PHYSICAL REVIEW VOLUME 148, NUMBER 2 12 AUGUST 1966

Thermoluminescence of Semiconducting Diamonds*

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(Received 30 March 1966)

The thermoluminescence (TL) of semiconducting diamonds was found to be composed of blue-emitting (at 150 and 260°K) and red-emitting peaks (at 175 and 285°K). The red peaks could be excited by light of wavelengths up to about 650 mμ (1.8 eV), the blue ones by light up to about 420 mμ (3 eV). The intensity of the red peaks and of the 150°K blue peak was found to increase linearly with the dose of excitation. The same was found for the 260°K blue peak on excitation at the absorption edge (225 mμ, 5.5 eV). Excitation of this peak at 260–400 mμ was found to be superlinear; the peak increased under suitable conditions with the third power of the dose of excitation. Other measurements included the thermal activation energies, the optical bleaching of the glow peaks, and the decay of phosphorescence after excitation at 77°K. A tentative model for the energy levels involved in the processes of excitation and emission of the TL is presented to account for the observations. A multiple-stage excitation is proposed to explain the superlinearity.

INTRODUCTION

THERMOLUMINESCENCE in diamond has been reported by several investigators. Chandrasekharan,[1] using visual methods, observed a blue glow at about 540°K. Bull and Garlick[2] recorded the glow curve obtained on heating together a large number of very small diamonds; it had two peaks, one below 400 and the other at 520°K. They also measured the activation energies of both glow peaks. No observation was made of the dependence of the glow on the type of diamond.[3] More recently Halperin and Nahum[4,5] have measured the thermoluminescence of diamonds of various types including the semiconducting (type-II$_b$) variety.[6] The glow curves were found to be specific for the type of diamond. In particular, those obtained for semiconducting diamonds had the following characteristics. On excitation with uv light at 77°K, the glow curves of type-II$_b$ diamonds[4] showed a comparatively weak peak near 150°K and an intense peak near 250°K. The excitation spectrum of the latter glow peak had a maximum near the absorption edge (at about 5.5 eV) with a sharp fall-off toward longer wavelengths. The emission consisted of a broad band with its maximum in the blue. A comparatively weak glow was observed above room temperature.

The present work deals with the thermoluminescence of type-II$_b$ diamonds, and specifically with the glow below room temperature.

A photomulitplier with high sensitivity in the red revealed red-emitting glow peaks in addition to the blue ones observed previously. These red peaks could be excited by wavelengths of up to 650 mμ. In addition, it has now been found that the blue-emitting glow could be excited by wavelengths of up to 400 mμ. While the intensity of the 250°K peak was increasing strictly linearly with the dose of previous irradiation when excited with light near the edge, it showed a strongly superlinear dependence on dose when longer wavelengths were used. This unusual superlinearity seems to bear interesting information concerning the defect levels within the forbidden gap of semiconducting diamonds. It will be described and discussed below.

EXPERIMENTAL

The experimental set-up was in general similar to that described in previous work.[4] The crystal was mounted in a metal vacuum cryostat, and was usually excited at liquid-nitrogen temperature. Monochromatic light for excitation was obtained from a Beckman DU monochromator using a Hanovia type 507C, 800W xenon compact arc lamp as light source. Irradiation doses were changed by varying either the irradiation time or the light intensity, the latter generally being achieved by introducing neutral density screens in the light path. Occasionally, light intensities were changed by varying the monochromator slit widths; however, in most of the experiments, slits were kept constant in order to avoid abrupt changes in the spectral widths of the exciting beam.

A photomultiplier with a tri-alkali photocathode (E.M.I. 9558 QB) sensitive up to about 9000 Å was used in most of the measurements. In the others, an E.M.I. 6256 B photomultiplier was used. The output of the photomultiplier was fed through a Keithley 410 micromicroammeter into a Leeds and Northrup Type G recorder.

Crude measurements of the emission spectrum, and especially separation of the blue emission from the red, were made by inserting suitable filters in front of the

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* The research reported in this document has been sponsored by the U. S. Air Force Cambridge Research Laboratories under contract AF61(052)-759 through the European Office of Aerospace Research (OAR), U. S. Air Force.

