

## Effects of High Pressure on the Thermoluminescence of $\gamma$ -Irradiated $\alpha$ - $\text{Al}_2\text{O}_3$ Single Crystals\*

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Thermoluminescent properties are reported here on  $\gamma$ -irradiated  $\alpha$ - $\text{Al}_2\text{O}_3$  and ruby single crystals, before and after the specimens were subjected to hydrostatic pressures of 24 kbar for 255 min at 773°K and at 30 and 40 kbar for 30-min periods at room temperature. Glow-curve changes and peak resolutions occur for white sapphire in the temperature range of 340 to 623°K. The graphs show regularity with regard to glow-peak temperatures and their sensitivity to higher annealing temperatures after pressure. A single pressure-sensitive peak at  $\sim 503^\circ\text{K}$  appears in ruby after applying pressure or after  $\gamma$  irradiation. Activation energies for several peaks as calculated from the results are also given.

### INTRODUCTION

Thermoluminescence of aluminum oxide and the effect of ionizing radiation on single crystals have been studied by several investigators.<sup>1-5</sup> The use of powder samples for luminescence studies might have complicated some results in that many peaks of unknown origin are observed during the warming cycle.<sup>6</sup> All past workers have restricted their glow experiments to effects of ionizing radiation. In the present work, glow curves (i.e., plots of light intensity versus temperature) were recorded for aged<sup>7</sup> single crystals of white sapphire and ruby. Glow curves are compared for specimens that were gamma irradiated ( $\text{Co}^{60}$ ) approximately 2 years ago, then subjected to pressures of 24 kbar at 773°K for 255 min and at 30 and 40 kbar at room temperature for 30 min. The same specimens were then annealed for 4 h at 1073°K. Some of the specimens were

then re-irradiated with  $\text{Co}^{60}$   $\gamma$  rays and again subjected to pressures of 30 kbar.

Well-defined glow peaks were obtained in these experiments on a white sapphire specimen after it was subjected to high pressure. The peaks showed regularities in their resolution and grouping when they were compared to the complexity of glow curves which were obtained from  $\gamma$ -irradiated samples that were not subjected to pressures. Examinations similar to those made on white sapphire were carried out on ruby. A prominent glow peak appears as a result of  $\gamma$  irradiation or the application of pressure. It is of interest to find that, because of pressure effects, restriction must be placed on the type of materials used for geological "age dating" by thermoluminescence. The apparent cumulative radiation-damage effects must take into account possible errors which pressure factors would introduce.

Exciting light from a mercury source induced additional glow peaks not present in the unexcited (not  $\gamma$  irradiated and/or subjected to pressure) crystals. Upon light irradiation of  $\gamma$ -damaged and/or pressured specimens, glow peaks were induced in white sapphire at 355°K and appeared to be further resolved in ruby at 473 and 503°K.

### EXPERIMENTAL

#### 1. Samples

The samples used in this study were obtained from the Linde Company, Crystal Products Division about 2 years ago and were fabricated from alumina powder which showed the following spectroscopic analysis (Table I). The ruby material was fabricated from powder containing a  $\text{Cr}_2\text{O}_3$  concentration of 0.75% but had an estimated 70% loss of dopant in the finished crystal.

The specimens used in this study were  $\gamma$  irradiated by a radiation source of approximately 4000 Ci of cobalt-60 in the form of five plates disposed about a cylindrical chamber.<sup>7</sup> The intensity of the gamma-ray field was

\* Studies have been made concerning the effects of high pressure on crystal-field strength by observing the spectrum in  $\text{Al}_2\text{O}_3$ . S. Minomura and H. G. Drickamer, *J. Chem. Phys.* **35**, 903 (1961); also in ruby, D. R. Stephens and H. G. Drickamer, *ibid.* **35**, 427 (1961).

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<sup>1</sup> O. Deutschbein, *Ann. Physik* **14**, 712 (1932), also G. F. J. Garlick and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **184**, 420 (1945), studied nonirradiated ruby and found light-induced luminescence, of a few milliseconds duration which was due to a forbidden transition in the  $\text{Cr}^{3+}$  impurity ion.

