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Synthetic diamonds as pulse counting radiation detectors

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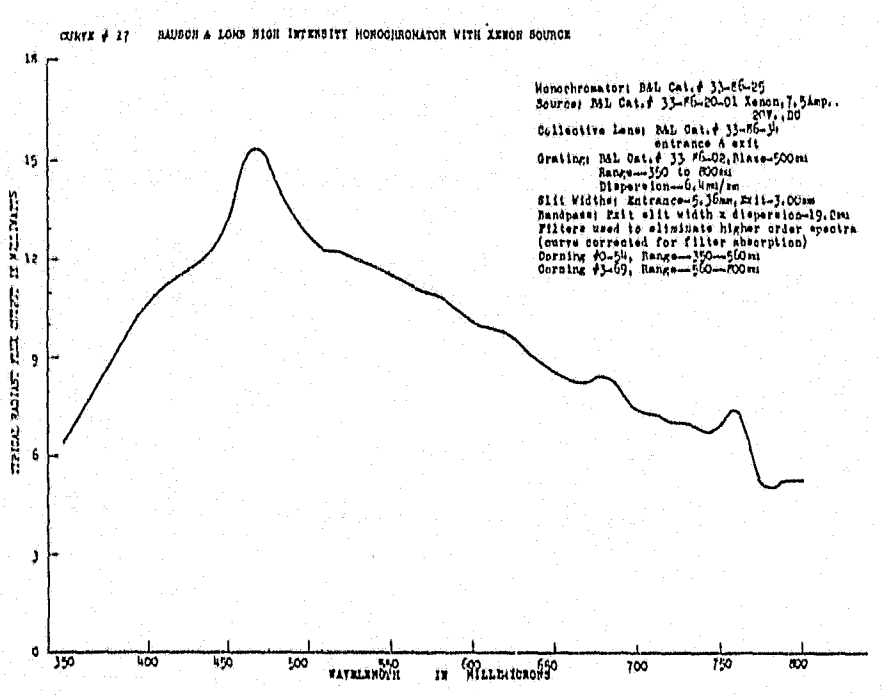


Figure 5.3. Intensity of the monochromator light as a function of wavelength.

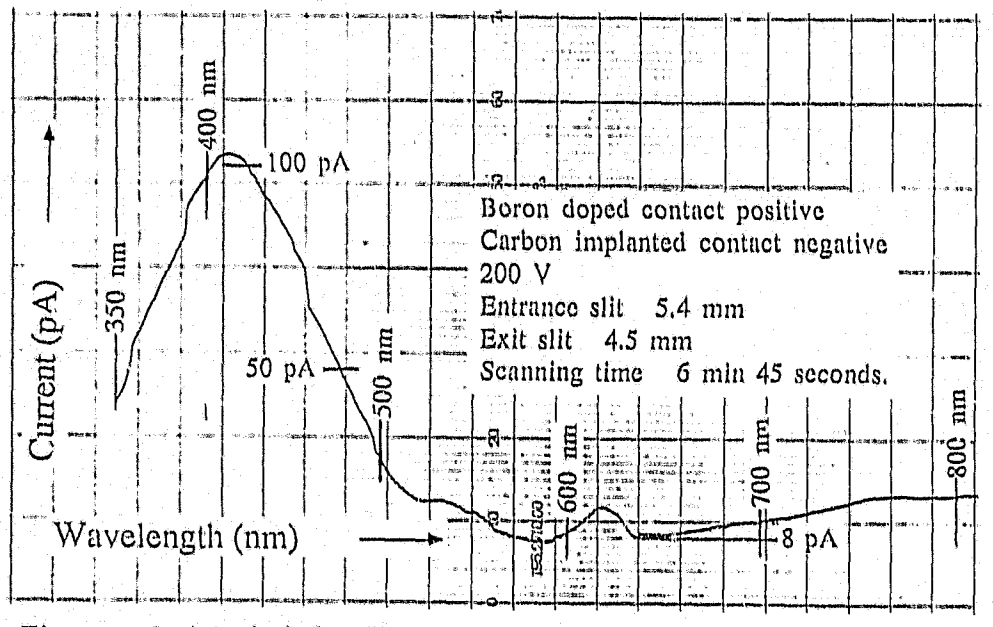


Figure 5.4. A typical photoconduction spectrum. Diamond: Suite 2. (Not corrected for light intensity variation).