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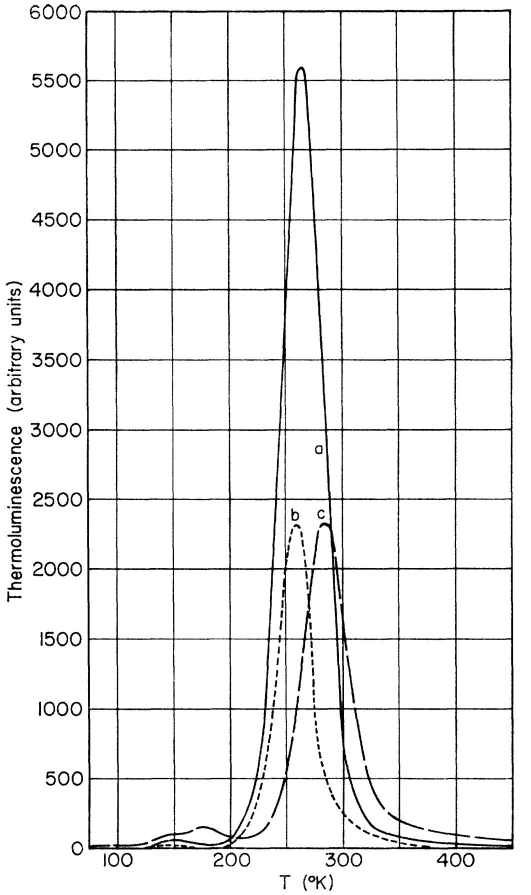

FIG. 1. Thermoluminescence of a semiconducting diamond: (a) blue-emitting glow peaks, excited with 225-mμ light, (b) blue peaks excited with 375 mμ, (c) red peaks excited with 475 mμ. Curve *c* was drawn with an extended (×20) ordinate.

photomultiplier. When the glow intensity was high, the spectrum was measured with a spectrophotometer.

A heating rate of about 35° per minute was used for most of the glow curves. This caused a shift of the peak temperatures toward higher temperatures than those obtained previously[4] when a lower heating rate was used.

The heating rate was kept linear by properly adjusting the heating current during the warm-up. This heating program was kept constant in all the measurements. In each measurement the crystal was heated up to about 525°K, which was found to bleach almost completely the effects of previous irradiation, at least as far as it affected the glow peaks appearing below room temperature.

In some experiments the photocurrent through the crystal was measured, using silver painted electrodes with dc voltage from a stabilized power supply applied across the crystal. Currents were measured with a Keithley 410 micromicroammeter, and the monochromatic light was supplied by the combination of the Beckman DU monochromator and the xenon arc lamp used for the excitation of the thermoluminescence.

RESULTS

A. The Glow Curves in General

Results were practically the same for the 5 specimens examined. Figure 1 shows representative glow curves obtained with one of the specimens (C4) after excitation at 77°K with different wavelengths. Excitation with light near the absorption edge (225 mμ, 5.5 eV) resulted in the glow shown in curve *a*. A very weak peak appears near 150°K and a strong one at 260°K. Although no filter was used in this case, the glow curve represents the blue emission which was dominant under the conditions of the excitation. Curve *b* (Fig. 1) was obtained after excitation with 375 mμ (3.3 eV). This time a blue transmitting filter (Wratten 47) was inserted in front of the photomultiplier in order to cut off the red emission. The glow has the same peaks as curve *a*. Curve *c* represents the red-emitting glow, as obtained after irradiation with 475-mμ light, with a Wratten 29 filter used for cutting off wavelengths below 610 mμ. In this case, the peaks are at about 175 and 285°K. An extended (×20) ordinate was used for the comparatively weak glow in curve *c*.

B. Excitation of the Glow Peaks

The superlinear excitation of the blue glow peaks is demonstrated in Fig. 2. All the curves were obtained by excitation at 77°K using the same wavelength (375 mμ) and the same intensity. Again a Wratten 47 filter was used to isolate the blue emission.

