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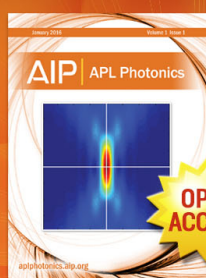
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Excitation and pre-excitation of glow curves in natural semiconducting diamonds

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The uv excited glow peaks at ~ 150 K and ~ 250 K were investigated. The mainly blue thermoluminescence (TL) peak appearing at 150 K in semiconducting diamonds was found to have also red and infrared components all appearing at the same temperature. Another red peak appearing at 260 K included an infrared component at a somewhat higher temperature. The intensity of this red peak behaved superlinearly with the dose of the 360 nm excitation. It was possible to pre-excite the 250 K blue peak using infrared light when the exciting light was 225 nm; however, this caused a partial bleaching of the 150 K blue peak. The investigation also included pre-excitation at various temperatures, intensity vs dose measurements of pre-excitation, and intensity vs dose measurements at various temperatures. It was found that the red TL peak produced by 500 nm could be excited more efficiently at 180 K than at liquid nitrogen temperature. The energy level model is reviewed in accordance with the new results.

INTRODUCTION

Thermoluminescence of the natural *p*-type semiconducting diamond was first investigated by Halperin and Nahum.¹ They found two blue TL peaks at ~ 150 K and ~ 250 K using 225 nm (5.5 eV) band to band excitation. The activation energies of the peaks were found to be 0.2 eV and 0.35 eV for the lower and higher temperature peaks respectively. The activation energy for the higher temperature peak was in good agreement with that of release of holes in semiconducting diamond, 0.37 eV, as found by electrical measurements.^{2,3} Halperin and Chen⁴ showed that the two TL peaks were excitable in the 300–400 nm region by employing high doses for excitation, although the absorption of light in this wavelength range is by far lower than the band to band absorption. The dependence on the dose (D) of the intensity of the 250 K glow peak was found to be superlinear at low doses of excitation in this wavelength range. The maximum intensity progressed like D^n where n assumed values of slightly above 2 in most of the above mentioned range and reached the value of 3 under certain conditions at 360 nm. It was also shown that the two TL blue peaks were accompanied by red components appearing at higher temperatures than their blue counterparts.

The superlinear excitation was explained to be due to a multistage transition of electrons, excited from the valence to the conduction band, before being trapped at the recombination center. This model was supported by the phenomenon of preexcitation.⁵ The sample was illuminated by red light (e.g., 700 nm), which by itself could not cause any detectable blue TL, and subsequently irradiated by the uv light in the "superlinear" 300–400 nm range. The resulting 250 K TL was subsequently higher than that observed after uv irradiation alone. The power of the dose dependence n , was reduced by preexcitation and attained values close to unity after long red light illumination. This preexcitation effect was explained as resulting from elevation of electrons to the intermediate stages from which uv light could later excite them through the conduction band to the centers.

Two works by Walsh, Lightowers, and Collins^{6,7} have given further insight into the emission spectrum of the band to band excited TL in semiconducting diamonds. They reported two emission bands, one between 3.1 and 2.2 eV and another between 2.1 and 1.5 eV. The spectra were similar for both the 150 and 250 K peaks and for each peak the blue emission occurred earlier than the red.

TL of semiconducting diamonds at various excitation temperatures (T_E) has recently been investigated in this laboratory.⁸ The results showed that the intensities of TL glow peaks both at 150 and 250 K excited with 360 nm, fell sharply as T_E approached 150 K. When T_E was above 150 K the lower temperature peak did not appear as we expected. Quite surprisingly, however, it was found that under these temperature conditions the 250 K peak did not appear as well. Results of a similar series of experiments, but with excitation corresponding to band to band excitation, did not show this effect. This difference in behavior was explained by the temperature instability of one of the levels involved in the 360 nm excitation, to which the superlinear dose dependence was attributed. In the present work the effect of preexcitation at various temperatures is investigated. Intensity vs dose measurements at various excitation wavelengths and temperature conditions are also performed, shedding light on the concepts of multistage transitions. These measurements were made separately for the blue and red emissions.