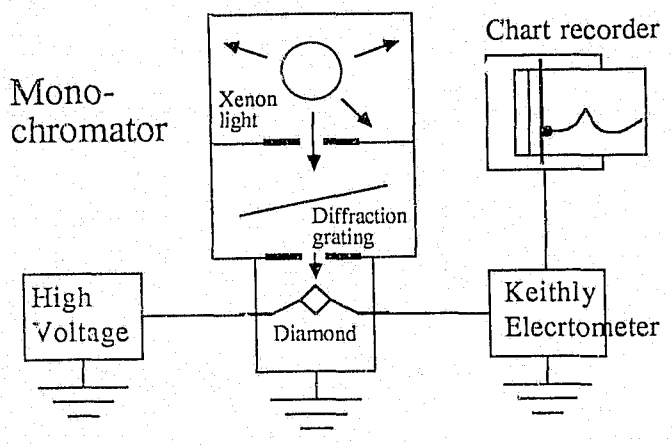


Figure 5.5. Schematic diagram of the photoconduction circuit.

All of the photoconduction spectra measured are similar to that shown in figure 5.4, and all have a broad peak starting at approximately 500 nm and peaking at approximately 400 nm. This indicates a level or band in the region 2.0 to 3.0 eV. Different scanning speeds and different potentials across the diamonds made no significant change to the spectra, and made it thus difficult to gain any further information about the trapping levels from the photoconduction spectra.

The results are similar to those obtained by Vermeulen and Farrer (1972) for photoconduction measurements of type Ib synthetic diamonds. They conclude that a trapping level exists and has an energy of 2.0 eV. From thermoelectric and photo-Hall measurements they deduce that the level lies below the conduction band, and tentatively attribute the level to the single substitutional nitrogen impurity.

5.3 Wavelength causing depopulation

To calculate the depth of the trap which was filled by pre-irradiation and depopulated by light, the pulse counting response of a primed diamond was measured after it had been exposed to monochromatic light. This measurement was repeated for many wavelengths so as to identify at what energy the depopulation started to occur.

A Cary 17 Spectrophotometer was used as a light source in place of the Bausch & Lomb monochromator. The monochromator diffraction grating produces second and

higher order diffractions (at $\frac{1}{2}$, $\frac{1}{3}$, etc. of the wavelength) which depopulate the traps, thus making it impossible to deduce at what wavelength the depopulation occurs. The Cary uses a diffraction grating and a prism in series, and so produces only a single wavelength of monochromatic light. The exit slit was opened as wide as possible (3 mm) because the light was of low intensity, and resulted in a 10 nm bandwidth resolution. The diamond was exposed to light for a time of 20 minutes to 1 hour. A dependance on the exposure time exists (figures 5.6 and 5.7) because saturation depopulation or filling of traps did not occur.

Only one diamond was selected for testing. The suite 2 diamond was chosen because it exhibited the best pulse counting response, and had a large response difference between the primed and unprimed states.

The procedure for each measurement was as follows :

i) The diamond was exposed to a Kaiser 1000 W photoflood light, to depopulated the trapping levels and thus give the diamond an almost zero pulse counting response. The diamond in its holder was surrounded by black tape for light protection and exposed to a 12 Gy or larger γ-ray radiation dose to fill trapping levels. This procedure enabled the initial conditions to be the same for each measurement.

ii) An initial ^{137}Cs pulse height spectra was recorded at a dose rate of 22 mGy·h^{-1} for a period of 100 seconds.

iii) The diamond was placed in the spectrophotometer and the light protection tape removed whilst in the dark. The diamond was exposed to monochromatic light of the desired wavelength. Because of the low light intensity, the diamond was left exposed for long periods of time in the hope that the filling and/or depopulation of trapping levels would reach a saturation level, making the response intensity independent. This situation was not reached, figures 5.6 and 5.7 indicate a time (i.e. light intensity) dependence.

iv) The black light protection tape was replaced, and a final ^{137}Cs pulse height spectrum was recorded at a dose rate of 22 mGy·h^{-1} for a period of 100 seconds. The final response (i.e. count rate) at each wavelength was calculated as the percentage of the initial count rate, and is shown graphically in figures 5.6 and 5.7.

