Thermally stimulated luminescence and conductivity in boron-doped diamonds

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Thermally stimulated luminescence and conductivity measurements have been performed in natural and synthetic semiconducting diamonds, in the temperature range 12–350 K, after excitation, near liquid-helium or liquid-nitrogen temperatures, with uv light, x-ray, 150-keV, and 0.5-MeV electrons. The glow curves observed in synthetic diamonds are similar to the glow curves obtained previously in natural diamonds. Two of the peaks which are reported have only been previously observed in types-I and -IIa diamonds. Conductivity measurements exhibit stages at 160, 230, and 340 K which correlate with thermoluminescence peaks. An additional stage at 50 K is observed after 0.5-MeV electron irradiation. The concentrations of the traps in these different stages have been deduced. The stage at 50 K is shown to be associated with a donor level situated at 0.02 eV below the conduction band.

I. INTRODUCTION

In the course of an investigation of the defects created by electron irradiation at low temperature in semiconducting diamonds using conductivity measurements, it appeared that carriers were thermally released from traps during the annealing process in the temperature range 12–250 K. This is illustrated in Fig. 1: several stages which are present after high-energy (0.5-MeV) electron irradiation are also observed after x-ray irradiation [uv illumination or low-energy (150-keV) electron irradiation produce similar effects to x-ray irradiation]. Because diamond is covalent, x-ray irradiation or uv illumination cannot create defects, but only induce electronic transitions between existing localized levels and the bands. As a result, the stages observed after such excitations can only be ascribed to thermally activated transitions of carriers from localized levels to the band in which the conductivity takes place. The only stages ascribable to the annealing of defects are those which are present after high-energy electron irradiation and which cannot be found anymore after the sample has been warmed up and excited again with uv light or x rays.

In order to study the defects created by high-energy electron irradiation using conductivity measurements it therefore appeared necessary to establish first the possible effect of these traps on the conductivity. We then investigated the presence of deep traps present in synthetic semiconducting diamonds using thermoluminescence and attempted to correlate the thermoluminescence measurements with conductivity measurements. We also compared these results with the results obtained on natural semiconducting (type-IIb) diamonds in

order to see if the traps are similar in synthetic and natural stones. We also studied the introduction of new traps by high-energy electron irradiation. The variations of conductivity are used to estimate the concentrations of the traps.

Section II is devoted to the experimental setup. Because the problems encountered during conductivity measurements, and because the experimental setup used for conductivity measurement and
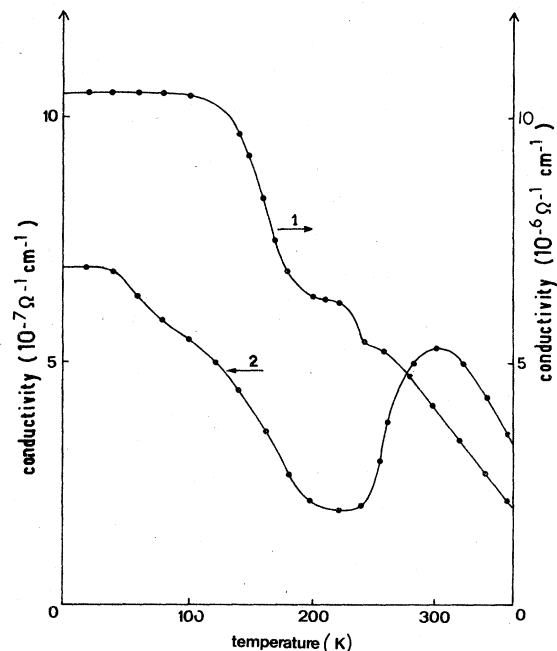

FIG. 1. Variations of conductivity at 12 K during isochronal warm-up (20 K×10 min^{-1}) following 20-keV x-ray irradiation (curve 1) and 500-keV electron irradiation (curve 2) performed around 20 K (sample GE48).

irradiation are described elsewhere,[1-3] only the experimental setup used for thermoluminescence and the method for the estimation of the trap concentrations are described here. The results concerning both thermoluminescence and conductivity measurements are described in Sec. III. Because the apparatus used for the thermoluminescence studies is not adapted for electron irradiation, only conductivity measurements have been performed after irradiation around helium temperature. In Sec. IV these results are analyzed and discussed in terms of the model for the thermoluminescence proposed in the literature.