EXPERIMENTAL

The experimental setup was similar to that described previously.^{1,4} The crystal was mounted in a metal vacuum cryostat and was excited at liquid nitrogen temperature (LNT) or higher temperatures between LNT and room temperature (RT). Monochromatic light for excitation was obtained from a Hilger and Watts D285 monochromator fitted with a quartz prism; in most cases an additional filter was used to avoid the stray light. A PEK Xe, 75 W lamp or a Hanovia 538C, 900 W, Xe arc lamp was used for excitation. The irradiation dose was varied by changing the irradiation time; it was

found that changing the dose by varying the light intensity using neutral density screens, gave essentially the same results.

An EMI 9558 QB (tri-alkali S-20) photomultiplier was used for the detection of the emitted light. In order to reduce the dark current of the photomultiplier and thus to measure a low intensity TL, a Products for Research thermoelectric cooling device was employed. The output of the photomultiplier was fed through a Keithley 414S picoammeter into the y axis of a YEW 3073 Yokogawa x - y recorder. The reading of a copper-constantan thermocouple attached to the crystal holder was fed into the x channel. Separation between the blue, red, and infrared emissions was done by inserting suitable filters in front of the photomultiplier. No correction was made in the figures for the wavelength response of the photomultiplier.

The heating rate used was ~ 35 K per minute. In each measurement the crystal was heated to about 500 K which was found to bleach completely the effects of previous irradiation. The samples used were the C_2 , C_3 , and C_4 specimens mentioned in the previous work.⁴ The samples were irregular in shape, and of dimensions varying from 2 to 6 mm. The results were practically the same for all the samples used. The bulk of the work was made on the C_3 sample.

RESULTS

The main glow peak appeared at ~ 250 K and a weaker one at ~ 150 K. These temperatures were in good agreement with previous observations.^{1,4-7} Spectral decomposition showed that most of the light was emitted in the blue region but weaker components appeared in the red and infrared. Curve (a) in Fig. 1 shows these two TL peaks appearing at 150 and 250 K on a semilog scale used to depict the widely varying intensities after ex-

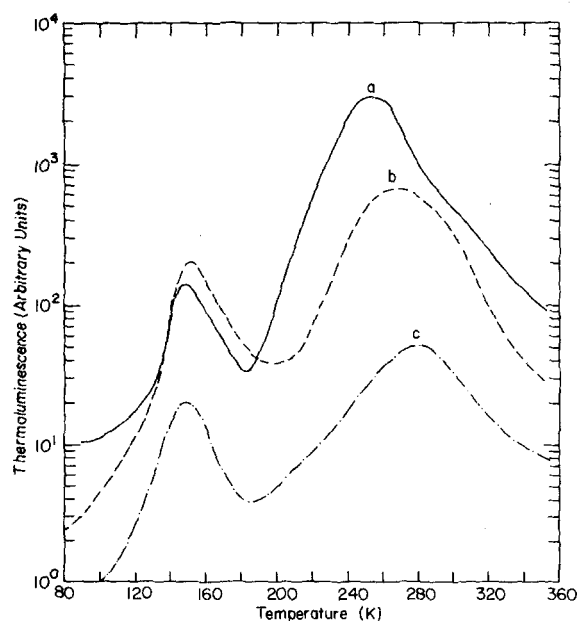


FIG. 1. Glow curves of semiconducting diamonds excited by 360 nm light, (a) blue emission, (b) red emission, (c) infrared emission.