<sup>2</sup> Thermoluminescence of various crystal phases of polycrystalline aluminum oxide was studied in the 5 to 425°C region by J. K. Rieke and F. Daniels, *J. Phys. Chem.* **61**, 629 (1957).

<sup>3</sup> Saturation limits and annealing temperature of the  $\gamma$ -ray-induced coloration, defects and their effect on the optical properties of  $\alpha$ - $\text{Al}_2\text{O}_3$  were first reported by R. A. Hunt and R. H. Schuler, *Phys. Rev.* **89**, 664 (1953); and later by P. W. Levy and G. J. Dienes, "Report of the Conference of Defects in Crystalline Solids," H. G. Wells Physical Laboratory, University of Bristol, Physical Society, London, pp. 256-60, 1954 (unpublished); *Phys. Rev.* **94**, 1409 (1954).

<sup>4</sup> J. T. Randall and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **A184**, 347, 366, 390 (1945).

<sup>5</sup> W. D. Compton and G. W. Arnold, *Discussions Faraday Soc.* **31**, 130 (1961).

<sup>6</sup> F. Seitz, *Rev. Mod. Phys.* **26**, 46 and 73 (1954).

<sup>7</sup> C. J. Christensen, A. T. Jacobsen, Q. Klingler, and M. D. Evans, Technical Report "Dugway Cobalt-60 Irradiation Facility," University of Utah (unpublished).

TABLE I. Impurity content in alumina obtained by spectroscopic analysis, in %.

CaO	0.0030	Mn <sub>2</sub> O <sub>3</sub>	0.0001
Cr <sub>2</sub> O <sub>3</sub>	0.0008	NiO	0.0020
CuO	0.0003	SiO <sub>2</sub>	0.0010
Ga <sub>2</sub> O <sub>3</sub>	0.0020	Na <sub>2</sub> O	0.0010
Fe <sub>2</sub> O <sub>3</sub>	0.0025	Ag <sub>2</sub> O	0.0001
PbO	0.0040	SnO <sub>2</sub>	0.0002
MgO	0.0001		

determined as  $1.4 \times 10^5$  rad/h by ceric sulfate dosimetry.<sup>8</sup> The white sapphire specimens were exposed for 1 h; the ruby had three successive 30-min exposures on the same day. Both the sapphire and ruby specimens remained in a clear-plastic box container during a period of 27 months.

After the first series of experiments were completed some of the samples were annealed at 800°C for 4 h and portions of each set were held as "background" controls. The remainder of the samples were exposed at room temperature for one hour to an 800-Ci source. The second set of experiments described below was conducted immediately after irradiation.

## 2. Pressure Apparatus

An unsupported tungsten-carbide piston  $\frac{1}{2}$  in. in diameter was moved in a  $\frac{1}{2}$  in. by 2 in. long supported tungsten-carbide pressure chamber. Talc was used as the pressure medium. Pressures up to 40 kbar were generated in the chamber and samples remained at this pressure for 30 min. A frictional correction for the single-stage piston was estimated from accurate results for a bismuth phase boundary previously determined as an absolute pressure indicator.<sup>9</sup> Essential features of the

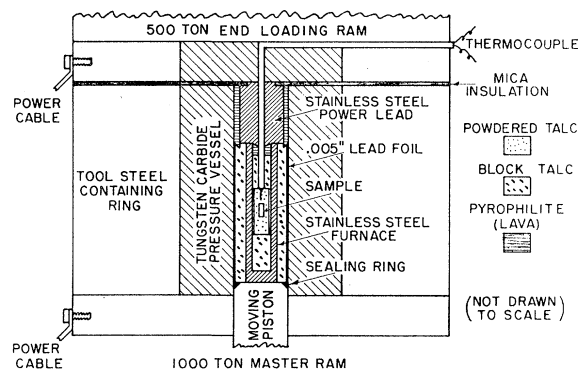


FIG. 1. Diagram of high-pressure cell and furnace assembly.

