noted in Figure 12. The height of peak 5 at 23°C (room temperature) is fixed at one, and the sensitivities at other temperatures are given with respect to the sensitivity at 23°C. Crystals 9, 10, and 11 are crystals with no previous exposure to UV and crystals 4, 5, and 6 are three crystals used in the repeated exposure study.

Table 3 indicates that the sensitivity varies considerably if the temperature range is large. However, only slight variations in sensitivity would be encountered in normal room temperature fluctuations. Assuming a Boltzmann dependence of crystal sensitivity, on temperature, the following relationship can be obtained:

$$\frac{TL}{TL_r} = \exp\left[-\frac{E}{k(1/T-1/T_r)}\right]$$

(6)

where:

- $T$ = the temperature (°K) of crystal during UV exposure
- $T_r$ = the room temperature (°K) of crystal
- $TL$ = the response of peak 5 at temperature $T$
- $TL_r$ = the response of peak 5 at room temperature
- $k$ = the Boltzmann constant
- $E$ = the energy

In this case, $E$ is interpreted to be the thermal activation energy of the first excited state of the center that is de-trapped during UV exposure. The natural logarithm of $TL/TL_r$ is plotted versus $(1/T-1/T_r)$ in Figures 16 and 17. Figure 16 corresponds to the average response of crystals 4, 5, and 6 while Figure 17 corresponds to crystals 9, 10, and 11.
<table>
<thead>
<tr>
<th>Crystal Temperature During UV Exposure</th>
<th>Average Relative Response of Peak 5 for Crystals 9, 10, and 11</th>
<th>Average Relative Response of Peak 5 for Crystals 4, 5, and 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>-56°C</td>
<td>0.44</td>
<td>----</td>
</tr>
<tr>
<td>-33°C</td>
<td>0.49</td>
<td>0.63</td>
</tr>
<tr>
<td>-3°C</td>
<td>0.70</td>
<td>0.73</td>
</tr>
<tr>
<td>23°C</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>29°C</td>
<td>1.13</td>
<td>1.13</td>
</tr>
<tr>
<td>36°C</td>
<td>1.30</td>
<td>1.22</td>
</tr>
<tr>
<td>42°C</td>
<td>1.43</td>
<td>1.38</td>
</tr>
<tr>
<td>46°C</td>
<td>1.54</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Crystals 9, 10, and 11 are crystals with no previous exposure to UV and crystals 4, 5, and 6 are the three crystals used in the repeated dose study.
Data points for average of crystals 4, 5, and 6

Theoretical curve

Temperature is in °K.

Figure 16. Temperature dependence of dosimeter during UV exposure for crystals 4, 5, and 6
Data points for average of crystals 9, 10, and 11

Theoretical curve

Temperature is in °K.

Figure 17. Temperature dependence of dosimeter during UV exposure for crystals 9, 10, and 11.
The emission lines of the lamp do not occur exactly at the same wavelength as the peak of the absorption bands. The half width of these absorption bands decreases with temperature; thus, at lower temperatures, a smaller percentage of the centers are being excited by the germicidal radiation. This phenomenon, along with the error in temperatures below 23°C as noted, explains the larger than predicted decrease in sensitivity at lower temperatures. Assuming that this effect is negligible around room temperature, the thermal activation energy of the first excited state may be determined. Further assuming that most of the thermoluminescence of crystal 7 is due to the de-trapping of F centers and most of the thermoluminescence of crystal 4 is due to the de-trapping of Z₃ centers, the thermal activation energy of the first excited state of the F center is determined to be less than 0.15 ev, while the Z₃ center is less than 0.13 ev.

RESPONSE TO OTHER SOURCES OF LIGHT

After a one hour exposure to cool-white fluorescent room light, no detectable thermoluminescence was observed. The attempt was made to excite the dosimeter by using the mercury line near 366 nm, however, no thermoluminescence was observed.