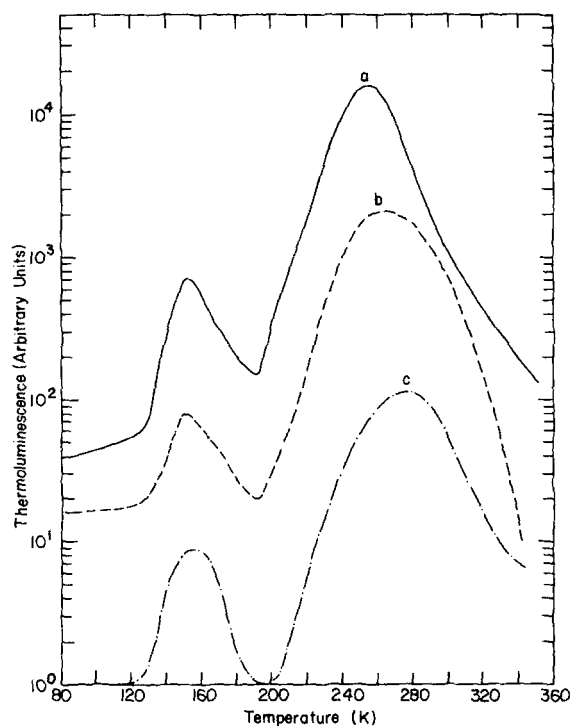


FIG. 2. Glow curves of semiconducting diamonds excited by 225 nm light (a) blue emission, (b) red emission, (c) infrared emission.

citation with light of 360 nm. A blue filter (Kodak Wrattened 47) was used in front of the photomultiplier. Curve (b) shows the glow curves when a red filter (Kodak Wrattened 26) is used. We see that while the lower temperature peak did not shift, the higher temperature peak shifted by about 15 deg from 250 K to 265 K. Curve (c) of this figure shows the results when an infrared filter is used (i. e., a combination of Kodak Wrattened filters 26 and 45 transmitting light of wavelength longer than 700 nm). Again it is noted that the lower temperature peak remains at 150 K, while the higher temperature peak shifts to 280 K. Figure 2 shows these results for excitation light of 225 nm, also on a semilog scale. The filters used are, as before, blue [curve (a)], red [curve (b)], and infrared [curve (c)]. We see that here too the lower temperature peak remains at about the same temperature, while the higher one shifts to higher temperatures as before, though not to the same extent. The lower temperature peak is at approximately 150 K in all three curves, while the higher temperature peak is at ~ 255 K, ~ 260 K, and ~ 275 K for curves (a), (b), and (c) respectively.

Curve (a) in Fig. 3 gives on a log-log scale a curve of the maximum intensity (I_m) of the blue peak at 250 K as a function of the excitation dose, the exciting light being 360 nm. For all the results given in Figs. 3, 5, 6, and 7, the dependence of the area under each glow curve has also been evaluated and these results were plotted vs the excitation dose. All the area curves behaved in the same way as the I_m vs D curves and therefore only the latter are given. The relation between the area under a glow curve, S , and the maximum intensity I_m has recently been studied theoretically by our group. It was found that there exists a practically linear rela-

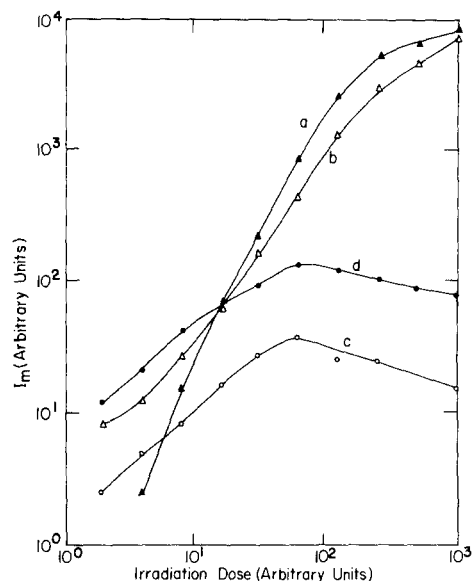


FIG. 3. Dependence of the maximum intensity (I_m) of the glow peak on the 360 nm excitation dose. (a) 250 K blue peak, (b) 265 K red peak, (c) 150 K blue peak, (d) 150 K red peak.

tion between these two, under rather general assumptions.⁹ The results in curve (a) of Fig. 3 are in agreement with those reported previously.⁴ The slope of the curve at the low dose range is seen to be ~ 2.6 and at higher doses the slope decreases gradually. Curve (b) shows results of similar measurements obtained when the red filter was inserted between the sample and the photomultiplier. The red peak is now also found to depend, in a superlinear manner, on the excitation dose, but as opposed to the behavior of the blue peak which starts with the maximum slope, the slope of curve (b) is seen to start with an approximately linear behavior, to gradually increase to a maximal slope value of 1.5, and then to decrease while tending to saturation. Curve (c) and (d) show the dependence of the maximum intensity of the ~ 150 K blue and red peaks respectively on the dose. As mentioned before⁴ the blue peak is seen to increase in a nearly linear rate at low doses, reach a maximum value at a certain dose and then to slightly decrease at higher doses. A similar behavior is now found for the red peak as depicted in curve (d).