<sup>8</sup> The term "aged" samples will mean that the specimens have in their history a one-hour exposure to a Co<sup>60</sup> source. The intensity of the  $\gamma$ -ray field was determined as  $1.4 \times 10^5$  rad/h by ceric sulfate dosimetry [J. Weiss, *Nucleonics* **10**, 28 (1952)]. The samples were investigated during a 3-week period, 27 months after the 1-h exposure.

<sup>9</sup> G. C. Kennedy and P. N. LaMori, *J. Geophys. Res.* **67**, 851 (1962).

pressure chamber are given in Fig. 1. Details of this and similar apparatus have been published elsewhere.<sup>10,11</sup>

One run was made where white sapphire samples were subjected to a pressure of 24.0 kbar at a temperature of 500°C. The time of the run was 255 min and the samples were lowered to room temperature in approximately 3 sec by a rapid quench. The pressure was then gently released.

## 3. Thermoluminescence

The experiments were carried out in a lighted room.<sup>12</sup> The technique was essentially the same as was used previously<sup>13,14</sup> with one exception; the sample was in a black-box chamber only during the warming cycle. The heating rate was about 50° per min. Lower heating rates (lowest was 20° per min) produced no additional glow peaks and the resulting broadened peaks offered difficulty to establishing the temperatures for peak maximums. A compact source Mineralight Model V-41 Hg

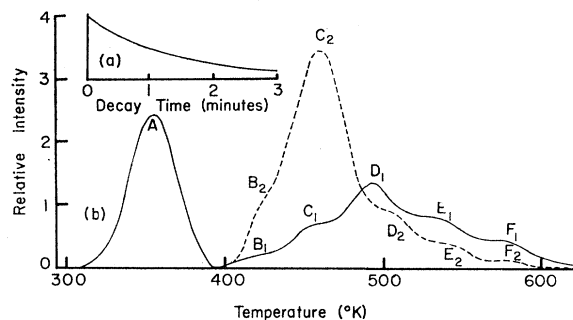


FIG. 2. Nonpressured sample: (a) Decay of light-induced luminescence, at 23°C, after 5-min exposure to mercury light, of an aged  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystal having in its history a 1-h exposure to a Co<sup>60</sup> source, over 2 years ago. (b) Glow curve (solid line) obtained from the sample used in (a), and glow curve (dash) obtained from an aged sample not exposed to uv light. (The heating rate was about 50°/min.)

lamp, obtained from Ultra-Violet Products, Inc., San Gabriel, California, supplied the light for exciting the white sapphire and ruby crystals used in this study. Recorder tracings of glow curves obtained from several white sapphire and ruby specimens are reproduced in Figs. 2 through 6.

## RESULTS

### 1. White Sapphire

#### *Nonpressured Sample*

Curves for light-induced luminescence and the glow curves for an aged crystal are given in Fig. 2. The

<sup>10</sup> F. R. Boyd and J. L. England, *J. Geophys. Res.* **65**, 741 (1960).

<sup>11</sup> G. C. Kennedy and R. C. Newton, *Solids Under Pressure* (McGraw-Hill Book Company, Inc., New York, 1962).

<sup>12</sup> The intensity of thermoluminescence peaks was found to be very sensitive to thermal pretreatment of the crystal and exposure to daylight.

<sup>13</sup> A. F. Gabrysh, H. Eyring, V. LeFebvre, and M. D. Evans, *J. Appl. Phys.* **33**, 3389 (1962).

<sup>14</sup> H. A. Woodbury, H. Eyring, and A. F. Gabrysh, *J. Phys. Chem.* **66**, 551 (1962).

light-induced luminescence in a  $\gamma$ -irradiated sample at 23°C and not subjected to pressure, Fig. 2(a), is similar to that discussed in an earlier paper.<sup>13</sup> Figure 2(b) shows (dashed curve) the effect remaining approximately 2 years after  $\gamma$  irradiation and the effect of mercury light (solid curve) on the emission of a similarly treated sample. The main peaks ( $B_1, C_1, D_1, E_1,$  and  $F_1$  for the non-light-irradiated and  $A, B_2, C_2, D_2, E_2,$  and  $F_2$  for the light-irradiated sample) were found to appear at 355, 419, 453, 500, 540, and at about 573°K, respectively.