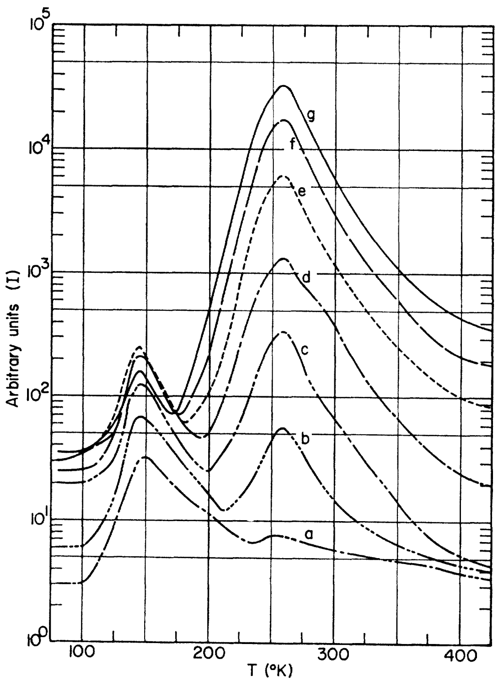

FIG. 2. Dependence of the blue thermoluminescence of a semiconducting diamond (specimen C3) excited with 375 mμ on time of excitation: *a*: 10, *b*: 20, *c*: 40, *d*: 80, *e*: 160, *f*: 320, *g*: 640 sec.

Doses were changed by doubling the irradiation time for each subsequent curve, starting with 10 sec in curve *a* and reaching 640 sec in curve *g*. A logarithmic intensity scale is used in the ordinate of Fig. 2 in order to accommodate all the curves which range in intensities over four orders of magnitude. At low doses (curve *a*) the 150°K peak is much stronger than the 260°K one. The low-temperature peak grows at first nearly linearly with the dose. After reaching a maximum (curve *e*), its intensity decreases with further increase in dose (curve *f*, *g*), The growth of the 260°K peak, however, is completely different. It rises superlinearly with the dose, overtaking the low-temperature peak very fast so that in curve *g* its intensity is already 200 times that of the 150°K peak.

The dependence of the intensity of the glow peaks on the dose is clearer in Figs. 3 and 4, giving plots of log intensity versus log dose. Curves *a*, *b*, and *c* of Fig. 3 depict the behavior of the 150°K peak on excitation with 225, 300, and 375 mμ, respectively. The curves were adjusted to the same dose scale, taking into account the spectral distribution of intensities in the light source and the change with wavelength of the dispersion of the monochromator. All the curves in Fig. 3 start to rise linearly with the dose (the initial part shows a slope of 1) and all reach their maximum value at about the same dose.

It should be noted that because of the comparatively low intensity of the light source at 225 mμ, the irradiation times used to excite the glow with this wavelength (curve *a*) were much longer than those used with the longer wavelengths (curves *b* and *c*).

It is interesting that the glow-peak intensities at the maxima of the curves in Fig. 3 are not the same. Thus, excitation near the absorption edge [Fig. 3(a)] produced the 150°K peak with an intensity higher by about an order of magnitude than that obtained with 300- or 375-mμ light. This seems to indicate that the maximum intensity results from an equilibrium between the excitation and bleaching processes which take place during irradiation [see also subsection (C) below].

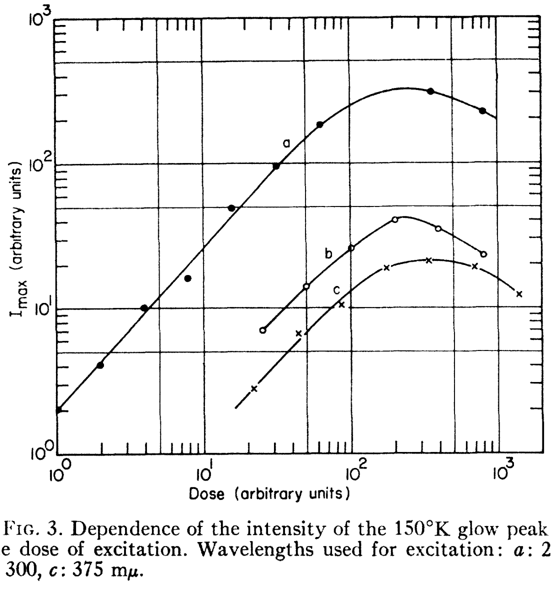

FIG. 3. Dependence of the intensity of the 150°K glow peak on the dose of excitation. Wavelengths used for excitation: *a*: 225, *b*: 300, *c*: 375 mμ.