The effect of infrared preexcitation which was previously observed after excitation with 360 nm light⁵ has now been found also after band to band excitation (Fig. 4). Curve (a) shows on a semilog scale the result of TL obtained with 225 nm excitation. Curve (b) shows the result of first preilluminating with light of 700 nm and then exciting with 225 nm as in curve (a). We see that the 255 K peak is enhanced by about 50%. We observed that the amount of enhancement depends on the dose of the infrared preillumination as well as on the uv excitation. It was also found that the 150 K peak was partly bleached by the ir preillumination and that the maximum of the peak shifted to lower temperatures. Figure 4 shows that the lower temperature peak was bleached to about 20% of its original value, and that the temperature at the maximum decreased by about 5 deg.

Reference was made⁸ in the introduction to the fact

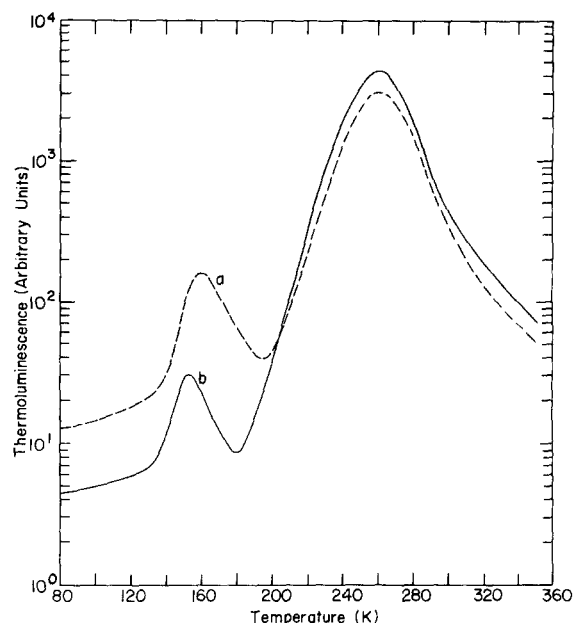


FIG. 4. Effects of preillumination on TL glow curves. (a) Sample excited by 225 nm only. (b) Sample preilluminated by light of 700 nm then excited as in (a).

that under 360 nm excitation, the 250 K peak could not be excited for T_p greater than 150 K. It was surmised that this is due to the instability of one of the levels involved in the superlinear excitation^{4,5} in this temperature range. In order to examine this assumption, a test of the temperature stability of the preexcitation was carried out. The sample was preilluminated at various temperatures (T_p) by light of 700 nm which was filtered using a Corning CS 2-64 glass filter so as to avoid any stray light that may pass through the monochromator. The sample was then quickly cooled to LNT and excited with 360 nm light. Curve (a) in Fig. 5 shows the result of this experiment. The y axis gives on a percentage basis the value of enhancement $[I_m(T_p) - I_m]/I_m$, where $I_m(T_p)$ is the intensity at the maximum of the 260 K peak when preexcitation is made at temperature T_p , and where I_m is the intensity at the maximum of the 250 K peak with no preexcitation. The x axis gives $T_p(K)$, the temperature at which preexcitation is made. We see

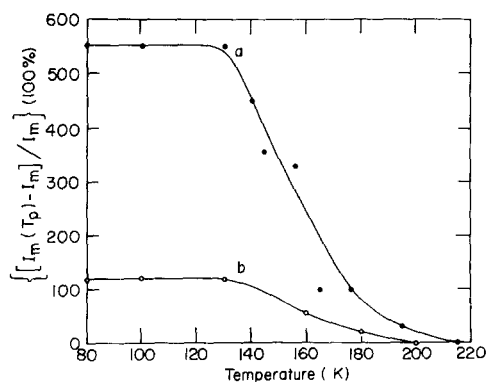


FIG. 5. Dependence of enhancement by 700 nm preexciting light as a function of the temperature at which preexcitation was made. The light used for excitation was (a) 360 nm, (b) 225 nm.

