PHYSICAL REVIEW B VOLUME 11, NUMBER 6 15 MARCH 1975

Point defects in hexagonal boron nitride. I. EPR, thermoluminescence, and thermally-stimulated-current measurements

A. Katzir and J. T. Suss
Department of Solid State Physics, Soreq Nuclear Research Center, Yavne, Israel

A. Zunger
Department of Theoretical Physics, Soreq Nuclear Research Center, Yavne, Israel and Department of Chemistry, Tel-Aviv University, Ramat Aviv, Israel

A. Halperin
The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

(Received 4 April 1974)

When hexagonal boron nitride is exposed to ionizing radiation two types of paramagnetic centers appear: three-boron centers and one-boron centers. Results of electron paramagnetic resonance, thermoluminescence, and thermally-stimulated-current measurements associated with these centers are described, and a model is proposed to explain these results. The model is consistent with views of others investigators on the role of carbon impurities in hexagonal boron nitride, and with the hypothesis that the three-boron centers are *F* centers. The three-boron centers and one-boron centers were found to introduce trapping levels at 1.0 and 0.7 eV, respectively, below the conduction band. It is suggested that carbon impurities produce luminescence centers, with an energy level at about 4.1 eV below the conduction band. Ionizing radiation frees electrons from these levels into the conduction band. Some of the electrons may then be trapped either in three-boron centers or in one-boron centers. Some may fall back to the centers, thus emitting blue photoluminescence. The unpaired trapped electrons give rise to the EPR signals. When the samples are heated, the electrons escape from the traps (first from the one-boron centers and then from three-boron centers and give rise to the glow curves and at the same time also cause a decrease in the EPR signal. This model was supported by quantum-mechanical defect-model calculations, given in part II of this study (following paper).

INTRODUCTION

Boron nitride (BN) is one of the most interesting solids among the III-V compounds, both from theoretical and practical points of view. A BN molecule is isoelectronic with a pair of carbon atoms and there is a great similarity between boron nitride and carbon solids. Like carbon, BN appears in two allotropic forms: (a) Hexagonal boron nitride, which resembles graphite in softness, in crystallographic layer structure, and in many other physical properties.[1,2] (b) Cubic boron nitride, which resembles diamond in hardness, in crystallographic structure, and in other physical properties.[2]

Two types of paramagnetic centers were identified and studied by Geist and by Romelt[3-5] in hexagonal boron nitride. In one type an unpaired electron was shown to interact with a single ^{11}B nucleus, giving rise to a four-line electron-paramagnetic (EPR) spectrum. These centers are referred to as the one-boron centers. The other type was shown to be due to an unpaired electron interacting with three equivalent ^{11}B nuclei, giving rise to a ten-line EPR spectrum, and these centers are referred to as the three-boron centers.

Boron consists of two isotopes, ^{11}B and ^{10}B, with natural abundance of 81.17% and 18.83%, respectively. These isotopes have different nuclear spins and magnetic moments. Romelt based his identification of the centers upon experiments with boron nitride samples enriched with ^{10}B. The EPR studies presented in this work deal only with phenomena related to ^{11}B.

Romelt found that both the one-boron and the three-boron centers could be produced by ionizing radiation. Khusidman *et al.*[6-8] suggested that the three-boron centers, were actually *F* centers. Their hypothesis was based on simplified π-electron quantum chemical calculations which suggested that a nitrogen atom carries a negative charge in the hexagonal structure. Electrons can therefore be trapped in nitrogen vacancies—thus forming *F* centers. Krasnoperov *et al.*[9] have also studied the production of the three-boron centers, and found two types: (a) centers which appeared in hexagonal boron nitride powder which had been heated to 1700 °C, cooled rapidly to room temperature, and then exposed to ionizing radiation. Under these conditions the powder assumed a light yellow color. Both the EPR signals associated with the three-boron centers and the yellow color disappeared on heating the powder to temperatures in the range (800–1000)°C. (b) Centers which appeared in hexagonal boron nitride powder heated to temperatures above 2000 °C. These did not disappear upon further heating.

Moore and Singer[10] confirmed the existence of the two types of three-boron centers, and proved that carbon impurities were necessary for the production of the centers. They also found a direct relation between the concentration of the three-boron centers and the strength of the yellow color. These workers also observed that both the g factor and the hyperfine splitting of the ten-line spectrum were anisotropic, and suggested that the unpaired electron had a π character.