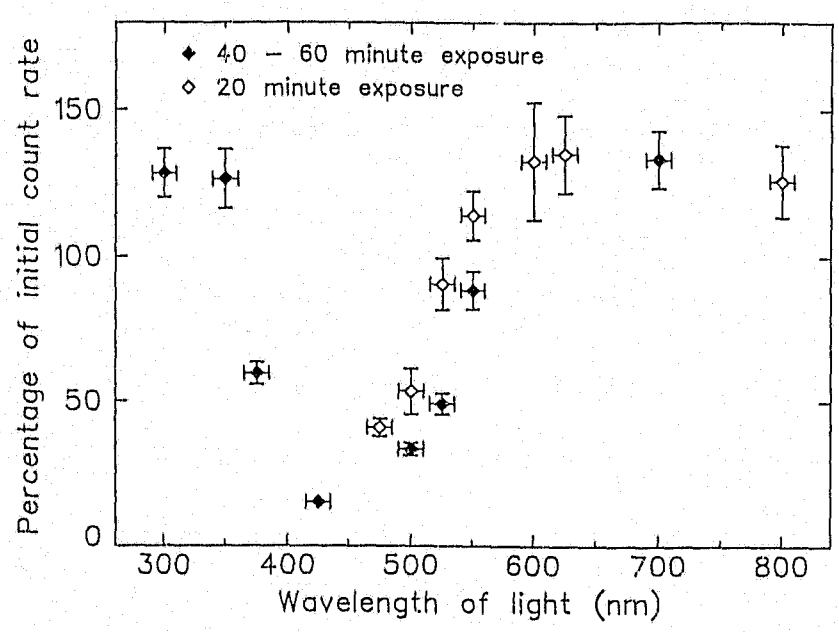


Figure 5.6. Effect on the pulse counting response as a function of wavelength after exposing the diamond to light. Diamond: Suite 2.

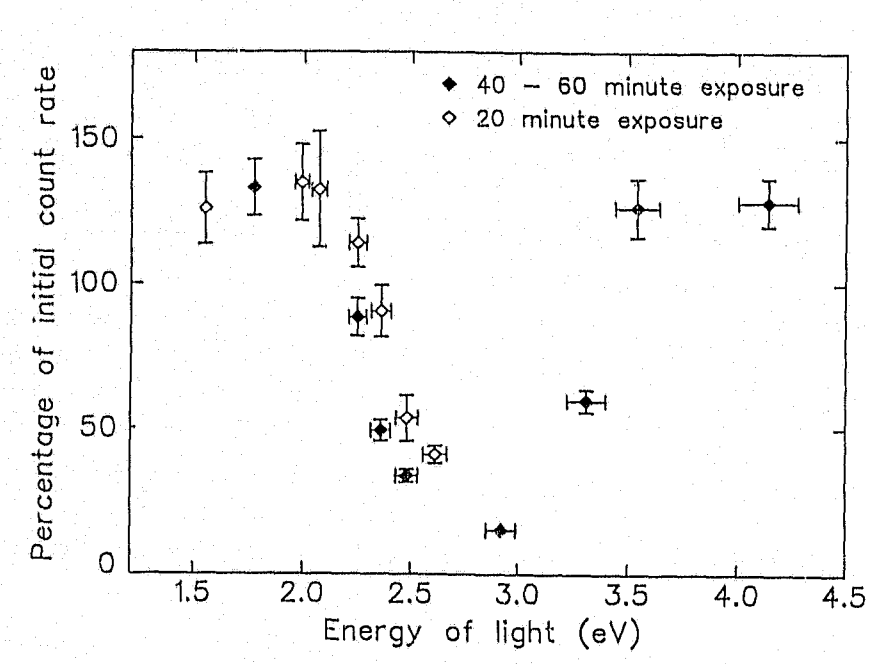


Figure 5.7. Effect on the pulse counting response as a function of energy after exposing the diamond to light. Diamond: Suite 2.

5.4 Shallow trapping levels

After exposure to light of energy less than 2.2 eV ($\lambda > 565$ nm) an increase in the count rate of approximately 30% was recorded. It is believed that this increase is due to the filling of shallow traps which have an energy of less than 1.55 eV. No measurements were made using light of lower energies, but it is believed that such measurements would make it possible to identify the level or levels of these traps. These traps are probably the shallow traps (20 - 200 °C) observed in thermoluminescent measurements (appendix A), which are known to be hole traps lying above the valence band (Nam 1989). These traps are also believed to be responsible for the initial increase in the count rate after the diamond has been pre-irradiated (figures 4.8 and 4.9). This initial increase does not occur after the diamond has been exposed to light of energy between 1.55 and 2.2 eV, indicating that both effects result from the same trapping level. The increase is also not observed if the pulse counting measurement is carried out several hours after pre-irradiation, indicating that these shallow traps are affected at room temperature. The pre-irradiation populates these traps, and depopulation occurs during pulse counting, by exposure to light of at least 1.55 eV, or by heat even at room temperatures.