that the enhancement with preexcitation at LNT is about 550%. Up to 130 K the glow intensity at the maximum is as high as that produced with $T_p = 80$ K. The enhancement is about half of its maximum value at $T_p \sim 155$ K, and gradually decreases in value as T_p increases to ~ 210 K. The intensity at the maximum of the glow peak preilluminated at $T_p \gtrsim 210$ K was the same as that produced with no preexcitation at all, so that no enhancement exists. Curve (b) in Fig. 5 shows results of a similar experiment, but with exciting light of 225 nm; the preexciting light remains 700 nm. It is seen that the behavior of the enhancement as a function of temperature, with an excitation of 225 nm [curve (b)], is similar in shape to that which occurs when the excitation is 360 nm [curve (a)]. We also see that in curve (b) the enhancement effect ceases to exist for $T_p \gtrsim 200$ K.

Examination to see whether the process associated with preexcitation is temperature stable was also carried out. This consisted of preilluminating the sample with 700 nm light at 155 K, letting it decay at that temperature for a specified period of time, then cooling to LNT, exciting with 360 nm and heating as usual. A similar examination, but with the decay at LNT, shows practically the same results.

Figure 6 shows on a log-log scale the dependence of the enhancement $[I_m(D_p) - I_m]$ of the 250 K peak on the 700 nm preexcitation dose for times ranging from ~ 1 to 1200 sec, followed by a specified dose of 360 nm excitation, where $I_m(D_p)$ is the intensity of the maximum of the TL peak after preexcitation of dose D_p , and I_m is the intensity of the peak without preexcitation. The slope, even at small 700 nm preexcitation dose is about unity and decreases with increasing dose.

As is known⁴ excitation above 400 nm and up to ~ 650 nm at LNT yields TL composed of only the red peaks which appear at ~ 175 and 285 K. Comparison between intensity vs dose measurements at LNT and at ~ 180 K has now been done using 500 nm excitation. Figure 7 depicts these results where excitation was made at LNT [curve (a)] and at 180 K [curve (b)]. The slope of the curves (a) and (b) on the log-log scale are approximately unity. It is seen that the TL obtained by excitation at 180 K was higher by about 50% than that obtained at LNT at each given excitation condition. At the lowest dose,

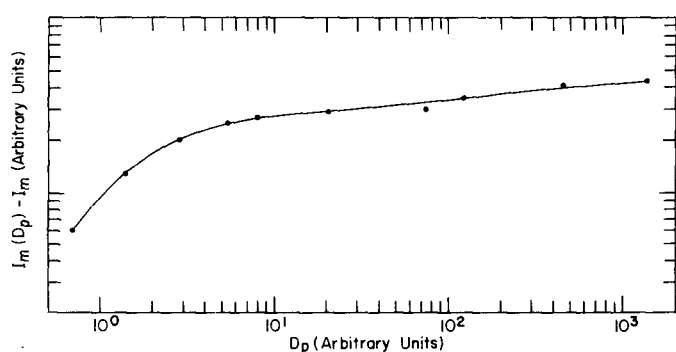


FIG. 6. Dependence of the enhancement $[I_m(D_p) - I_m]$ of the 250 K blue peak on the 700 nm preexcitation dose (D_p). The exciting light was 360 nm.

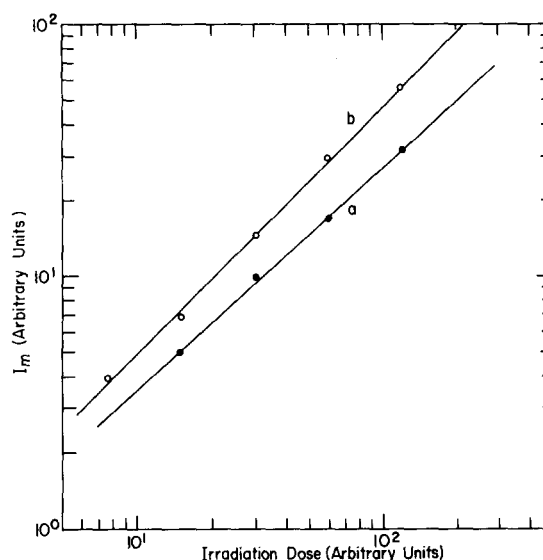


FIG. 7. Dependence of the maximum glow intensity I_m of the ~ 280 K red peak on the 500 nm excitation dose. The temperature of excitation was (a) 80 K, (b) 180 K.