Moore and Singer assumed the thermal production of the three-boron centers to be due to diffusion of carbon into hexagonal boron nitride at 2000 °C, in a manner similar to the additive coloration in alkali halides.[11] The formation of the three-boron centers by ionizing radiation was explained as due to displacement of a nitrogen ion from its place, and its stabilization by a nearby carbon atom.

Tiede and Tomaschek[12] observed a blue photoluminescence (PL) emission upon uv excitation and they were first to note the significant role of carbon impurities. Larach and Shrader[13] studied the photoluminescence of hexagonal boron nitride powder in more detail. They found a broad emission with structure throughout the range 3000–5000 Å. The excitation spectrum showed a structure at shorter wavelengths. From the temperature quenching of the photoluminescence at high temperature these authors obtained an activation energy of 1.1 eV. Bose and Henisch[14] examined the photoluminescence of carborundum "grade HP" (hot-pressed) powder, and obtained results similar to those mentioned above.

The electroluminescence of hexagonal boron nitride was found[13] to show the same structure as the photoluminescence. Dzhuzeev[15] showed that the electroluminescence was emitted only by hexagonal boron nitride samples which were preheated to high temperatures (most likely in the presence of carbon).

The thermoluminescence of hexagonal boron nitride was studied by Krasnoperov *et al.*[9] They found the thermoluminescence in samples prepared at temperatures below 1100 °C to be much weaker than in those prepared above 1600 °C. Two peaks were observed in the uv-excited high-temperature treated samples, near 100 °C and near 400 °C. The thermoluminescence peaks were found to increase tremendously in samples intentionally doped with carbon. The enhancement was more pronounced in the 400 °C peak. This latter peak was found to emit at 4000 Å independent of the carbon doping. Hexagonal boron nitride powder exposed to γ rays was found to give a weak thermoluminescence at (250–400)°C. Bose and Henisch[14] found only a weak thermoluminescence at 450 °C in grade HP powder.

Most of the earlier investigators studied either the EPR or the luminescence phenomena. In the present work we have combined EPR, photoluminescence and thermoluminescence techniques, and suggested a phenomenological model, which enabled us to explain most of our results and many results of other investigators. A far better understanding of the properties of defects in boron nitride has been gained by quantum mechanical calculations, which are given in Paper II of our study of point defects in boron nitride.[16] The results of these calculations are in agreement with the experimental results.

EXPERIMENTAL METHODS

A. Samples

Three types of polycrystalline material were investigated in the present work: hot-pressed boron nitride (HPBN), pyrolytic boron nitride (PBN) and compression-annealed pyrolytic boron nitride (CAPBN). "Grade HP" hot-pressed powder rods were purchased from the Carborundum Co., and are claimed to contain (1.5–2)% oxygen, 1.5% calcium, 0.2% chlorine, less than 0.1% B_2O_3, and less than 0.05% carbon.[17] "Boralloy" PBN plates, containing less than 10-ppm metallic impurities, were purchased from the Union Carbide Co.[18] CAPBN plates were prepared by Moore and Singer.[19]

All three types of boron nitride investigated consisted of small crystallites which were partially ordered with respect to a preferential axis. X-ray studies showed that in CAPBN the order of preferential orientation was so high that in some respects it resembled a single crystal.[19] The crystallite platelets were ordered with their crystallographic c axis parallel to the preferential axis, and the boron nitride layers perpendicular to it. PBN is much more ordered than hot-pressed boron nitride.[20]

B. EPR measurements

EPR measurements were carried out on a Varian type EC-365 X-band spectrometer. Most measurements were taken at room temperature, but some were at lower temperatures, down to 77 °K. In the later cases we used a Varian type E-257 variable temperature accessory.

Thin boron nitride plates were prepared from larger pieces of boron nitride in such a way that their larger surfaces were perpendicular to the c axis. A special holder enabled us to vary the angle θ between the c axis of the sample and the direction of the external magnetic field H_{dc}.