The increase in counting response when the diamond is exposed to red light has also been observed by Willardson and Danielson (1950), Willardson (1950), Urlau et al (1961) and Vermeulen and Nabarro (1967b). These traps are probably responsible for the trapping of space charge near the contacts, Willardson and Danielson (1950) report that space charge is removed from traps by exposure to monochromatic red light. Red light would excite electrons from the valence band, allowing them to recombine with the trapped holes, returning the level to its neutral state (figure 5.8). A symmetric trapped charge distribution will result, removing the space charge effect. The space charge returns if the red light is switched off (Willardson and Danielson 1950), indicating that the traps responsible for space charge are sufficiently shallow to depopulate or fill at room temperature. This is consistent with the finding that the space charge develops in the opposite direction if the high voltage polarity is switched (figure 4.3), and dissipates if the high voltage is switched off (section 4.1).

Pre-irradiation also removes the space charge for several minutes (figure 4.6), it is most probably because the irradiation excites electrons to the conduction band, leaving a trapped hole at the shallow trap. Note that is the opposite to what occurs if the diamond

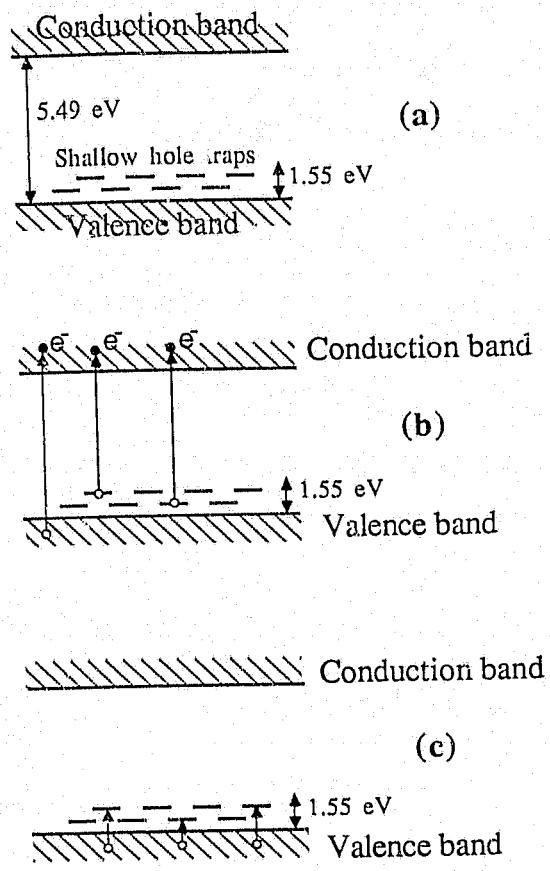


Figure 5.8. Procedures affecting the shallow hole traps in diamond. (a) Position of possible hole trapping levels above the valence band. (b) Pre-irradiation causing hole to be trapped. (c) Red light or heat exciting electron from valence band, releasing trapped hole and returning the trap to its neutral state.

is exposed to red light, but also results in a symmetrical charge distribution. The energy deposited by pre-irradiation is large and it is more probable to excite electrons from the valence band and from shallow traps above the valence band into the conduction band, rather than into shallow traps above the valence band (figure 5.8). This would result in trapped holes at the shallow traps, and is in agreement with Nam's (1989) model for holes trapped during irradiation and released by heating for thermoluminescence. The space charge effect still occurs after pre-irradiation, but takes several minutes as opposed to seconds if no pre-irradiation was carried out. The pre-irradiation probably

causes hole trapping at levels that do not populate and depopulate immediately at room temperature. Such traps would take longer to trap space charge, explaining the longer time before the onset of the space charge decrease.

It is believed that the trapped hole at these shallow levels will act as an effective electron trap. Electron 'capture' by the trapped hole would reduce the size of the radiation induced pulse, and thus the number of pulses recorded in the ROI. Red light releases the trapped hole and removes the possibility of electron trapping, thus explaining the observed increase in pulse counting response after exposure to red light. The initial increase in pulse counting response after pre-irradiation is explained by the reducing concentration of trapped holes as electrons are 'captured', fewer electrons are then trapped resulting in a higher pulse counting response.