II. EXPERIMENTAL SET UP

A. Samples

The diamonds used in this study are synthetic stones (B190, GE47, GE48, GE4A, GE5A), doped with boron, grown by General Electric, and one natural type-IIb stone (DB2B) furnished by De Beers. The natural stone is a cube of $2 \times 2 \times 2$ mm^3 of resistivity 5×10^5 Ω at room temperature; its resistivity at low temperature is too high to be measured, so it can be used only for luminescence studies, for comparison with the synthetic stones. The concentration of boron impurities N_A in the synthetic stones, as well as the concentration N_D of compensating centers, has been evaluated[4] using resistivity and optical absorption, the latter being more reliable.[4] The results are given in Table I. The evaluation of the concentration of traps has been determined in samples GE48 and

B190 using the values of N_A and N_D obtained from optical measurements.

B. Evaluation of the trap concentration

Low concentrations of traps in semiconducting diamonds can be detected using conductivity measurements at low temperature. Conductivity in synthetic semiconducting diamonds, sufficiently doped with boron, occurs through a variable range hopping mechanism[4] below approximately 150 K. The variation of conductivity, from an initial value σ_i to a value σ, due to a variation ΔN_D in the concentration of compensating centers (which occurs when traps release their carriers by thermal excitation), can be calculated[2] from

$$\ln\sigma = \ln\sigma_i - \beta\Delta N_D, \qquad (1)$$

where β is a term depending upon both the doping (boron) concentration N_A and the concentration N_D of the compensating centers; in the samples (B190 and GE48) in which ΔN_D has been evaluated, the compensation $K = N_D/N_A$ is larger than 0.5 and the expression of β is then[2]

$$\beta = 0.66(\alpha^3 e^2/2k\chi T)^{1/4}N_A^{1/6}(N_A - N_D)^{-4/3}, \qquad (2)$$

where χ is the dielectric constant, e the electronic charge, α^{-1} a length characterizing the extension in space of the wave function of the hole bound on boron impurities; α^{-1} is[4] about 2×10^{-7} cm. The values of ΔN_D calculated this way are only approximate since N_A, N_D, and α are not known accurately.

TABLE I. Concentrations (cm^{-3}) of boron (N_A) and of compensating centers (N_D) in the synthetic stones studied. [a]

Sample	N_A	N_D	N_A-N_D	K (%)	Method of determination
B190	1.3×10^{17}	1.0×10^{17}	3.0×10^{16}	77	Resistivity
	1.5×10^{18}	1.2×10^{18}	2.5×10^{17}	83	Absorption
GE47	1.2×10^{17}	5.0×10^{16}	7.0×10^{16}	44	Resistivity
	3.6×10^{17}	2.4×10^{17}	1.2×10^{17}		Absorption
GE48	1.7×10^{18}	1.6×10^{18}	6.5×10^{16}	96	Absorption
GE4A	2.0×10^{16}	6.0×10^{13}	2.0×10^{16}	0.3	Resistivity
GE5A	9.0×10^{16}	2.0×10^{14}	9.0×10^{16}	0.2	Resistivity

[a] In the method of determination called "resistivity" N_A and N_D are determined (Ref. 4) graphically from the resistivity ρ-vs-temperature T curve taking for the mobility experimental results obtained on similar samples. In the "absorption" method N_A and N_D are obtained (Ref. 4) from the magnitude of the optical absorption at 0.348 eV and from the resistivity at room temperature. The difference in the results obtained by these two methods comes from the fact that $\rho(T)$ has to be studied at very high temperatures (above 1000 °C), temperatures at which defects—associated with N_D—annealed. The best values to consider are those given by the absorption method because the experiments performed in this paper, as well as the absorption measurements, have been done prior to the study of $\rho(T)$, i.e., prior to any high-temperature annealing.