Rieke and Daniels<sup>2</sup> have reported peaks similar to  $C_2$  and  $D_2$  for  $\gamma$ -irradiated  $\alpha$ - $\text{Al}_2\text{O}_3$  powder. Absence in their results of the  $B_2, E_2,$  and  $F_2$  peaks is perhaps due to instrumentation and/or sample structure characteristics.

The trap responsible for the  $C_2$  peak in an aged sample is greatly influenced by uv light. An aged sample which was exposed for 5 min to uv light gave the luminescence

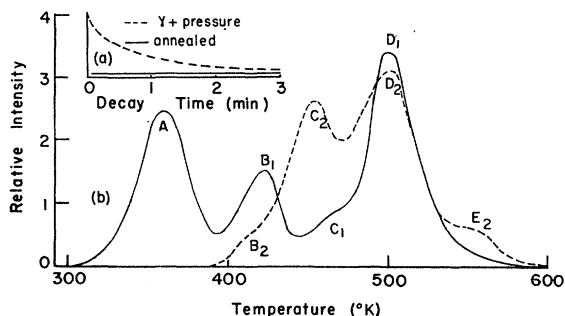


FIG. 3. Sample pressured to 40 kbar: (a) Mercury-light-induced luminescence (dash curve) of an aged  $\alpha$ - $\text{Al}_2\text{O}_3$  crystal immediately after the crystal was subjected to 40 kbar of pressure (dashed curve) and after the crystal was subjected to 24 kbar and at 500°C (solid curve). (b) Glow curves obtained on aged  $\alpha$ - $\text{Al}_2\text{O}_3$  samples immediately after 40 kbar pressure (dash) and after exposure first to mercury light after being pressured (solid).

decay curve of Fig. 2(a) and the thermoluminescence glow shown by the solid curve of Fig. 2(b). The trap responsible for the dominant  $C_2$  peak in an aged sample, not exposed to uv energy, is greatly influenced by Hg light. The  $C_2$  trap is ionized by the incident Hg radiation and the electron thus liberated is then captured by another luminescence center to form a new and dominant peak,  $A$ .

#### Pressured Sample

Representative luminescent decay and glow curves of aged crystals which were subjected to a pressure of 40 kbar for a period of 30 min are given in Fig. 3. The luminescence decay of a sample which was Hg irradiated after being pressured is given by the dashed curve in Fig. 3(a). It should be noted that in every case the decay was appreciably steeper for the first part of the curve for samples that were subjected to pressure when compared to curves for nonpressured samples, Fig. 2(a). A sample that was pressured to 24 kbar and heated to

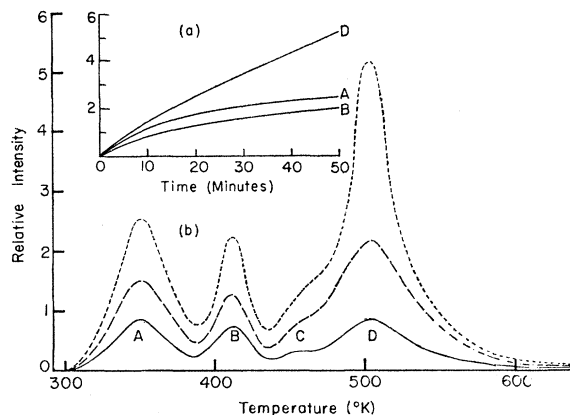


FIG. 4. (a) Dependence, in pressured samples, of intensities of the different glow peaks on time of exposure to mercury radiation. (b) Selective enhancement of glow peaks by radiation from a mercury light on an aged sample pressured to 40 kbar.

500°C while under pressure, for a period of 255 min, indicated an annealing out [solid line, Fig. 3(a)] of all luminescent centers.