C. Glow curve and luminescence measurements

Glow curve and luminescence measurements

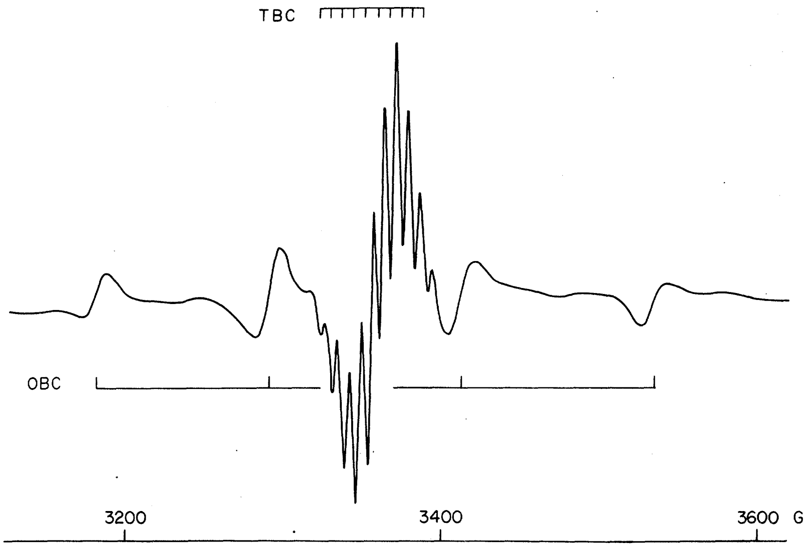

FIG. 1. EPR spectrum of γ-irradiated hot-pressed boron nitride. Positions of the one-boron-centers (OBC) and three-boron-centers (TBC) lines are indicated.

were carried out in a specially designed optical cryostat, similar to that described by other investigators,[21] with a controller[22] which regulated the temperature of the cold finger. With this setup we were able to perform measurements at any temperature in the range (77–800)°K, or to raise the temperature linearly at rates in the range (3–50)°K/min.

Simultaneous measurements of thermoluminescence and thermally stimulated current (TSC) were carried out in a setup described earlier.[23] Two aluminum electrodes were evaporated onto the upper surface of the sample. The sample was mounted on the cold finger of the cryostat, cooled to 77 °K, and excited through suitable windows either by uv or x rays. The temperature was then raised linearly (usually at a rate of 20 °K/min) and the thermoluminescence emitted by the sample in the area between the electrodes was detected by a cooled 9558 QB EMI photomultiplier. For the thermally stimulated current measurements we connected one of the electrodes to a dc power supply, and the other electrode to a type 401 Cary vibrating reed electrometer.

X-rays for excitation were supplied from a tube with a copper target operated at 40 kV and 20 mA. uv light was supplied by a stabilized xenon arc lamp.[24]

Using the same experimental setup, we also carried out photoluminescence and phosphorescence measurements at various temperatures.

EXPERIMENTAL RESULTS

A. EPR measurements

Large ten-line and four-line signals (due to three-boron centers and one-boron centers, respectively) were measured in hot pressed boron nitride samples which were exposed to γ rays at room temperature (see Fig. 1). No such signals were obtained in pyrolytic boron nitride. The samples of CAPBN were found to contain thermally produced three-boron centers, which gave rise to a ten-line signal. Exposure of CAPBN to γ radiation caused the three-boron center signals to increase and also produced some one-boron-center signals.

A more detailed study of the signals in HPBN showed that they saturate at high doses of ionizing radiation. Under x-ray excitation (40 kV, 20 mA) saturation was reached after several hours. The excitation spectrum of the EPR signals produced by uv light was found to be centered around 3000 Å (4.1 eV), as shown in Fig. 2 (a).

The EPR signals produced by ionizing radiation could be bleached by heating, which enabled us to measure the isochronal annealing of the signals. In these measurements the sample was excited at room temperature T_0. The amplitude $I(T_0)$ of the EPR signals (either the one or the three-boron-center signals) was then measured, and the sample was heated rapidly to temperature T_1 and kept at this temperature for 2 min. It was then cooled down to room temperature when the amplitude was measured again and denoted by $I(T_1)$. Such cycles were repeated for a series of exceedingly higher temperatures $T_2, \ldots, T_n$. The isochronal annealing curve was obtained by plotting $I(T_n)/I(T_0)$ vs T_n, and is shown in Fig. 3 (a) (see also Ref. 25).

The EPR signals were also bleachable optically by light in the range 4000–7000 Å. This optical bleaching was not very efficient, and with the intensity of the available light sources the decrease in the signals was quite small. Nevertheless, it was noted that the one-boron-center signals were