C. Thermoluminescence measurements

The sample is held by tungsten wires in a vacuum chamber equipped with a quartz window on a holder which can be cooled to liquid-nitrogen temperature. This holder contains a heater which allows linear variations of temperature with time (within 10%) between 80 and 360 K. Temperature rates vary from 0.5 to 15 K min⁻¹. These rates are similar to the rates used in conductivity measurements (2 K min⁻¹), but different from the rates usually taken by other authors. These rates are imposed by the experiments we used. Behind the window are a diaphragm, a filter, and a cooled photomultiplier (RCA C31034) whose response is nearly constant between 2000 and 9000 Å. The transmission of the filters used are in the blue (3800–4800 Å), green (5000–5600 Å), and red (5800–9000 Å). The sample is excited by uv light (4.88 eV), through the quartz window, or by electrons emitted by field effect, from a needle raised to a voltage of about 10 kV; the intensity of the current (on the order of 1 μA) is adjusted by varying the voltage applied on the needle.

D. Irradiation

Electron irradiations have been performed at 12 K, only in the case of resistivity measurements, with a 3-MeV Van de Graaff. 500 keV was used to create defects and 150 keV to excite the traps while creating a negligible concentration of defects (the threshold energy for atomic displacement corresponds to an energy of about 150 keV.)[5]

III. EXPERIMENTAL RESULTS

A. Thermoluminescence measurements

The glow curves observed in all the samples are qualitatively similar. The difference between curves of different samples comes mostly from the relative heights of the peaks; besides, depending upon the time during which the excitation is applied or depending upon the mode of excitation (uv illumination or field effect) some peaks can appear or be masked by others. Typically, with uv excitation, peaks are present (Fig. 2) around 105 K [(a), weak], 140 K [(b), weak], 210 K (c), and 265 K (d) for a heating rate of 0.15 K sec⁻¹. With field-effect excitation (Fig. 2) new peaks appear at 160 (e) and 320 K (f). The temperatures of the different peaks observed in all the samples are given in Table II. The results obtained with the natural stone are given for comparison; there are two prominent peaks (Fig. 3) around 250 (g) and 265 K (d), and three weak peaks around 105 (a), 320 (f), and 415 K (h), which are the peaks found in the

synthetic stones, with the exception of peak g (probably masked by peak d) and of peak h. The glow curves obtained with spectral filters, for synthetic and natural stones, show that peaks c, d, and e lie in the blue range, the others in the red range (Table II).

We have determined the depth E_T of the traps which give rise to the best defined luminescence peaks. Since the value of E_T depends strongly upon the method of determination used, in order to be able to compare the present results with those previously published by Halperin et al.,[6] we determined E_T using their method, i.e., we calculate

$$E_T = 1.72kT_g^2(1 - 2.58\Delta)/\tau \qquad (3)$$

from the peak temperature T_g, the temperature at half intensity on the low-temperature side of the peak T_1, and from $\tau = T_g - T_1$. The correcting factor Δ is given by $\Delta = 2kT/E_T$. This formula assumes a first-order process with carrier recombination occuring through the conduction or valence band; it therefore applies to the model proposed for the thermoluminescence mechanism (see Sec. IV).

B. Conductivity measurements

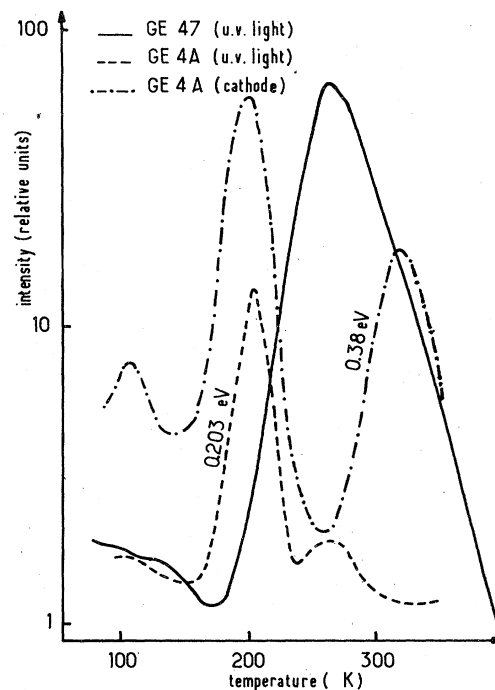Excitation has been performed at 12 K with uv light, 20-keV x-ray, or 150-keV electron irradia-

FIG. 2. Thermoluminescence spectra of samples GE4A and GE47 excited at 77 K by uv light and by field effect.