corresponding to 7.5 seconds of excitation, only the glow excitation at 180 K could be observed.

DISCUSSION

The energy levels and transitions connected with the excitation and TL emission processes are schematically shown in Fig. 8. T_1 and T_2 represent the hole traps with the depths of 0.2 and 0.35 eV respectively. A_1 and A_2 are the two intermediate steps for raising electrons from the valence band (VB) to the conduction band (CB) by energies smaller than the band gap. These two levels were, as mentioned, associated with the super-linear dose dependence. It can be seen from Fig. 1 that the red TL peak which was reported previously⁴ is actually composed of two components, red and infrared. This may be explained by the existence of three different recombination centers. Levels B , R , and IR in Fig. 8 represent electron traps, which may act as recombination centers for the thermally released holes, thus yielding blue, red, and infrared TL emission bands respectively. The delay in the appearance of the infrared peak in comparison with the red, indicated that the recombination probability of the IR center is small as compared with that of R , which is in turn smaller than that of B , since we expect the center with the highest recombination probability to peak first. In this process,

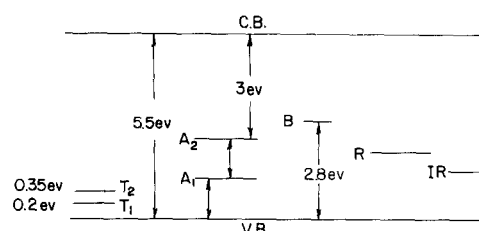


FIG. 8. Schematic model for the energy levels and the transitions involved in the excitation of the blue, red, and infrared TL. Arrows indicate electron transitions.

electrons may be excited into the CB either directly (by 5.5 eV excitation) or in stages (by 3–4 eV excitation) and may then fall either to the B , R , or IR . The electrons may also be excited directly to R and IR by light below 3 eV. Upon heating the sample, holes which were trapped in T_1 are first released and recombine with the electrons at B , R , and IR . The lower temperature TL peaks behavior is dominated by the emptying of the T_1 trap of holes rather than by the exhaustion of the electrons in the centers. This can be seen by the fact that all the components of the peak appear at the same temperature 150 K even though the recombination probabilities of a free hole with an electron are different for B , R , and IR . Upon further heating, the T_2 trap, which is responsible for the hole conductivity of semiconducting diamonds, comes into play. It is the filling of the centers now which causes the appearance of the peaks.

Luminescence has previously¹⁰ been explained to be due to donor–acceptor pair recombination involving the 0.2 and 0.37 eV acceptors. Walsh *et al.*⁶ explained that the blue and red TL emission of the higher temperature peak are also due to a donor–acceptor recombination as explained in the following manner. At the start of the heating period a certain number of these acceptors still exist which contains holes. As the temperature is increased, the holes from the 0.2 eV level and later, those from the 0.35 eV level recombine in two stages. The holes are first captured at an ionized acceptor, then recombination takes place with an electron on a nearby donor. The similarity to the luminescence spectrum¹⁰ is explained in this way. They thus pointed out that the probability for donor–acceptor pair recombination, as well as the spectrum of the resulting emission, depended on the distance between the constituents of the pair. They concluded that the recombination probability, as well as the energy of the emission, decreases as the separation increases, and explained in this way the appearance of the red peak at higher temperatures. This explanation met some difficulty due to the fact that according to Dean¹⁰ the lifetime of a donor–acceptor recombination process is ~ 0.5 msec for nearest neighboring pairs, and ~ 100 msec for fifth nearest neighbors and above. This relatively short lifetime can hardly explain the substantial temperature difference (5–15 K) between the appearance of the blue and red glow peaks. At a heating rate of 0.6 K/sec as measured in the present work, this corresponds to a time difference of 10–25 sec. It is also difficult to explain by their theory how the red and infrared peaks can be excited by light of wavelength in the 400–800 nm range, whereas the blue TL is not excitable, as shown in the present work.