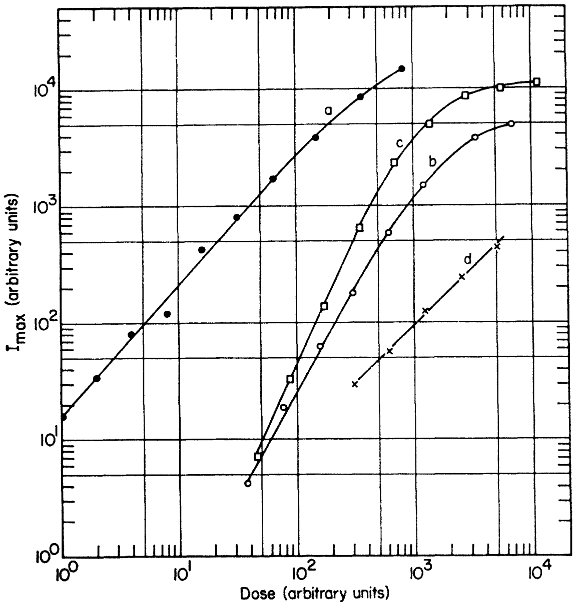

FIG. 4. Same as Fig. 3, but for the 260°K (curves *a*, *b*, *c*) and 285°K peaks (curve *d*). Excitation: *a*: 225, *b*: 300, *c*: 375 and *d*: 425 mμ.

Figure 4 shows the dependence of the intensity on dose for the 260°K glow peak (curves *a–c*) and for the 285°K peak (curve *d*). On excitation with 225 mμ (curve *a*), the 260°K peak rises linearly with the dose over a wide range of doses; only with the highest dose used (irradiation time of 135 min) does the curve show a tendency toward saturation.

The superlinear behavior is shown in curves *b* and *c* (Fig. 4) where wavelengths of 300 and 375 mμ, respectively, were used for excitation. The slopes in the low-dose portions of the curves, before saturation effects start, are about 2 for curve *b* and 3 for curve *c*. Both curves *b* and *c* were obtained with a blue (W47) filter, and represent the blue-emitting 260°K glow peak.

Curve *d* illustrates the behavior of the red-emitting 285°K glow peak. 425-mμ light served for excitation and a Wratten 70 filter was used to cut off the blue emission. In contrast with the superlinear behavior of the 260°K peak, the 285°K peak is seen to rise linearly with the dose. This linearity was observed on excitation with other wavelengths ranging from 225 to 650 mμ.

Figure 5 shows, again for the 260° K peak, the dependence of the initial slopes on the wavelength of the exciting light. Near the absorption edge (up to about 275 mμ), the slope remains nearly one. At 275 mμ there is an abrupt rise in the slope. The behavior on excitation with wavelengths of 280–400 mμ depended to some extent on the conditions of excitation. Each point in curve

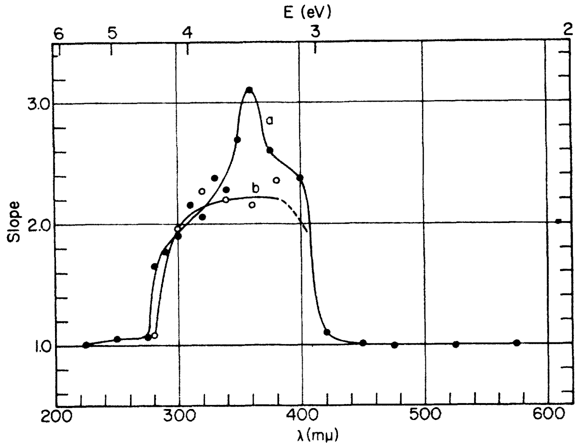

FIG. 5. Dependence of the power factor p (the slope in Fig. 4) on the wavelength of the exciting light. Curve b was obtained by reducing the intensities of the exciting light by a factor of 10.

a (Fig. 5) gives the slope obtained from a set of measurements in which the intensity of the exciting light was kept constant and excitation times were changed. The maximum value of about 3 was reached with wavelengths near 360 mμ. Similar results were obtained by keeping the time constant and varying the intensities by using neutral density screens. The results, however, differed when considerably lower intensities and longer excitations were used. This is shown in curve b of Fig. 5 which was obtained in the same way as curve a but with intensities nearly 10 times lower. This curve reaches only slightly above 2, a value which remains nearly constant between 300 and 400 mμ.