The spectra for an aged sample which was annealed immediately after pressure shows main peaks  $B_2, C_2$  and  $D_2$  comparable to those of Fig. 2(b). However,  $D$  is now the dominant peak and the resolved peaks  $E$  and  $F$  combined to form a peak  $E_2$  at an intermediate temperature of about 560°K.

The exposure of a pressured specimen, before annealing, to Hg light [luminescence decay curve given in Fig. 3(a)] produced the solid-line glow curve of Fig. 3(b). Here again the trap effecting the  $C$  peak is destroyed and the  $A$  trap is enhanced. Complex changes at curves  $B, D,$  and  $E$  are noted.

Figure 4 shows the effect of additional irradiation with Hg light of a sample annealed after pressure was applied for 5 (solid), 15 (long dash), and 50 (short dash) min. Exposures were increased by 5-min time intervals, however only 3 curves are shown. Prolonged Hg irradiation of an aged and pressured crystal effected a faster rate of intensity increase in the  $D$  (500°K) trap such that the intensity increased by a factor of 10 or more. The intensity of glow peaks  $A$  and  $B$  have about the same rates of increase, Fig. 4(a). The intensities, Fig. 4(b), were reduced by a factor of 10 in order to keep peak heights on scale.

## 2. Ruby

As already reported in the literature,<sup>4,14</sup> characteristic thermoluminescence in doped  $\text{Al}_2\text{O}_3$  single crystals arises from transitions involving the impurities. Figure 5 shows glow peaks, for  $\gamma$ -damaged, pressured, and mercury-light irradiated ruby. The heating to 450°C of "as received" or virgin crystals not subjected to previous cycles of irradiation, pressure, heating, and cooling resulted in a glow curve which coincided with the black-body tracing of the heating element. Peak  $A$  at 473°K

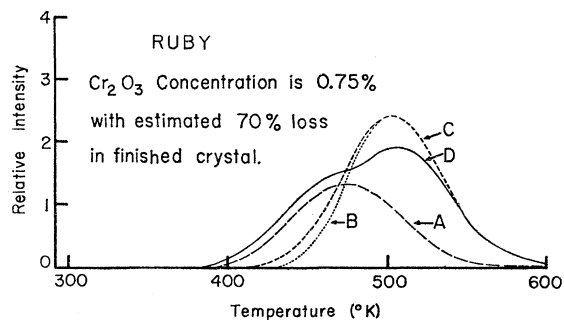


FIG. 5. Glow curves for as received and aged ruby: Sample was annealed after being  $\gamma$  damaged (long dash); as received sample pressured to 40 kbar (dot); sample  $\gamma$  damaged and pressured to 40 kbar (short dash); and sample  $\gamma$  damaged also pressured to 40 kbar and exposed for 5 min to radiation from a mercury-light source before annealing (solid curve).

is representative of glow peaks resulting from the annealing of aged ( $\gamma$ -irradiated two years ago) ruby specimens. Peak *B*, at 503°K, represents a typical glow curve obtained from virgin crystals which were pressured to 40 kbar. Glow peak *C*, at 503°K, represents annealing glow curves of aged ruby samples that were pressured to 40 kbar.

The compound peak *D* resulted from the annealing of an aged specimen which was pressured to 40 kbar and exposed to radiation from a mercury light source before the sample was heated. Slight variation in sample sizes made difficult any assignment of corresponding increases or decreases of intensity to the destruction of one type of luminescent center and favor by another in the process. It is intended to investigate, on identical samples, the distribution of luminescence intensities as a function of pressure, time under pressure, and time of exposure to uv light.

### 3. Kinetics of Thermoluminescence

The glow curves shown in Figs. 2 through 5 consist of a series of single or overlapping peaks, each of which corresponds to a particular type of electron trap. Each trap is emptied of its captured electrons as the rising temperature provides the necessary energy. The methods of calculating the number of electrons in the trap level and their activation energies require comment:

First Randall and Wilkins (Ref. 4, pp. 366–374) and later several other authors based their kinetic treatments on the assumption that the escape of the electron from a trap is the only event in a sequence of events leading to thermoluminescence which requires thermal activation. Elaborate analyses have been developed by Williams and Eyring,<sup>15</sup> Hill and Schwed,<sup>16</sup> Kikuchi<sup>17</sup>

<sup>15</sup> F. E. Williams and H. Eyring, *J. Chem. Phys.* **15**, 289 (1947); also F. E. Williams, Ph.D. dissertation, Princeton University, 1946 (unpublished).