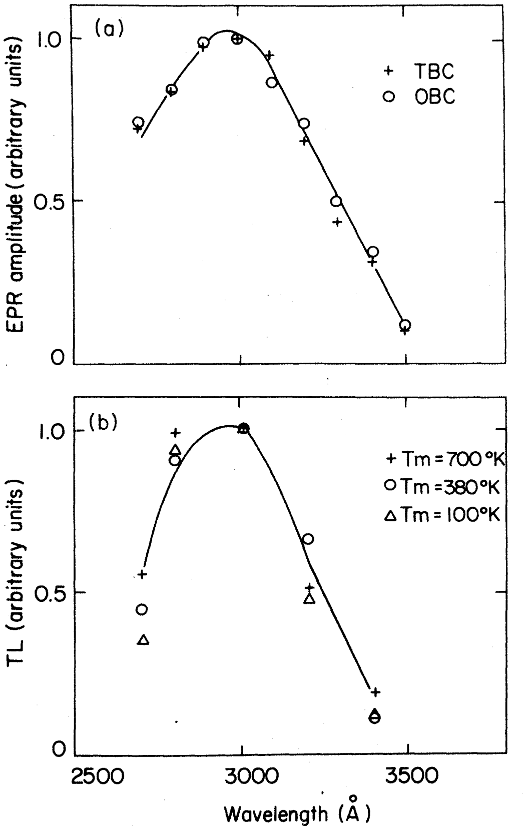

FIG. 2. (a) Excitation spectrum of the EPR signals as measured at 300 °K. (b) Excitation spectrum of the thermoluminescence (TL) peaks at 100°, 380° and 700 °K.

affected mainly by green light (5500 ± 100 Å) and the three-boron-center signals, by blue light (4500 ± 100 Å). We have not succeeded in measuring the detailed spectrum of optical bleaching.

Compression-annealed pyrolytic boron nitride resembles a single crystal in many respects, which is one of the reasons why Moore and Singer chose it for studies of the anisotropy of the three-boron centers.[10] We carried out similar measurements on one-boron centers in CAPBN, and measured the anisotropy of the g factor and of the hyperfine splitting ΔH between the two central EPR lines. The sample was rotated about an axis in the plane of the boron nitride hexagons (perpendicular to the c axis), thus varying the angle θ between the c axis and the external magnetic field H_{dc}. The dependence of ΔH on θ is shown in Fig. 4. It was found that $\Delta H(\theta)$ fits the expression $\Delta H = a + b \cos^2\theta$ G with $a = 116.5 \pm 3.0$ G and $b = 28.0 \pm 3.0$ G. No change in $\Delta H(\theta)$ was detected when the sample was rotated about the c axis, with c perpendicular to H_{dc}. The measured value of $g = 2.002 \pm 0.003$ was found to remain constant, within the experimental error, when θ was varied.

In the search for other thermally bleachable centers we performed measurements at low temperatures. The samples were γ irradiated at 77 °K, and EPR measurements were carried out at the same temperature, but no new EPR centers were found.

B. Glow-curve measurements

Useful information can be gained by combined EPR and glow-curve measurements.[26,27] The former can help to establish the chemical nature of the defect and the symmetry of the charge distribution, while the latter may be used to determine the energy of the trapping level.

Our measurements were carried out on grade HP samples which had been exposed to ionizing radiation (uv, x rays, or γ rays). Some of the results on the thermoluminescence and the thermally stimulated current measurements of samples excited by x rays at room temperature were reported elsewhere.[25] Two glow peaks at 380 and at 700 °K were observed, and are shown in Fig. 3(b). The activation energies of the two peaks were determined by the "initial-rise" method,[28] and found to be 0.7 ± 0.1 and 1.0 ± 0.1 eV for the 380 and 700 °K peaks, respectively. Using uv light for the excitation we were able to measure the excitation spec-

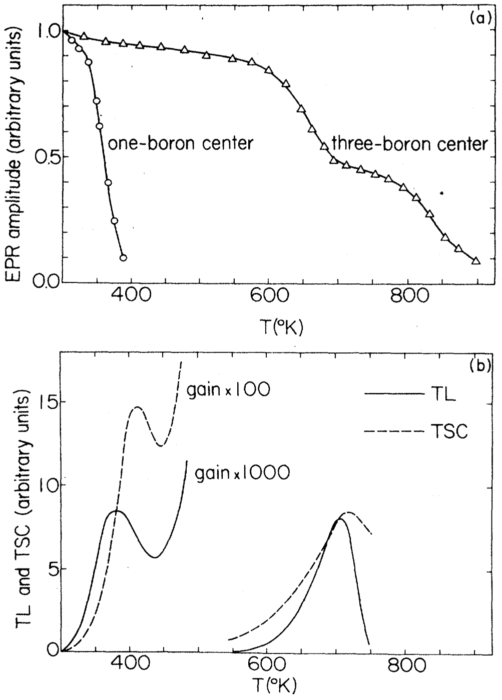

FIG. 3. (a) Isochronal annealing curves of the EPR spectra of the OBC and the TBC of hot-pressed boron nitride. (b) Thermoluminescence and thermally stimulated currents of the same samples as in (a).