TABLE II. Temperatures of the peaks, spectral response, and associated activation energies (E_T) (excitation: uv, light; e, field effect).

Temperature (K)	GE4A [a] uv	GE4A [a] e	GE47 [a] uv	GE47 [a] e	B190 [a] uv	B190 [a] e	DB2B [b] uv	DB2B [b] e	Spectral response	E_T (eV)
105 (a)	×	×	×	×			×	×	Red	0.09
140 (b)			×		×				Red	
160 (e)			×		×				Blue	~0.2
210 (c)	×	×	c	c		c			Blue	0.20–0.24 [a]
250 (g)							×	×	Red	
265 (d)	×		c	c	c	c	×	×	Blue	0.37 ± 0.2 [b]
320 (f)	×	×			×			×	Red	0.38
415 (h)							×		Red	~0.8

[a] Synthetic stones.
[b] Natural stone.
[c] The two peaks c and d are mixed up.

tions at 12 K. The measurements are taken 5 min after the excitation has been stopped, a time after which conductivity variations are negligible during the course of the experiment.[3] Figures 4 a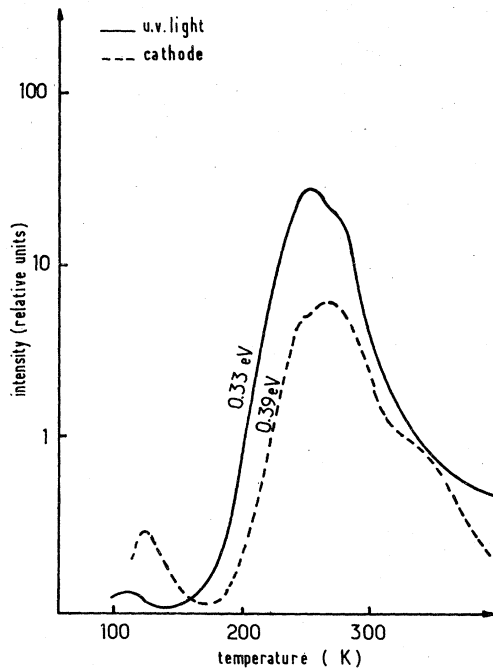nd 5 give the variations of conductivity, measured at 12 K, with the duration of the excitation. The conductivity increases until it saturates, indicating a new equilibrium in the distribution of charged carriers between traps. The variations of conductivity are larger for x rays or electron irradiations than for uv illumination (which does not induce direct band-to-band transitions). In the case of electron ir-

FIG. 3. Thermoluminescence spectra of a natural sample (DB2B) excited at 77 K by uv light and by field effect.
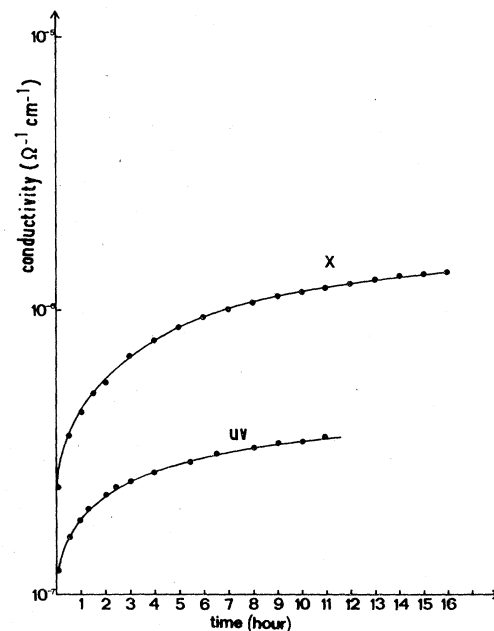

FIG. 4. Conductivity changes due to uv illumination and x-ray irradiation at 12 K (sample GE48).