<sup>16</sup> J. Hill and P. Schwed, *J. Chem. Phys.* **23**, 652 (1955).

<sup>17</sup> T. Kikuchi, *J. Phys. Soc. Japan* **13**, 526 (1958).

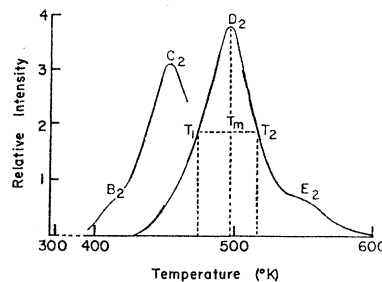


FIG. 6. Glow curves resolved by "saw-tooth" annealing of an aged sample which was pressured to 40 kbar.

and more recently by Medlin<sup>18</sup> to account for the multiple peaks found in the glow curves. The simpler work of Hill and Schwed was extended by Bonfiglioli, Brovotto, and Cortese.<sup>19</sup> They assumed that a transition of conduction-band electrons to a luminescence level  $n$  has a probability,  $p_n$ , which is temperature-independent. With increasing temperatures the trapped electrons are activated into the conduction band followed by their capture at various luminescence centers according to respective probabilities,  $p_n$ , which can differ by several orders of magnitude; the subscript  $n$  designates a particular center. A linear heating rate,  $R$ , results in light emission from a given luminescence level through second-order kinetics of the form

$$-\frac{dN_n}{dt} = \frac{p_n N_n N_t}{R} e^{-E/kT}. \quad (1)$$

Here  $N_t$  is the number of electrons in the trap level, and  $N_n$  the number of luminescence centers.

Randall and Wilkins proposed that the energy of the trap level corresponding to an experimental peak is about  $25 kT_m$ , where  $k$  is the Boltzmann constant and  $T_m$  is the temperature of the peak maximum. A disadvantage is that this estimate is based on an assumed constant value for a frequency factor. Assuming the first-order reaction, Grossweiner<sup>20</sup> developed an estimate of trap depth which is

$$E = 1.51 k T_m T_1 / (T_m - T_1), \quad (2)$$

where  $k$  is the Boltzmann constant,  $T_m$  is the absolute temperature of the peak maximum, and  $T_1$  is the temperature (on the low-temperature or leading edge of the glow curve) at which the intensity is one-half of the maximum value. This method also makes use of unaccountable<sup>15</sup> assumptions concerning the frequency factor.

Hill and Schwed, and also Bonfiglioli used the slope in an Arrhenius plot (i.e., log intensity versus  $1/T$ ) of the ascending portion of a peak to find activation energies,  $E$ . This method does not require an assumed fre-

<sup>18</sup> W. L. Medlin, *Phys. Rev.* **122**, 837 (1961); **123**, 502 (1961).

<sup>19</sup> G. Bonfiglioli, P. Brovotto, and C. Cortese, *Phys. Rev.* **114**, 951 (1959); **114**, 956 (1959).

<sup>20</sup> L. I. Grossweiner, *J. Appl. Phys.* **24**, 1306 (1953).

quency factor but it does assume that a first-order process is critically involved in the thermoluminescence. The  $\log I$  versus  $1/T$  plots did not form completely straight lines when  $T$  and the related  $I$  values were taken from the beginning of the glow up to about one-half of the maximum and, indeed, it should not. In this case the peaks are probably not simple ones but are composed of more than one component. Peak resolution was achieved by "saw-tooth" annealing which is described by Ghormly and Levy.<sup>21</sup> Example of resolved peaks is given in Fig. 6 for an aged sample which was treated in exactly the same manner as the sample whose glow peaks are given by the dash curve in Fig. 3.