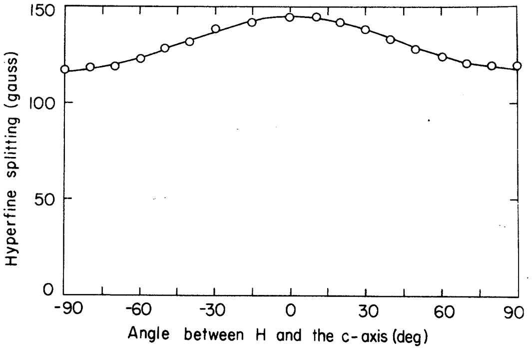

FIG. 4. Hyperfine splitting ΔH between two one-boron-center EPR lines as function of the angle θ between c axis and the external magnetic field H_{dc}.

trum of the peaks, and found that they were very similar to those observed in the EPR measurements, as shown in Fig. 2 (b). Another point of similarity was found in the optical bleaching of the peaks. The 700 °K peak could be bleached partially by blue light (4500 Å), and the 380 °K peak mainly by 5500-Å light.

Measurements were also taken with the samples excited at 77 °K. Another thermoluminescence peak was observed at 100 °K, accompanied by a thermally stimulated current peak. The activation energy of the former was also determined and found to be 0.3 ± 0.05 eV. The excitation spectrum of the thermoluminescence peak was similar to the previous ones, and it is also indicated in Fig. 2(b).

The thermoluminescent emission of all three peaks was measured through various optical filters. The light intensity through green, orange, or uv transmitting filters was much lower than that through a blue filter (Corning 5-58), and thus it seems that the emission is centered in the region 3600–4700 Å. A detailed study of the emission spectrum was difficult because of its low intensity.

C. Photoluminescence and phosphorescence

Photoluminescence measurements were carried out only on grade HP hot-pressed powder samples. They were excited by uv at or below room temperature, and a blue photoluminescence was observed. The excitation spectrum was found to peak at 3200 Å, and the emission spectrum covered the region 3900–5000 Å, with a peak near 4200 Å. These results are similar to those reported by others,[13,14] although we were not able to observe the fine structure.

On excitation by uv or x rays at 77 °K, we observed a blue phosphorescence after termination of the excitation. The phosphorescence emission looked to be similar to that of the photoluminescence. At 77 °K the phosphorescence decayed slowly with time, while heating for a very short time to 200 °K caused it to disappear completely.

PROPOSED MODEL AND DISCUSSION

A. Proposed model

We shall first summarize the main results of the present work and then propose a model of the energy levels of the point defects consistent with the experimental results.

1. EPR results

(i) The excitation spectra of the three-boron centers and of the one-boron centers peak at about 4.1 eV [Fig. 2(a)].

(ii) The isochronal annealing curves show a drop in the one-boron-center curve at about 350 °K, and two "knees" in the three-boron-center curve at 650 and 800 °K [Fig. 3(a)].

(iii) The one- and three-boron centers are partially bleached by green and blue light, respectively.

2. Glow-curve and photoluminescence results

(i) Three thermoluminescence peaks were observed [Fig. 3(b)] at about 100, 380, and 700 °K with activation energies of 0.3, 0.7, and 1.0 eV, respectively.

(ii) The excitation spectra of these peaks were similar to those of the EPR signals [compare Figs. 2(a) and 2(b)].

(iii) All the thermoluminescence curves were accompanied by the thermally stimulated current curves [Fig. 3(b)].

(iv) The 380 and 700 °K peaks can be bleached by green and blue light, respectively.

(v) The emission in the thermoluminescence, photoluminescence, and phosphorescence was in the blue.

To the above list we add some important results of other workers.

(i) The luminescence phenomena were correlated with carbon impurities.[12,15]

(ii) The three-boron centers appear only in the presence of carbon.[10]

(iii) Temperature quenching of the photoluminescence took place with an activation energy of nearly 1.1 eV.[13]

(iv) The band structure of pure hexagonal boron nitride has not yet been determined conclusively, but various experiments gave for the band gap a value of $E_g = 5.5 \pm 0.3$ eV.[13,29,30]

Our proposed model of the energy levels of electrons trapped in the three- and one-boron centers and shallow traps (ST) and those associated with carbon impurities is given schematically in Fig. 5.