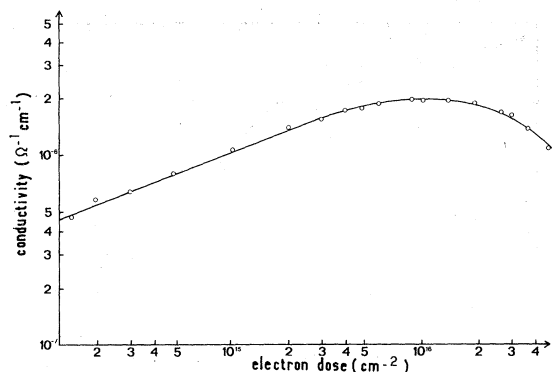FIG. 5. Conductivity changes with the dose of 150-keV electron irradiation at 12 K (sample GE48).

radiation, for doses larger than 10^{16} cm^{-2}, the conductivity decreases; this can be explained in two ways: either the electron irradiation introduced enough defects[5] or (and) the concentration of the compensating centers become lower than 0.5.[7] In sample GE48 (90% compensation) the excitation induces an increase of conductivity (Figs. 4 and 5) and therefore a decrease in the compensation, i.e., a decrease in the concentration of the carriers trapped on the compensating centers.

During isochronal warm-up (conductivity measured at 12 K) we observe the thermal deexcitation of carriers. The conductivity exhibits stages
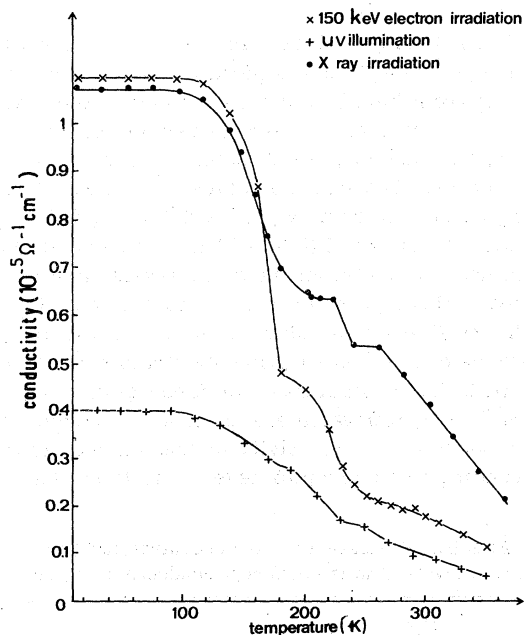
around 160, 230, and 340 K (Fig. 6); the temperatures at which these stages occur are independent of the mode of excitation (Fig. 6). In some stones only the first stage (between 150 and 190 K) is observed (Fig. 7).

After 0.5-MeV electron irradiation at 12 K, sample GE48 exhibits an additional stage at 50 K and a reverse stage around 250 K (Fig. 8). The reverse stage at 250 K cannot be found after warm-up at 300–320 K followed by a new excitation with 150-keV electron irradiation; it therefore must be attributed to the annealing of defects introduced by 0.5-MeV electrons[8] (the increase in conductivity corresponds to a decrease in concentration of the compensating centers). The stage at 50 K is still observed after warm-up at a temperature lower than 250 K followed by a new excitation (Fig. 8); it must therefore be attributed to the thermal release of carriers from a new trap, introduced by the irradiation. This trap is associated with the defects which anneal at 250 K since, after warm-up at 360 K followed by an excitation at 12 K, the 50-K stage is not observed anymore (Fig. 8).

We have attempted to measure the activation energies E_A associated with the thermal release of carriers in the 50- and 230-K stages (in sample GE48). (Due to difficulties of the measurements it has not been possible to determine the activation energies associated with the other stages.) Since $\ln \sigma$ varies linearly with the concentration ΔN_D of