Our calculations were carried out by a method suggested by Urbach<sup>22</sup> and modified by Lushchik.<sup>23</sup> The activation energy,  $E$ , related to a glow peak is given as

$$E = kT_m^2 / (T_2 - T_m). \quad (3)$$

where  $k$  is the Boltzmann constant,  $T_m$  the absolute temperature of peak maximum, and  $T_2$  the temperature at half the intensity on the fall off of the peak.

Use of Eq. (2) requires resolution of the leading edge of each glow peak from the interfering luminescence of preceding peaks. Equation (3) requires resolution of the fall-off edge from the interfering luminescence of succeeding peaks. Figures 2 through 5 indicate well-defined peaks where no further resolution was required. Trap energies calculated by Eqs. (2) and (3) are compared in Table II. The value of energies, when obtained from the Arrhenius plot, were lower (e.g., Table II; peak C,  $E = 0.72$  eV) for all peaks. Equation (3) gives an approximate "average" value of  $E$  for the three methods.

## DISCUSSION

Additional work is needed before one tries to give a model for the observed effects. The luminescence results (glow curves) obtained in the present work show a complexity not resolved by many and repeated variations in the method of investigation and of the samples used. A measurement of the spectral distribution of the light for each peak can only help to establish a model to account for effects of  $\gamma$  irradiation and pressure. Also, two significant conclusions must be drawn from this and related work:

(1) In triboluminescence work, as well as in the high-pressure work reported here, it was determined that the application of pressure induces thermoluminescence peaks in some materials. Thus, the interpreted value of geological age-dating by measurements of radiation induced thermoluminescence from materials must take account of the past history for transient dynamic pressure changes on these materials.

<sup>21</sup> J. A. Ghormly and H. Levy, *J. Phys. Chem.* **56**, 548 (1952).

<sup>22</sup> F. Urbach, *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley & Sons, Inc., New York, 1948).

<sup>23</sup> C. B. Lushchik, *Zh. Eksperim. i Teor. Fiz.* **30**, 488 (1956) [translation: *Soviet Phys.—JETP* **3**, 390 (1956)].

TABLE II. Activation energies calculated from Eq. 2 ( $E_2$ ) and Eq. 3 ( $E_3$ ): In each case the calculations result from average values taken from many glow curves. The dots signify that peak resolution was not good enough to be meaningful.

Sample	Peak	$T_m$ (°K)	$T_1$ (°K)	$T_2$ (°K)	$E_2$ (eV)	$E_3$ (eV)
White sapphire	A	355	336	375	0.82	0.55
	B	419	400	435	1.15	0.95
	C	453	433	469	1.27	1.11
	D	500	480	517	1.56	1.20
	E	540	...	555	...	1.68
	F	573	...	...	...	...
Ruby	A	473	436	505	0.72	0.60
	B	503	474	532	1.07	0.75
	C	503	468	532	0.87	0.75

(2) The heating of the ruby rod by a flash tube during laser<sup>24,25</sup> operation is a direct function of the average power in the system. Some preliminary investigations<sup>26</sup> show that either the heating of the rod caused by optical pumping while in laser configuration or simply the optical pumping itself anneals out the  $\gamma$ -induced traps responsible for the related glow curve at 473°K, Fig. 5. Thus, even though  $\gamma$ -damaged ruby may give rise to the visually observed broadening of near-field patterns and to laser action of higher efficiency at low pump energies, this effect would be gone after one pulse.

There is much similarity between the  $\gamma$ -ray-induced and pressure-induced glow peaks, Fig. 5. Perhaps faster pulse rates of reduced energy could be achieved on rods which are continuously subjected to changes in pressure (not yet known) that induces the glow peak at 503°K.

Mention should be made of some uncertainty as to whether, in ruby, changes in pressure induces triboluminescence,<sup>27</sup> metastable defects, or simply helps to fill existing defects. The absence of any glow peaks during the annealing cycle on "as-received" ruby, before and after exposure to the uv light, is suggestive of pressure-change-induced defects; however, further work is needed to prove this point.