Beyond 400 mμ the 260°K peak decreases very rapidly and measurements at these wavelengths were taken on the red 285°K peak, which accounts for the drop to the value of 1 in the curves of Fig. 5.

C. Optical Bleaching of the Glow Peaks

The dependence of the maximum of the 150°K glow peak on the exciting wavelength (see Fig. 3) was interpreted above as being due to an equilibrium between the excitation and bleaching effects. To check this, the crystal was irradiated by 225-mμ light with a dose which would produce nearly the maximum intensity of the 150°K peak obtainable with this wavelength. Then, before warming up, it was illuminated with 375-mμ light. The result was a decrease in the intensity of the 150°K peak which, with sufficient illumination with 375-mμ light, came down to the equilibrium intensity reached after irradiation with the 375-mμ light alone. No effect of bleaching of the 260°K peak was observed under these conditions.

Similar bleaching of the 150°K peak could also be obtained using wavelengths other than 375 mμ. This is shown in Fig. 6 for wavelengths up to 3.4 μ (0.36 eV), the upper limit being set by the monochromator used. All the points on the curves in Fig. 6 were obtained by using a fixed excitation with 225-mμ light followed by irradiation with monochromatic light of longer wavelengths, after which the glow curve was recorded. The light sum of the latter irradiation was kept constant for each curve in Fig. 6; it was varied, however, from curve to curve. Thus, the light sum used in curve b was four times that of curve a, and that used in curve c was greater by about an order of magnitude than that of curve b.

A Beckman DU monochromator was used for curves a and b, but for curve c it was replaced by a Hilger quartz monochromator (D 246) to enable extension of the measurements up to 3.4 μ. It is obvious from the curves in Fig. 6 that

(1) Wavelengths of 300 to 400 mμ, which were previously shown to excite the 150°K peak (see Fig. 3), also bleach the same peak.

(2) This peak is bleached by still longer wavelengths up to at least 3.4 μ.

D. Activation Energies

The method of initial rise[7] was used for the determination of the thermal activation energies. Values obtained in the present work for the blue-emitting peaks fitted those reported previously,[4] namely 0.20 and 0.37 eV for the 150 and 260°K peaks, respectively. The values were independent of the wavelength used to excite the glow peaks (225-400 mμ in the present work).

Measurements on the red-emitting peaks were somewhat more difficult because of their comparatively low intensities. For the 285°K peak we obtained a value of 0.38 eV (measured values varied between 0.36 and 0.41 eV). The good agreement with the value of 0.37 eV obtained for the 260°K peak, indicates that carriers (positive holes) excited from the same level are involved in both peaks. The difference in the peak temperatures (285°K for the red peak versus 260°K for the blue) should then be attributed to differences in

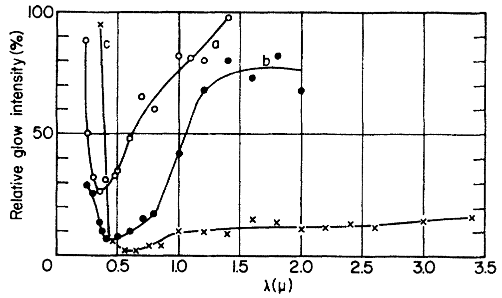

FIG. 6. Optical bleaching with various wavelengths of the 150°K glow peak after excitation with 225 mμ. The ratio of the doses of the bleaching light was approximately 1:4:40 in curves a, b, and c, respectively.

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the transition probabilities of the recombination centers involved.[8]

More difficult was the case of the very weak 175°K peak. The measured value in this case was about 0.20 eV which fits the activation energy obtained for the 150°K peak. The uncertainty in the measurement, however, does not permit any definite conclusions as to the origin of the carriers involved in the formation of the 175°K peak.

E. Phosphorescence at 77°K

The crystals usually phosphoresced when kept at 77°K after excitation. The emission was in both the blue and the red regions.

In a set of experiments, the self-decay of this phosphorescence was measured after excitation with various wavelengths. Attempts fo fit the results into simple combinations of exponential decay curves were unsuccessful, which indicates that the process is not of first order. The Becquerel-type formula[9]: $I=\text{const}/(t+t_0)^p$ proved more useful. In this formula, I is the phosphorescence intensity, t is the decay time, t_0 and p are constants. The power constant p should depend, according to Adirowitch,[10] on the ratio of the probability for retrapping to that for recombination.