It has been mentioned above that the three-boron centers consist of unpaired electrons trapped in the

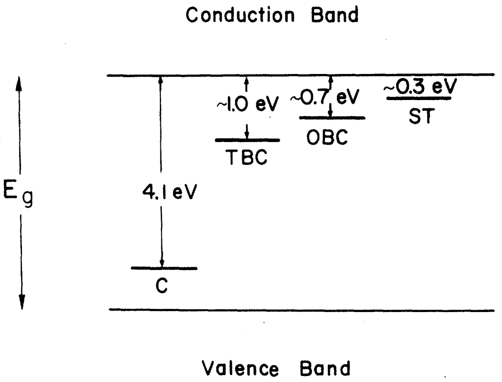

FIG. 5. Schematic energy level diagram of the point defects in hexagonal boron nitride. OBC—one-boron-center, TBC—three-boron-center, ST—shallow trap, C—carbon impurity level.

vicinity of three ^{11}B nuclei. Our results suggest that the electron energy level is located about 1.0 eV below the conduction band. For the one-boron center, the electron is localized on one ^{11}B nucleus and it is proposed that its energy level is 0.7 eV below the conduction band. Another set of levels, ST, is located at about 0.3 eV below the conduction band.

We assume that carbon impurities serve as luminescent centers, and they introduce an energy level (level C in Fig. 5) located 4.1 eV below the conduction band. If it is assumed that the value E_g lies in the range 5.3–5.7 eV, then the distance of the carbon impurity level from the valence band is between 1.2 and 1.6 eV.

Microwave absorption in a sample in a magnetic field should be proportional to the density n of unpaired electrons, and the amplitude of the EPR signals is approximately proportional to n. In our measurements n is the density of the trapped electrons. These electrons when released upon heating give rise to the phenomenon of isochronal annealing. The curve of isochronal annealing is proportional to that of a plot of n vs T. The release of electrons from traps can be accompanied by a luminescence glow curve which should then be proportional to $-dn/dT$.[31] If the same set of electron traps is responsible for both phenomena, the glow curve will be proportional to the negative of the derivative of the isochronal annealing curve. This is really the case as is evident when comparing the isochronal annealing curves in Fig. 3(a) with the glow curves in Fig. 3(b).

The negative of the derivative of the three-boron-center curve in Fig. 3(a) has actually two peaks, at 650 and 800 °K. The one at 650 °K is proportional to the thermoluminescence peak shown in Fig. 3(b), which indicates that the three-boron centers are responsible for both phenomena in this temperature range. The thermal activation energy calculated from the thermoluminescence peak was $E^{\mathrm{th}}_{\mathrm{TBC}} = 1.0$ eV. The thermoluminescence peak was accompanied by a thermally stimulated current peak, which indicates that the trapping level lies about 1.0 eV below the conduction band, as shown in our model. The optical bleaching experiments indicated that partial bleaching of the three-boron centers was caused by light with an energy $E^{\mathrm{opt}}_{\mathrm{TBC}} \approx 2.8$ eV, and thus $E^{\mathrm{opt}}_{\mathrm{TBC}} > E^{\mathrm{th}}_{\mathrm{TBC}}$. The "knee" at 800 °K in Fig. 3(a) seems to be related to electrons in deeper traps. These electrons are again related to the three-boron centers, but are more strongly bonded. The strong black-body radiation at 800 °K did not permit the observation of the thermoluminescence temperature.

A similar comparison of the one-boron-center isochronal curve [in Fig. 3(a)] with the glow curves in the 380 °K range [Fig. 3(b)] shows that the energy level of the one-boron center is located at $E^{\mathrm{th}}_{\mathrm{OBC}} = 0.7$ eV below the conduction band. Optical bleaching occurred in this case with light of an energy $E^{\mathrm{opt}}_{\mathrm{OBC}} \approx 2.2$ eV.

A careful examination of Fig. 3 shows that the thermoluminescence peaks appear at temperatures slightly higher than the corresponding "knees" in the isochronal annealing curves. This shift seems to have resulted from the different heating rates in the two experiments. A shift was also observed between the thermoluminescence and the thermally stimulated current peaks. This type of shift stems from the differences in the two processes.[32]

The thermoluminescence and the thermally stimulated currents obtained after excitation at 77 °K show that electrons can be trapped in a set of shallow traps (ST in Fig. 5), at $E^{\mathrm{th}}_{\mathrm{ST}} = 0.3$ eV below the conduction band. Electrons escaping from these traps at 77 °K were responsible for the phosphorescence described earlier. Heating the samples to 200 °K emptied these traps, and the phosphorescence disappeared and was not observed again when the samples were cooled back to 77 °K.