*Note added in proof.* While this paper was in review, relative experimental data was published by W. Flowers and J. Jenney, *Proc. IEEE*, **51**, 858 (1963). Their data shows that the  $\gamma$ -ray damage is not annealed out of a rod after a single laser pulse, as we suggested, but that several pulses are required. We based our suggestion on a visual observation of the near-field pattern from a rod exposed at room temperature to pulses of nonfiltered light. Work done (by V. R. J., while the manuscript was in review) at liquid nitrogen temperatures and

<sup>24</sup> A. L. Schawlow and C. H. Townes, *Phys. Rev.*, **112**, 1940 (1958).

<sup>25</sup> A. L. Schawlow, *Sci. Am.* **204**, 52 (1961).

<sup>26</sup> Some results of this work by A. F. Gabrysh, V. R. Johnson, O. H. Bezirjian, H. Eyring, J. H. Merrill, Hardin Eyring, and R. W. Grow were reported in informal discussion at UCLA and The Battelle Memorial Institute (unpublished).

<sup>27</sup> G. Wolff, F. Gross, and I. N. Stranski, *Z. Elektrochem.* **56**, 420 (1952).

with pyrex tubing around the ruby rod indicates that Flowers and Jenney are, in fact, correct.

#### ACKNOWLEDGMENTS

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## Diffusion with Interstitial-Substitutional Equilibrium. Zinc in GaAs

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The diffusion of an impurity existing in a substitutional-interstitial equilibrium in an extrinsic semiconductor is considered. The dependence of the effective diffusion coefficient  $D$  on the impurity concentration can be simplified by assuming that the concentrations of the substitutional species and electrical carriers are nearly equal and that the diffusion of the substitutional species can be neglected. Then  $D$  is shown to vary as the first, second, or third power of the impurity concentration depending on the charge states of the substitutional and interstitial species. Universal calculated results are presented for these three cases for a constant surface concentration and semi-infinite medium. The results are used to explain the anomalous diffusion of zinc in GaAs, for which the model predicts that  $D$  should vary as the square of the concentration. Six available diffusion profiles at 1000°C can be fit using a single parameter, and the small temperature dependence of available diffusion profiles is in accordance with the theory. The interstitial zinc concentration is estimated to be several orders of magnitude below that of the substitutional zinc.

### I. INTRODUCTION

THE diffusion of zinc in many semiconductors is frequently unusual. For example, although it diffuses substitutionally in germanium,<sup>1</sup> it diffuses interstitially in silicon.<sup>2</sup> There are conflicting reports of zinc diffusion in InSb,<sup>3-4</sup> and in GaP, zinc diffusion is concentration dependent.<sup>6,7</sup>

The case studied most fully is that of zinc diffusion in GaAs. Here it was found that the diffusion is rapid, the diffusion front is anomalously sharp, and the diffusion profile depends on the surface concentration of zinc.<sup>8-11</sup> The first attempt to explain this behavior was made by Allen,<sup>12</sup> who proposed that the zinc diffuses in both

a neutral and ionized state. However, Goldstein soon refuted this explanation by pointing out that the zinc forms an impurity band merging with the valence band,<sup>9</sup> and, furthermore, demonstrated that within an experimental error of 10%, all the zinc is ionized.<sup>13</sup> Next, Kendall and Jones<sup>11</sup> advanced the suggestion that the zinc diffuses substitutionally but is enhanced due to an increase in the gallium vacancy concentration. However, they have not yet published a quantitative fit to the data. More recently, Longini<sup>14</sup> has suggested that zinc can exist as an interstitial species at high zinc concentrations, and thereby dominate the diffusion process. However, Longini only provided plausibility arguments for this explanation, with no quantitative treatment of the diffusion problem.

In the present work, the problem of the diffusion of a species in interstitial-substitutional equilibrium is shown to be reducible to a concentration-dependent diffusion process, by applying several appropriate restrictions. General solutions are presented for diffusion profiles for the cases when the diffusion constant varies as the first, second, and third power of the concentration. The results are shown to provide a good quantitative fit to data of zinc diffusion in GaAs.

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