EMISSION SPECTRA

The emission spectrum of the UV stimulated thermoluminescence was observed and found to consist of a broad band with maximum emission at about 400 nm. This agrees with the emission spectra observed after gamma irradiation and X irradiation by other investigators, and with the gamma induced thermoluminescence observed by this investigator.
CHANGE IN PEAK RATIOS

The ratio of peaks 2, 3, and 5 remained relatively constant for a range of total UV exposure from 1000 μjoules/cm² to 24,000 μjoules/cm². This phenomenon was independent of dose rate and exposure time. Above 24,000 μjoules/cm², the peak ratio changed. After a 48,000 μjoule/cm² UV exposure, peak 5 was 4.24 times larger than peak 3 and 6.44 times larger than peak 2 compared to twice as large as both peaks 2 and 3 for an exposure below 24,000 μjoule/cm². After 52 exposures, each consisting of 480,000 μjoule/cm², peak 5 was 2.68 times larger than peak 3 and 5.52 times larger than peak 2. The change in peak ratio from an exposure of 240,000 μjoule/cm² to 480,000 μjoule/cm² suggests that the available traps responsible for peak 2 are becoming filled at a faster rate than those traps corresponding to peak 3. In the same manner, traps corresponding to peak 3 are becoming filled faster than those of peak 5.

The change in peak ratios after 52 UV exposures suggests two possibilities: (1) the defects responsible for the traps corresponding to peaks 2 and 5 are being converted into the type of defect responsible for the traps corresponding to peak 3; or (2) these two types of defects are becoming bleached at a faster rate than the type of defect responsible for peak 3.
SUMMARY AND MODEL

The most obvious interpretation of the results leads to a model with the following characteristics: exposure to UV ionizes electrons from the F and $Z_3$ bands. These electrons are then free to move through the crystal until they are retrapped at defects corresponding to the different glow peaks. Upon heating the crystal, these electrons are ionized and some are retrapped at defects corresponding to F and $Z_3$ centers. A few recombine at luminescence centers giving off the observed light.

The main problem with this process is the failure to observe photo luminescence of the F center. A model that accounts for this failure and other observed data is summarized by the following assumptions:

1. Upon UV illumination, the F centers, by a type of tunneling process, are converted into $Z_3$ centers and into the centers responsible for peaks 2, 3, and 5 of the glow curve.

2. The defects corresponding to the peaks 2, 3, and 5 are aggregates of F centers modified by the presence of Mg, i.e., perturbed M and R centers.

3. Upon heating the perturbed M and R centers are converted back into F and $Z_3$ centers with a few being ionized and recombined with holes or tunneling to a luminescence center.

Assumption 1 is justified as follows: Since all other models assume ionization of the F center during F band illumination, these theories do not account for the failure to observe photo luminescence of the F center, (i.e., if electrons are ionized when excited by F band light, then some of these electrons should...
be trapped in luminescence centers and give off luminescence). If the assumption is made that the F center electrons tunnel through to other trapping centers during UV stimulation, then this discrepancy is resolved.

The small increase in the 310 and 380 nm absorption bands during UV stimulation coupled with a relatively large decrease in the F and 270 nm band (re: Figure 10) justifies assumption 2 since two or more F centers form one aggregate center. This assumption is further supported by the observation that the centers responsible for the 310 and 380 nm bands also absorb 250 nm light and aggregates of F centers absorb 250 nm light.

Assumption 3 is justified by the observation that upon heating the crystal, the F and Z3 bands are increased in the height of their peak absorptions (re: Figure 11).

Assumption 1, coupled with the observation that peak 4 is not restimulated during UV photo stimulation (re: Figure 12), leads to the following discrepancy. Podgorsak, Moran, and Cameron on the basis of the failure to restimulate peaks -4 and -1 of the glow curve, associated these peaks with hole traps. Peak 4 has been ascribed to electron traps by Mayhugh, Christy, and Johnson. Either Podgorsak, Moran, or Cameron are in error since the same mechanism responsible for the failure to restimulate peak 4 might be responsible for the failure of Podgorsak, Moran, and Cameron to restimulate peaks -4 and -1 or the arguments leading to the determination that peak 4 is an electron trap are in error.

Mayhugh and Christy ascribe the 110 nm absorption band in TLD-100 to the V3 center instead of the 8 band, upon the following arguments:
(1) The F band is smaller in peak absorption than the \( \beta \) band and (2) the F absorption band bleaches at a faster rate than the \( \beta \) band. These two arguments do tend to rule out ascribing the 110 nm band to the \( \beta \) band since the \( \beta \) band should be bleached at the same rate as the F band; and the \( \beta \) band and the F band should have approximately the same peak absorption.\(^{59}\)