The superlinear dose dependence of the 265 K red TL is shown in Fig. 3, curve (b). This may be due to the fact that electrons can be brought to the center either through CB or by direct transition from the VB. At low doses of excitation most of the red TL may be attributed to those electrons that were directly raised to R from VB, in agreement with the initial linear behavior of the curve. As the dose of excitation is raised, more electrons reach R through the CB. The resulting superlinear portion of the curve represents then the sum of the two linear functions, one being due to the electrons

raised directly, and the other to those which are raised to R via the CB. As the center becomes saturated, the slope drops. The behavior of curves (c) and (d) will be discussed further on.

The effect of the enhancement of the 255 K blue peak by preillumination (Fig. 4) can be explained as follows. During the 225 nm excitation, electrons are raised directly from the VB to the CB. The intermediate levels A_1 and A_2 then compete with the recombination centers B , R , and IR for these free electrons. The competition is less effective after preexcitation, since the intermediate levels already contain electrons. This enables more electrons to reach the recombination centers leading to an enhanced 255 K peak. On the other hand, the effect of bleaching of the 150 K peak by the same 700 nm preilluminating light (Fig. 4) can be explained as follows. Preillumination fills the IR center directly, and the subsequent excitation with uv light fills the B and R center. Thus, holes thermally released from T_1 , may recombine either in the IR or B (and R) center. This would bring about a partial bleaching of the 150 K peak, as fewer holes (compared with a case where no preillumination was made) would recombine in the B center, because of the competing IR center.

A similar explanation as above serves also to explain the strange dose dependence of the red and blue 150 K peaks as shown in Fig. 3, curves (c) and (d). These peaks reach a maximum value at a certain dose of excitation, then slightly decrease (see also Ref. 4). It seems that both the B and R reach a saturation at a certain irradiation dose; however as the dose is further increased, the IR or possibly some irradiationless center receives more electrons, which by competition during heating finally lowers the value of the blue and red peaks.

The effect of preexcitation is dependent on the existence of the intermediate levels A_1 and A_2 . It was previously reported⁹ that it is possibly the A_2 level which is unstable at temperatures of excitation above 150 K. Figure 5 shows the combined temperature stability behavior of levels A_1 and A_2 . When the temperature at which preexcitation is made (T_p) is higher than 150 K, only A_1 is responsible for the preexcitation effect. Its efficiency goes down as T_p increases, and vanishes at $T_p > 210$ K.

The phenomenon shown in Fig. 7 can now be understood as follows. The maximum intensity I_m of the ~ 280 K peak excited with 500 nm behaves linearly with respect to the dose of excitation both at LNT and at 180 K. It is therefore to be expected that at both excitation temperatures the same number of electrons will be excited into the IR center. If the excitation is at LNT, however, a certain number of electrons accumulate at A_1 and A_2 . During heating, A_1 and A_2 compete with the IR center for thermally released holes. This competition is decreased when the excitation is made at 180 K since at least one of the intermediate levels is unstable.⁸ Since transitions to A_1 and A_2 seem to be radiationless, the 280 K peak is larger after excitation at 180 K than after LNT.

As mentioned in the introduction, the value of the

slope describing the dependence of the 255 K peak intensity on the dose of the 360 nm irradiation was reduced to unity after a large dose of preexcitation. This was attributed to the raising of electrons to A_2 by the preexciting light. It would seem reasonable to expect a superlinear behavior with a power of up to 2 for the dependence of the enhancement on the preexcitation dose. We see though, from Fig. 6, that even at low doses the behavior is about linear. The explanation for this is not yet fully understood, though possibly it may be due to the fact that it is difficult to accurately measure the difference $I_m(D_p) - I_m$ in the limit of low dosage of excitation.

ACKNOWLEDGMENT

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