Plots on a log-log scale with $t+t_0$ in the abscissa and I in the ordinate should give, if the Bacquerel formula is obeyed, striaght lines with a slope p. Figure 7 shows a few such curves obtained for the blue phosphorescence. Curves a, b, and c were obtained after excitation with 375, 300, and 225 mμ, respectively. The value of t_0 was only 3 sec in curves a and b, but was as great as 20 sec for curve c. This seems to have originated from the low intensity of the light source at 225 mμ, which seems also to be the cause of the low slope ($p=0.96$) in curve c as compared with slopes of 1.4 and 1.35 in curves a and b, respectively. More detailed experiments showed that the measured slopes were indeed reduced on lowering the intensities of the exciting light.

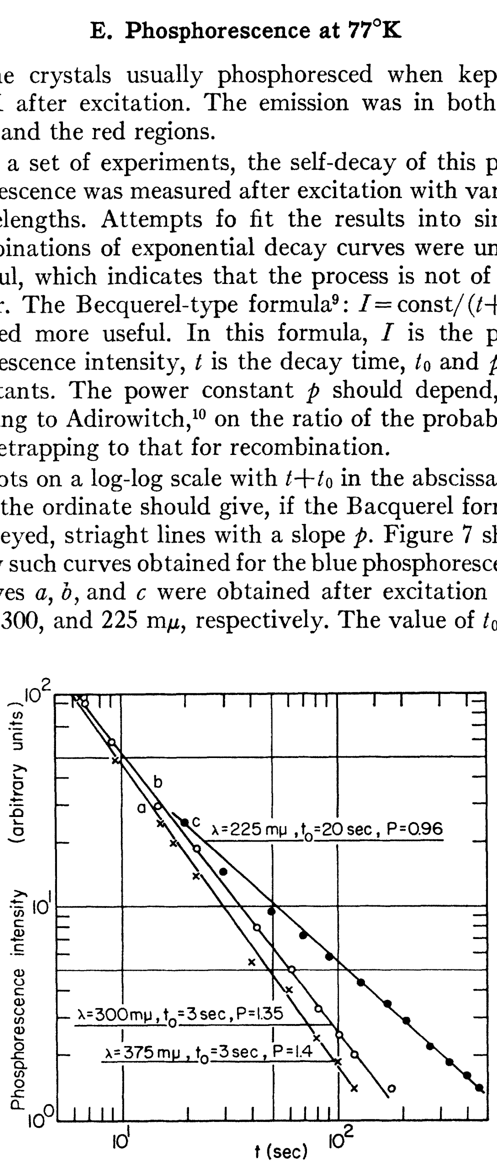

FIG. 7. Decay curves for the blue phosphorescence at 80°K. Wavelengths used for excitation and parameters of the Becquerel formula are indicated in the figure.

Similar measurements were made on the red phosphorescence. Again striaght lines were obtained, this time the slopes being of 1 or less. The importance of this difference is not clear, however, because of the dependence on intensity of the measured slopes, as mentioned above.

DISCUSSION

The new observations reported in the present work seem to give a better insight into the processes involved in excitation and emission of thermoluminescence in semiconducting diamonds.

Red emission from semiconducting diamonds has been observed in photoluminescence[11–13] and recently also in electroluminescence.[14] In thermoluminescence, it was not observed before. The blue-glow peaks were reported previously[4] to be excitable with light near the absorption edge (225 mμ) only. They have now been obtained by excitation with much longer wavelengths (up to 400 mμ or about 3 eV). This fact in itself is not surprising. In insulating diamonds, for example, it was also possible to excite some glow peaks by energies of 3 eV or even less.[5] The situation in the present work, however, seems to be different. While the intensity of thermoluminescence was linear with the dose of exciting light, on excitation at the edge, it became superlinear when longer wavelengths were used, which seems to indicate a compound transition. Excitation by multiple-photon absorption[15–17] would, of course, show a superlinear dependence on the light intensity with a power factor equal to the number of photons involved in each transition. However, with the comparatively low light intensiteis used in the present work (10^{10}–10^{13} photons/cm^2 sec), multiple-photon transitions should be very improbable. Besides, this would not explain the superlinear dependence on the dose when the intensity is kept constant and only the time is varied (see Fig. 2). This behavior can be accounted for, assuming a multiple-stage transition, when the dependence on the third power of the dose would indicate that the excitation involves three stages.