We observed that the excitation spectrum of the one-boron center was similar to that of the three-boron center, and this was clearly seen both in EPR and in the related glow peaks. Excitation at low temperature caused the shallow traps to be filled, and the excitation spectrum in this case was exactly the same as that for the other centers. This indicates that the same luminescence centers were involved in the process of excitation of all the thermoluminescence peaks. Some of the electrons excited at 77 °K are then trapped in one-boron centers, some in three-boron centers, and others in shallow traps.

All the phenomena mentioned above appeared only in carbon-containing samples, which indicates that the luminescence centers are associated with carbon. The centers are assumed to introduce the energy level C (Fig. 5) at 4.1 eV below the conduction band, which fits the peak of the excitation spectrum. Upon heating, the trapped electrons are excited to the conduction band, and emit blue light on recombination. The emission spectrum of the thermoluminescence has not been determined precisely, and we are still unable to tell whether the recombination takes place at the centers C or at other centers. Other workers have already concluded that the photoluminescence, electroluminescence, and even cathodoluminescence are connected with carbon.[12,13,15]

In our model the energy difference W between the level C and the valence band is somewhat above 1.0 eV. Therefore the temperature quenching of the photoluminescence would be expected to occur in the temperature range studied,[31] where the dependence of the photoluminescence on the temperature would be given by $L(T)=L(0)/(1+Ae^{-W/kT})$. This was indeed found by Larach and Shrader,[13] who obtained the value $W=1.08$ eV. It may be noted here that the thermoluminescence peak at 700 °K is asymmetric [see Fig. 3(b)], and drops very steeply on the high-temperature side. Furthermore, the "knee" at 800 °K in the isochronal annealing curve is not accompanied by a thermoluminescence peak. Both effects may serve as an indication that temperature quenching is taking place in this temperature range, which is in agreement with our model.

B. Nature of the defects

We shall now discuss the nature of the defects. Starting with the three-boron centers, Romelt[4] proved that these centers consist of unpaired electrons which interact with three equivalent ^{11}B nuclei. Krashoperov *et al.*[9] calculated the electrical charges in boron nitride and came to the conclusion that the three-boron centers are electrons trapped in nitrogen vacancies. Moore and Singer[10] studied the anisotropy of the hyperfine splitting ΔH between a pair of lines in the EPR signal associated with the three-boron centers. They found that $\Delta H=a+b\cos^2\theta$, with $a=7.85$ G and $b=-1.27$ G, where θ is the angle between the c axis and the external magnetic field H_{dc}, and inferred that the unpaired electron had a π character.

Our thermoluminescence experiments have shown that the electrons were trapped at about 1.0 eV below the conduction band. The problem of a nitrogen vacancy in hexagonal boron nitride was then solved theoretically. The details of calculations using a quantum mechanical defect-model are given in Paper II.[16] These calculations indicate that the electron is trapped in a π defect orbital with its charge symmetrically distributed on the three boron atoms neighboring the vacancy, and that it should be located in the range 1.1–1.4 eV below the conduction band. The charge distribution on the three boron atoms in this defect orbital was shown to agree with the experimental EPR hyperfine coupling constants.[33] Thus support is given to the hypothesis that the three-boron centers are actually F centers by nature. Conclusive experimental evidence for this hypothesis could be given by experiments where nitrogen vacancies are produced by electron bombardment. Preliminary measurements of the production of three-boron centers by electrons are now under way.

As for the one-boron centers, Romelt[5] proved that these consist of an unpaired electron which interacts with one ^{11}B nucleus. We have found (Fig. 4) that the anisotropy of the four-line signal associated with this center is given by the expression $\Delta H=a+b\cos^2\theta$, with $a=116.5\pm 3.0$ G and $b=28.0\pm 3.0$ G, so that for $\theta=0°$, $\Delta H_{\parallel}=144.5$ G and for $\theta=90°$, $\Delta H_{\perp}=116.5$ G. If the Fermi-contact hyperfine interaction is denoted by A_s, and the dipolar interaction by A_p, then one can write[34] $\Delta H_{\parallel}=A_s+2A_p$, $\Delta H_{\perp}=A_s-A_p$, and thus $A_s=125.8$ G, $A_p=9.3$ G. Simple considerations show that $\Delta H_{\parallel}$ and $\Delta H_{\perp}$ must have the same sign, different signs would lead to an unreasonable value of A_p. A_s and A_p were calculated for a free ^{11}B atom, with the results[34] $A_s=720$ G and $A_p=18.9$ G. This suggests that the trapped electron has a considerable π character.