FIG. 6. Isochronal warm-up (20 K×10 min^{-1}) of conductivity at 12 K (sample GE48) after the sample has been excited at 12 K by uv light, x-ray, and 150-keV electron irradiations.
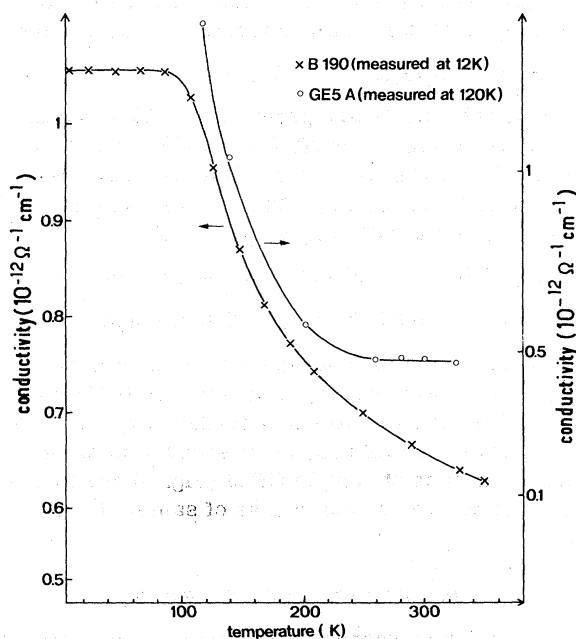

FIG. 7. Isochronal warm-up of conductivity (samples B190 and GE5A) after the samples have been excited at 12 K by 150-keV electron irradiation.
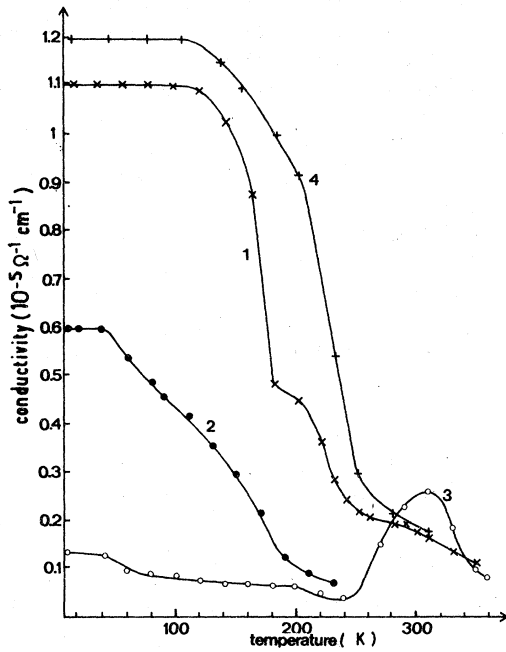
FIG. 8. Isochronal warm-up of conductivity (sample
GE48): (1) after excitation with 150-keV electron irrad-
iation; (2) after 0.5-MeV electron irradiation and heat-
ing up to 230 K; (3) after a new excitation at 12 K with
150-keV electron irradiation and heating up to 360 K; (4)
after a new electron excitation.

FIG. 9. Variation of conductivity during isothermal
runs around 50 and 250 K (sample GE48).

the traps [Eq. (1)] the ratio of the slopes S_1 and S_2
of $\ln(\ln\sigma)$ versus time during isothermal runs at
two slightly different temperatures T_1 and T_2 gives

$$E_A = k\,\ln(S_1/S_2)/(1/T_2 - 1/T_1)\,. \qquad (4)$$

The measurements are performed at 12 K because
at temperatures T_1 and T_2 (around 50 and 230 K)
the conductivities are too small to be measured
with sufficient accuracy. The results, shown in
Fig. 9, give the following values for E_A:

$E_A = 0.0024 \pm 0.0005$ eV for the 50-K stage,

$E_A = 0.16 \pm 0.04$ eV for the 230-K stage.

The concentrations of the traps in the different
stages have been calculated in samples GE48 and
B190, from the variations of conductivity. The re-
sults, given in Table III, correspond to x-ray ex-
citation in case of sample GE48 (Fig. 6) and to 150-
keV electron excitation in case of sample B190
(Fig. 7).