Assumptions 1 and 2 contradict the arguments of Mayhugh and Christy for assigning the 110 nm band to the \( V_3 \) center instead of the B band. After gamma or x-ray exposure, many electrons would be trapped at F center aggregates and the \( \beta \) band would have a higher peak absorption than the F band. Furthermore, any bleaching of the F band that only transfers F centers into aggregates of F centers would not decrease the \( \beta \) band. Also, the formation of a band (\( \alpha \) band) between the F band and the \( \beta \) band should occur as the F band and \( \beta \) band are bleached. Since the \( \alpha \) band is associated with isolated anion vacancies,\(^{59}\) the formation of this band would not be directly proportional to the decrease of the F and \( \beta \) bands in heavily doped crystals as observed in LiF crystals. Mayhugh and Christy did observe such a band occurring at 130 nm.\(^{51}\) These arguments are consistent with associating the 110 nm absorption band with the \( \beta \) band and the 130 nm absorption band with the \( \alpha \) band as reported by other investigators.\(^{22,37,50}\)

As observed in Figure 11, heating through peak 2 of the glow curve increases the F band peak absorption. Heating through successively higher temperature peaks increases the F band but in each case, the increase in absorption is less than the preceding increase indicating that either the lower temperature glow peaks are larger aggregates of F centers than the
higher temperature peaks or more electrons in the high temperature peaks are trapped at luminescent centers during heating than in the lower temperature peaks. The second premise is concluded to be the more probable of the two premises on the basis of the following argument. When a crystal containing only the F band is illuminated with F band light near room temperature, the M band is the first of the F center aggregates to appear with the larger F center aggregates (R, N, etc. centers) only appearing after prolonged illumination. Thus, the rate of production of M centers during F band illumination would decrease at a faster rate than the larger F center aggregates since the production of M centers would reach an equilibrium with the bleaching of the F centers before the production of larger F center aggregates due to the F center aggregates also absorbing F band light. The change in peak ratios after various exposures to UV suggests that the rate of filling of the traps responsible for peak 2 decreases faster than the rate of filling of the traps responsible for peak 3. In the same manner, the rate corresponding to peak 3 decreases faster than the rate corresponding to peak 5. Therefore, it is concluded that peak 5 is a more efficient thermoluminescence center.

The change in peak ratios after repeated exposures to 480,000 μ joule/cm² germicidal radiation with subsequent readout of the glow curve after each exposure yields some insight into the nature of the traps responsible for the thermoluminescence.

When a divalent ion is incorporated in the lattice of LiF, there exists one cation vacancy for each divalent ion. When LiF containing Mg is
heated to 400°C and quenched to room temperature, most of the Mg divalent ions and cation vacancies are paired to form dipoles. Upon annealing the crystals at a fixed temperature, the dipole concentration decreases with time. The deduction has been made from features of dipole decay that the dipoles aggregate into groups of three (trimers) and if the annealing temperature is high enough, the dipoles aggregate into larger aggregates with trimers as nuclei.\textsuperscript{61, 62} Dryden and Shuter,\textsuperscript{63} on the basis of comparison of peak heights of TLD-100 with dipole decay curves, determined that one of the factors governing the heights of peaks 2 and 3 of the glow curve was the concentration of dipoles present at the time of irradiation with trimers and larger aggregates making no contribution. They also concluded that dipoles and trimers both contribute to the heights of peaks 4 and 5 with larger aggregates making no contribution.\textsuperscript{63} Since the glow curve in the present investigation was recorded to above 200°C, the number of traps responsible for peaks 2 - 5 should decrease with repeated glow curve readouts, i.e., dipoles forming aggregates larger than trimers. Furthermore, the change in peak ratios should occur between peak 5 and both peaks 2 and 3. But, this investigation showed that the relative height of peak 3 alone was increased. Therefore, it is concluded that the height of peak 3 is not determined by the concentration of dipoles.

The defect responsible for peak 3 is suggested to be a $Z_2$ center associated with Mg. If the model of Ohkura\textsuperscript{42} is correct, the $Z_3$ center is an ionized $Z_2$ center. Observe in Figure 11, that upon heating through peak 2, the peak of the $Z_3$ band is increased, and heating through peak 3 produces a larger
increase in the $Z_3$ band. Heating through peak 5 decreases the height of the $Z_3$ band slightly, leading to the supposition that heating through peak 3 ionizes one of the electrons in a $Z_2$ center leaving a $Z_3$ center in its place.