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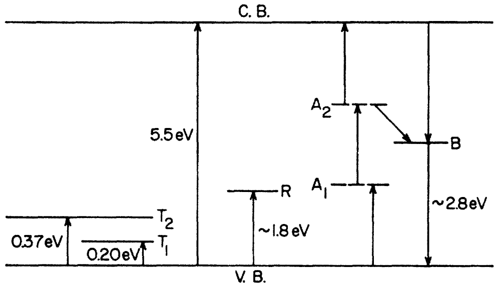

FIG. 8. Schematic model for the transitions involved in the excitation of the blue and red thermoluminescence of semiconducting diamonds. Arrows indicate electron transitions.

A schematic model is presented in Fig. 8. The mechanism of the excitation of the blue-glow peaks by light at the absorption edge (225 mμ) has already been described.[4] Referring to our model (Fig. 8), the 225-mμ light raises valence-band electrons to the conduction band. The electrons fall into the centers B, while the holes left at the valence band become trapped at T_1 and T_2. When the crystal is warmed, the blue-glow peaks at 150 and 260°K appear on recombination at B of the positive holes released from T_1 and T_2, respectively. Longer wavelengths (280–420 mμ) would not produce the interband transition, and intermediate stages seem necessary. To get a third power dependence on the dose, the exciting light is assumed to raise the electrons to the level A_1 where they accumulate at a concentration proportional to the dose (d). In the second stage, electrons at A_1 are excited to A_2, with a concentration proportional to d^2, and in the third, the electrons are excited to the conduction band whence they get trapped at B with a concentration proportional to d^3.

To account for the reduction from the third to the second power of the dose on long excitations with low intensities, as mentioned above, we assume the electrons at A_2 to leak directly, by tunnelling, into B. The rest of the process will be the same as on excitation at the edge, which explains the appearance of exactly the same glow peaks.

The red-glow peak at 285°K was found to have the same thermal activation energy as that of the blue 260°K peak. We assume therefore, that it arises from holes released from T_2. Recombination occurs in this case with electrons at R. This level is located about 1.8 eV above the valence band, and light of wavelengths up to 650 mμ produces direct excitation of electrons from the valence band to R, thus exciting the 285°K glow peak.

The assumption that both the blue peak at 260°K and the red one at 285°K arise from T_2 implies second-order kinetics of the process.[8] This in fact was concluded previously[4] and is to some extent supported by the second-order character of the decay of the phosphorescence at liquid-nitrogen temperature which was observed in the present work. The delay in the appearance of the red peak, as compared with that of the blue, indicates that the cross section for recombination at R is small compared with that at B.

According to Adirowitch's theory,[10] the slope in the phosphorescence decay curves (Fig. 7) should depend on the ratio of the probability for retrapping to that for recombination. Assuming the former to be equal for both the red and blue phosphorescence, a higher value of the slope in the decay curves should correspond to a higher recombination probability. Although the results of the measurements of the slopes were not decisive, as noted above, they seem to fit well into the general picture.

The energy levels involved in the emission of the red peak at 175°K are more difficult to locate. The very low intensity of this peak did not enable an exact measurement of its activation energy. Neither was it possible to measure the emission spectrum, and only by using filters was it possible to classify it as a "red" peak. It is therefore preferable not to propose any model for this glow peak until more experimental evidence is available.

The experiments on the optical bleaching of the 150°K peak can be explained as follows. In the excited crystal there is a certain concentration of trapped holes at T_1. Further irradiation may produce more positive holes in the valence band by exciting electrons to one or another of the centers. Some of these holes may get trapped in T_1 and eventually increase the 150°K peak. On the other hand, the irradiation may also raise electrons into T_1 which would annihilate the holes and cause a reduction in the glow peak. Bleaching occurs when the latter effect is dominant. This is especially true with long wavelengths when excitation of valence-band electrons up to luminescence centers is negligibly small or even impossible. The result should then be pure bleaching, as was actually observed with wavelengths exceeding 420 mμ. By this model, bleaching of the 150°K peak should occur with wavelengths up to about 6 μ (0.20 eV). Unfortunately, our experimental set-up was limited to 3.5 μ.