The exact nature of the one-boron center has not yet been determined, but these centers may be related to boric oxide. A large four-line signal is obtained in hot-pressed boron nitride, containing boric oxide, whereas no such signal is obtained in pyrolytic boron nitride, which is free of the oxide. Moreover, similar one-boron centers have been found in BeO doped with boron.[35] This suggestion can be checked in samples with known concentrations of boric oxide.

The conclusion that carbon centers introduce an energy level at 4.1 eV below the conduction band has been supported by quantum chemical calculations of carbon impurities in boron nitride, which are discussed in Paper II. But, again, conclusive evidence for the role of carbon should be obtained by measurements in samples with known concentrations of carbon.

ACKNOWLEDGMENTS

The authors wish to thank Dr. L. S. Singer and Dr. A. W. Moore of Union Carbide Corp., for supplying some of the samples used in this study. We are grateful to Professor Z. Luz for many helpful discussions.

[1] M. Neuberger, Hughes Aircraft Co., 1969 (unpublished).

[2] R. C. DeVries, General Electric Co. Report, 1972 (unpublished).

[3] D. Geist and C. Romelt, Solid State Commun. 2, 149 (1964).

[4] G. Romelt, Z. Naturforsch. A 21, 1970 (1966).

[5] G. Romelt, Proc. Int. Symposium on Lattice Defects, Tokyo, 1966, pp. 407–417.

[6] M. B. Khusidman and V. S. Neshpor, Teor. Eksp. Khim. 3, 270 (1967) [Theor. Exp. Chem. 3, 152 (1967)].

[7] M. B. Khusidman and V. S. Neshpor, Fiz. Tverd. Tela 10, 1229 (1968) [Soviet Phys.-Solid State 10, 975 (1968)].

[8] M. B. Khusidman and V. S. Neshpor, Poroshk. Metall. 8, 72 (1970).

[9] V. A. Krasnoperov, N. V. Vekshina, M. B. Khusidman, and V. S. Neshpor, Zh. Prikl. Spektrosk. 11, 299 (1969).

[10] A. W. Moore and L. S. Singer, J. Phys. Chem. Solids 33, 343 (1972).

[11] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, London, 1963).

[12] E. Tiede and H. Tomaschek, Z. Anorg. Allg. Chem. 47, 111 (1925).

[13] S. Larach and R. E. Shrader, Phys. Rev. 104, 68 (1956).

[14] D. N. Bose and H. K. Henisch, J. Am. Cer. Soc. 53, 281 (1970).

[15] U. D. Dzhuzeev and P. E. Ramazanov, Izv. Viz. Fiz. USSR 7, 81 (1969).

[16] A. Zunger and A. Katzir, following paper, Phys. Rev. B 11, 2378 (1975).

[17] Information on boron nitride supplied by Carborundum Co. in technical bulletins.

[18] Union Carbide Corp., 1965 (unpublished).

[19] A. W. Moore, Nature (Lond.) 221, 1133 (1969).

[20] O. J. Guentert and R. L. Mozzi, Nature (Lond.) 193, 570 (1962).

[21] J. L. Brebner and E. Mooser, J. Sci. Instrum. 39, 69 (1962).

[22] E. G. Manning, M. A. Littlejohn, J. A. Hutchby, and E. M. Oakley, Rev. Sci. Instrum. 43, 324 (1972).

[23] A. Halperin and J. Nahum, J. Phys. Chem. Solids 18, 297 (1961).

[24] A. Katzir and M. Rosmann, Rev. Sci. Instrum. 45, 453 (1974).

[25] A. Katzir, J. T. Suss, and A. Halperin, Phys. Lett. A 41, 117 (1972).

[26] G. K. Born, R. J. Grasser, and A. O. Scharmann, Phys. Status Solidi 28, 583 (1968).

[27] C. Bettinali and L. Guidoni, Z. Phys. Chem. Neue Folge 78, 17 (1972).

[28] A. Halperin, A. A. Braner, A. Ben-Zvi, and N. Kristianpoller, Phys. Rev. 117, 416 (1960).

[29] A. J. Noreika and M. H. Francombe, J. Vac. Sci. Technol. 6, 722 (1969).

[30] W. Baronian, Mater. Res. Bull 7, 119 (1972).

[31] D. Curie, *Luminescence in Crystals* (Methuen, London, 1963).

[32] R. Chen, J. Appl. Phys. 42, 5899 (1971).

[33] A. Zunger, J. Chem. Phys. (to be published).

[34] P. B. Ayscough, *Electron Spin Resonance in Chemistry* (Methuen, London, 1967), Chap. 3.

[35] A. R. Reinberg, J. Chem. Phys. 41, 850 (1964).