The decrease in the $F$ band during the first few minutes of UV exposure can be related to the formation of the $B$ center at the expense of the $F$ center as observed in KCl. The increase back in height is suggested to occur due to the bleaching of the 270 nm band (re: Figures 3, 4, and 5). The same type of process seems to be occurring with the $Z_3$ center during the first few minutes of UV exposure (re: Figures 9 and 10). The present investigator knows of no model that has been presented for the $B$ center (bleached $F$ center) or that the same effect is noted for $Z_3$ centers that have been formed by thermal bleaching. Another observation is that while the half widths of both the $Z_3$ and $F$ bands appear to increase as noted for the $B$ band in KCl, the half widths appear to decrease again when the bands are restimulated in height.

The $Z_3$ absorption band appears to consist of two types of centers. One is a fast decaying band (re: Curve A, Figure 11) while the other is the $Z_3$ absorption band as identified by Mort. 40, 41

There appears to be an absorption band occurring at shorter wavelengths than 190 nm in all the optical absorption measurements, but no consistent variations occur in the shoulder of this band.

The comparison of the UV stimulated glow curve emission spectra with the gamma stimulated glow curve emission spectra indicates that the same luminescent center is responsible for both types of glow curves. The
suggestion is made that while Equations 4, 5 and 6 give good empirical fits to the results, the interpretations of the parameters have not been proven conclusively. For instance, the assumption is made that the 190° peak has been correctly identified as peak 5. However, due to the high gamma irradiations, peaks 2, 3, 4, and 5 could not be resolved and since the 310 nm light bleaches peak 5 with a subsequent enhancement of peak 4, a possibility exists that the 190° peak is peak 4. If this is true, then the interpretation of the parameters of Equations 4, 5, and 6 will have to be revised. The assumption has also been made that the 250 nm light bleaches the Z band with the subsequent restimulation of peaks 1, 2, 3, and 5. This has not been shown conclusively by these experiments.

SUGGESTED FUTURE RESEARCH

Due to the slight uncertainty of the identification of peak 5, it is suggested that some non-gamma irradiated crystals be x-rayed at low levels and the glow curve read out on the equipment used in the investigation. Since the glow curve peak structure is well resolved for low level x-ray exposure, the identity of peak 5 could be confirmed. To determine the validity of this author's argument (the 110 nm absorption band is actually the beta band), it is suggested that crystals in which the beta band is well identified be doped with impurities and exposed to high levels of ionizing radiation to produce M and R bands. Upon elimination with the M band light, the M center is disassociated with an enhancement of the F band. If the author's arguments are correct, the beta band should remain the same or decrease and the F band should increase.
Another suggestion is that an action spectra (exciting the crystal with different wavelengths of light) be run to determine if the $Z_3$ band does contribute to the restimulation of the glow peaks, i.e., a peak in the action spectra corresponding to the $Z_3$ band peak.

Another experiment that would be helpful in determining whether the 310 nm line actually bleaches peak 5 would be to expose crystals to equal intensities of the 257 nm line of mercury with one set of crystals being exposed to filtered light. Comparisons of the TL response of the two sets of crystals would determine the effect of the 310 nm line of the germicidal lamp.
CONCLUSIONS

TLD-100 ionizing radiation dosimeters may also be used to measure germicidal radiation. The wide distribution of radiation sources and thermoluminescence readers, should enable many individuals and institutions to use this method of ultraviolet radiation detection. The temperature of the dosimeter during ultraviolet exposure must be controlled for accurate measurements; however, room temperature variations usually introduce less than 10 percent error.

The TLD-100 gamma-irradiated crystals had the following characteristics:

1. They were sensitive to low levels (0.1 μwatt/cm²) of germicidal radiation. Since these are integrating dosimeters, they may detect lower levels by allowing longer exposure times.

2. Response was linear from low exposures (-5 percent) up to 4,800 μ joule/cm² (-20 percent). A single crystal can be calibrated and used, with meticulous care, to measure dosages with a precision of about 1 percent.

3. The dosimeters were exposure-rate independent over the experimental range from 0.1 μ watt/cm² to 50 μ watt/cm².

4. The dosimeters could be used repeatably to measure germicidal radiation after only one high level gamma exposure.

5. The dosimeters were insensitive to cool white fluorescent room lights.

The actual mechanisms involved in the TL process are still too complex to present a detailed model of the TL process in TLD-100, but the partial model presented does account for the observations noted in this investigation.
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55. G. C. Moore (private communication).

56. F. B. Podgorsak, P. R. Moran, and J. R. Cameron (private communication).