Using a combination of two (or even three) different wavelengths for the excitation of the 260°K glow peak, should yield interesting information of the individual stages of the multi-stage transition. In preliminary experiments we have excited the crystal with long wavelengths (500–1000 mμ) followed by 360-mμ light. The 260°K peak was enhanced compared to excitation with 360 mμ only, and the power factor of the dependence of its intensity on the dose was reduced (by roughly 1). This supports strongly our model. A detailed investigation along these lines is now underway and its results will be published elsewhere.

The high efficiency of the multiple-stage excitation is surprising. A rough calculation showed that 10^{16} photons of 360-mμ light which reached the crystal (during a 640-sec irradiation period) produced the 260°K glow with an integrated emission of 10^{10} photons. The absorption of the crystal at 360 mμ seems to be less than 1%. Assuming that each of the electrons at B will emit a photon during the glow, one gets about 10^{-4} as a lower limit for the efficiency of the excitation. Practically, absorption in the transition from A_1 to A_2 or from A_2 to the conduction band (see Fig. 8) might be much less than 1% and the actual efficiency is probably not far from 1, which is quite surprising for such an unusual process.

ACKNOWLEDGMENTS

We wish to thank Dr. J. F. H. Custers and Dr. H. B. Dyer of the Diamond Research Laboratory, Johannesburg, who provided the semiconducting diamonds used in this work. Thanks are also due to M. Sinuany for making some of the measurements.

PHYSICAL REVIEW VOLUME 148, NUMBER 2 12 AUGUST 1966

Anharmonic Decay of Optical Phonons*

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(Received 28 March 1966)

An expression is derived from perturbation theory for the lifetime of an optical phonon decaying into two acoustical phonons, and its temperature dependence. The strength of the interaction is expressed in terms of the Grüneisen constant and the effect of a strain, equivalent to the instantaneous strain of an optical mode, on the frequency spectrum of a linear chain with alternating force constants. This interaction depends on the ratio of the acoustical and optical mode frequencies at the zone boundary. Fitting the theory to silicon, the optical mode at $\mathbf{k}=0$ has a calculated half-width at 300°K of about 1.2% of its frequency. This result is compared with experimental data.

I. INTRODUCTION

BECAUSE of the anharmonicity of the lattice forces, an optical mode can interchange energy with other lattice modes, and in this way maintain a thermal equilibrium energy content. In this respect, an optical mode behaves similarly to an acoustical mode. The rate at which an acoustic mode approaches equilibrium can be related to the relaxation time which enters the expressions for the thermal conductivity; optical modes, however, do not contribute substantially to thermal conduction. The relaxation time of optical modes does, however, determine such properties as the linewidth in infrared absorption measurements, in Raman scattering, and in inelastic neutron scattering experiments, and theoretical estimates of this lifetime are therefore of interest.

The principal anharmonic interaction is due to the cubic anharmonicities, resulting in the splitting of an optical phonon into two acoustic phonons of opposite momentum. This process will be estimated here from second-order perturbation theory. This method has been used extensively in thermal conductivity problems,[1] and has also been applied to the problem of the lifetime of a local mode.[2] The latter problem has many similarities to that of the optical mode: in one case, the local mode phonon splits into two acoustic phonons; in the other, the optical phonon splits into two acoustic phonons. The main difference is that in the case of the optical phonon one must consider momentum conservation, and in the case of the local mode the interaction is localized and there is no momentum conservation.

From physical intuition one would be led to believe that the lifetime of an optical phonon should be comparable to that of a local mode phonon of the same frequency, since the strain field of a local mode, in a small region about a defect, is similar in character to that of an optical mode. This expectation will indeed be verified. Nevertheless, we shall see that there is an important difference in the theory of these two cases—the method used in the local mode calculation cannot be simply taken over for the optical mode. It is therefore of some interest to describe the calculation for the lifetime of an optical mode.

A calculation of the lifetime of optical phonons has been reported by Cowley.[3] His calculation is based on the same principles as the present one, but differs in the method of estimating the interaction strength, and in that he sums over all interactions numerically by means of a computer. In principle his method is thus capable of greater precision than the present one, but the present calculation can be followed step by step, and has the advantage of greater physical insight and didactic value. It seems difficult to compare the

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* Supported in part by the U. S. Air Force Office of Scientific Research under Contract No. AF 49(638)-1589.

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