IV. DISCUSSION OF THE RESULTS

Thermoluminescence measurements have already
been performed in natural semi conducting (type-
IIb)[9-18] as well as in types-I and -IIa[11-13] diamonds.
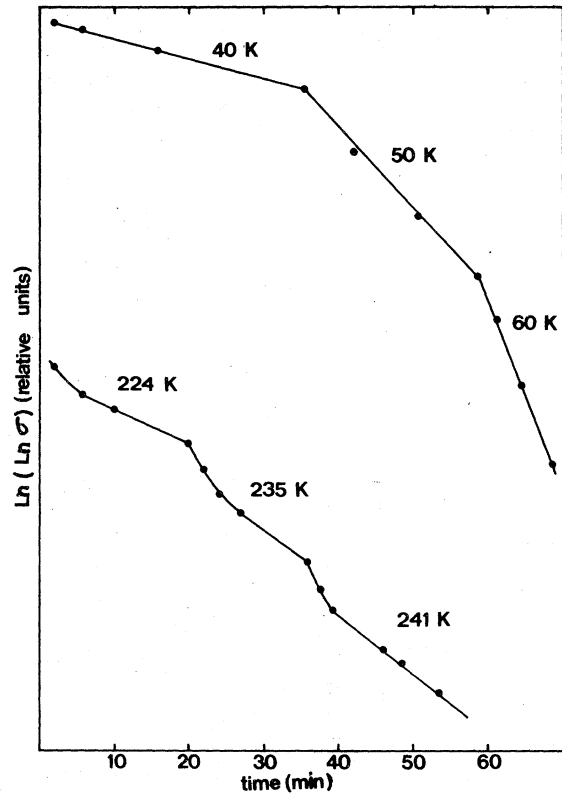In particular two fairly well separated peaks at 150

and 250 K having emission in the blue and red have
been reported,[9,10] the temperatures of the maxima
shifting from blue to red towards higher tempera-
tures. The activation energies associated with
these peaks have been measured; they are given
in Table IV. Because the values of the activation
energies are the same at 150 and 175 K (~0.2 eV)
and at 250 and 285 K (0.37 eV) it is suggested that
carriers, excited from the same levels, are in-
volved in these pairs of peaks. As shown by Hal-
perin and Nahun[12] the blue emission has the ap-
pearance of the A absorption spectrum now identi-
fied with the recombination of donor-acceptor
pairs.[19] The activation energy of 0.37 eV which ap-
pears as well in conductivity measurements as cor-
responding to an acceptor level, was first attribu-

TABLE III. Evaluation of the concentrations (cm^{-3}) of
the traps involved in the different conductivity stages.

Sample	N_D (cm^{-3})	N_A (cm^{-3})	160 K	230 K	340 K
GE48	1.6×10^{18}	1.7×10^{18}	1.1×10^{15}	1×10^{15}	1×10^{15}
B190	1.2×10^{18}	1.5×10^{18}		4.8×10^{15}	

TABLE IV. Thermoluminescence peaks reported in the literature for semiconducting diamond.

T (K)	Spectral response	E_A (eV)	Type of sample	Reference
150	Blue + red	0.17–0.21	IIb	13
		0.2	IIb	10
		0.19 ± 0.05	Synthetic (B doped)	11, 18
175	Red	0.2	IIb	10, 12
		0.3		16
250	Blue + red	0.35 ± 0.02	IIb	11, 18
		0.33 ± 0.02	Synthetic (Al doped)	11, 18
		0.30 ± 0.05	Synthetic (B doped)	11, 18
		0.36–0.39	IIb	13
		0.37	IIb	10, 12
285	Red	0.36–0.41	IIb	10
350		0.52	IIb	12
~420		0.7	IIb	12

ted to a substitutional aluminum center,[20,21] then to a substitutional boron center.[22] The peaks having an activation of 0.37 eV are therefore thought to be due to the thermal release of holes from the boron level.

The model proposed to account for the thermoluminescence peaks observed is due to Halperin and Chen[10] [Fig. 10(a)]. Electrons are raised by the excitation into the conduction band, directly or through the intermediary of traps depending upon the energy of the excitation (larger or smaller than the band gap). These electrons are then trapped on B or R levels and holes on T_1 and T_2 levels (situated at 0.2 and 0.37 eV from the valence band, respectively). When the holes are thermally released from the T_2 (at 150 K) and T_1 (at 250 K) states, they recombine with electrons on B and R states giving rise to blue (~2.8 eV) and red (~1.8 eV) luminescence. We note that the 0.2-eV activation energy is not observed in conductivity; this implies that the T_1 level could rather be at $E_c - 0.2$ eV and correspond to electrons excited in the conduction band which recombine with holes on a deeper level R' [Fig. 10(b)].

The results described here are in agreement with those previously reported. In the natural IIb stone we observed the red and blue emissions (d and f peaks) characterized by an activation energy of ~0.37 eV. However, the blue emission (0.2 eV) at 150–160 K (peak e) is not seen as well as the other peaks previously reported, except for the peak h. But two new peaks at 105 (a) and 320 K (f) are present (the peak f cannot be the peak at 350 K previously reported since it has not the same activation energy, but it could be the peak reported at 285 K). These two new peaks have however been

seen in natural I and IIa diamonds.[13] In synthetic stones the red emission (peak g), probably masked by the large intensity of the blue emission, is not observed; but peaks b and e (150 K) are observed. The other peaks are also present, as well as the new ones (a and f) and blue emission at 210 K. It can therefore be concluded that, with the exception of the traps corresponding to the blue emission at 210 K present only in synthetic stones and to the red emission at 415 K present only in natural stones, the nature of the traps is identical in synthetic boron-doped and natural IIb diamonds.

The activation energies E_T, calculated using formula 3, which implies — as mentioned in Sec. III A — a recombination through the valence or conduction band, are in agreement with values we determined from the slope of $\ln I$ (I: thermoluminescence intensity) vs T

$$E_T = k \frac{\ln(I_2/I_1)}{1/T_1 - 1/T_2} \tag{5}$$

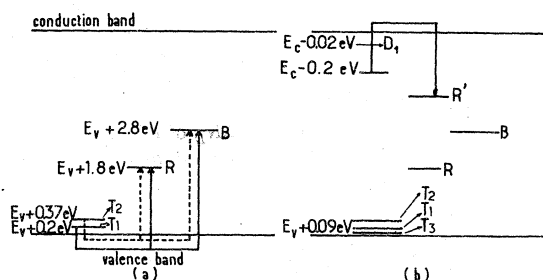(I_1 and I_2 are the intensities at temperatures T_1 and

FIG. 10. Thermoluminescence model of Halperin and Chen (Ref. 10) (a) and modified model (b) taking into account the results obtained.

T_2, respectively). This is a good indication that carriers indeed recombine through one of the bands, i.e., that the model proposed by Halperin and Nahum applies. The results reported here allow us only to add a new level T_3 [Fig. 10(b)] at E_v + 0.09 eV responsible for the red emission at 105 K.

Conductivity measurements provide results which correlate with thermoluminescence results. Since the conductivity at low temperature (12 K) is sensitive to the concentration of holes on the boron level (T_2) and to the concentration of compensating centers (B and R), the stages observed during isochronal warm-up indicate changes in the distribution of the carrier population among the different levels when these are thermally excited. The conductivity stages which occur around 160 and 340 K could correspond to emissions e and f, respectively. The activation energy for the 230-K stage (0.16 ± 0.04 eV) indicates that this stage probably corresponds to the c emission (210 K). It is also possible that, because some of the conductivity stages take place in a large temperature range, they correspond to several emission peaks (for instance the d and g emissions could be mixed with the c emission in the 230-K stage).

The stage at 50 K (associated with an activation energy of 0.02 eV) is, as shown in Sec. IIIb, associated with the defects which anneal around 270 K. It has been proposed that this annealing stage is due to the recombination of vacancy-interstitial pairs through the mobility of interstitials.[3] Since vacancies do not disppear completely after such

annealing, the 50-K stage can only be due to the thermal release of carriers from a level D_1 associated with the interstitial. Interstitials being donors, this level D_1 is therefore at E_c − 0.02 eV [Fig. 10(b)].

V. CONCLUSION

The results obtained with thermoluminescence measurements, in agreement with previously published results, have shown that the nature of the traps is the same in synthetic boron-doped diamonds and type-IIb natural diamonds. Two thermoluminescence peaks (around 105 and 320 K) are reported, which had already been observed only in natural type-I and -IIa diamonds. Thermally stimulated conductivity which exhibits three stages (160, 230, and 340 K) before the introduction of defects by high-energy electron irradiation and one additional stage (50 K) after irradiation correlates with thermoluminescence results. The results are consistent with the model for the thermoluminescence proposed by Halperin and Chen. Conductivity measurements allow us to ascribe the 50-K stage to the defect (the interstitial) which anneals around 270 K and to determine the level associated with this defect (E_c − 0.02 eV).

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