The initial increase not being observed if the pulse counting measurement was performed several hours after pre-irradiation, is explained by electrons in the valence band having sufficient thermal energy at room temperature to recombine with the trapped hole. The valence band electrons would have only a small probability of having sufficient thermal energy at room temperature to reach the trapping level, since it takes several hours for the process to occur. The position of a trapping level at the limit of room temperature thermal energy, indicates the existence of a trapping level closer to the valence band which can populate and depopulate within seconds at room temperature. The level closer to the valence band would be the major trapping level for space charge, explaining the switching of the space charge field in less than a minute (figure 4.3). Vermeulen and Nabarro (1967a,b) measured trapping levels at 0.9 eV and 1.5 eV above the valence band in their pulse counting type Ia diamonds, and their levels may be the same levels that are described in this section.

5.5 The pre-irradiation trapping level

The major effect to the pulse counting response as the result of light is a large decrease after exposure to wavelengths less than 560 ± 20 nm (an energy greater than 2.2 ± 0.1 eV). The response decrease is not observed if the diamond is exposed to 375 ± 10 nm or lower wavelengths of light (an energy of 3.3 ± 0.1 eV or higher). The two energies add to 5.5 ± 0.2 eV which is the band gap of diamond (5.49 eV), indicating that the decrease and increase in response correspond to opposing processes occurring to the

same trapping level. This is the trapping level mentioned in section 4.4, which is filled by pre-irradiation and depopulated when the diamond is exposed to ambient light.

A measurement showed that illuminating an initially unprimed diamond with 300 nm (4.14 eV) ultraviolet light, caused the trapping level to be filled. Exposing the diamond to sufficiently intense ultraviolet light, therefore has the same effect as pre-irradiation and exposure to light which fills the shallow hole traps. Sunlight and most ambient lighting does not fill this trapping level, because the intensity of light causing trap depopulation is higher than the intensity of ultraviolet light which causes filling of the trapping level.

The single energy level has two possible positions, either an electron trapping level 2.2 eV below the conduction band, or a hole trapping level 2.2 eV above the valence band (figure 5.9).

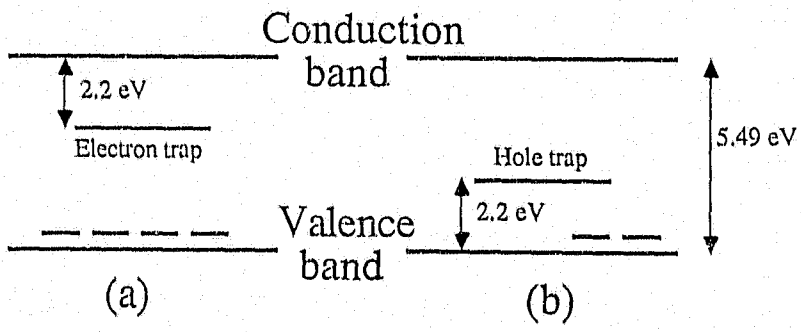


Figure 5.9. Band structure diagram with the trapping level which causes decreased counting response - (a) possible electron trap 2.2 eV below the conduction band, or (b) possible hole trap 2.2 eV above the valence band.

No energy level of approximately 2.2 eV appears in the thermoluminescent spectrum (Appendix A). It would occur in the region of 300 °C to 400 °C, and would indicate the existence of a trapping level lying above the valence band. This fact would tend to support the existence of an electron trapping level 2.2 eV below the conduction band.

The energy of 2.2 eV indicates that this may be the same level that is observed in the photoconduction spectra, described in section 5.2. It is also in agreement with a level observed by Urlau et al (1961) for pulse counting measurements of one type IIa and two type I diamonds. Vermeulen and Nabarro (1967b) see the same energy level for pulse counting with type Ia diamonds. They consider it to be a hole trapping level above the valence band, because private communication with Farrer suggested counting diamonds are *p*-type when exposed to green light. Later Vermeulen and Farrer (1975) describe a level 2.0 eV below the conduction band measured by means of thermoelectric and photo-Hall techniques. This may be the same level that is measured here, but they make no connection or reference to the level measured earlier by Vermeulen and Nabarro.

Recently Prins (1989c) has postulated that the negative vacancy (ND1 centre) could be a very effective hole trap, and would lie 2.25 eV above the valence band. The energy is in very good agreement with the 2.2 ± 0.1 eV that has been measured. The negative vacancy would 'trap a hole' by recombination with the electron at the vacancy, leaving the vacancy in a neutral state. What has been referred to as depopulation of the trapping level by exposure to light, would be the excitation by light of an electron from the valence band to the neutral vacancy, creating a negative vacancy which can act as a hole trap. Pre-irradiation or exposure to ultraviolet light will excite the electron from the negative vacancy to the conduction, leaving a neutral vacancy which will not act as a hole trap. A level lies between this hole trapping level and the valence band (Prins 1989c), and may be the reason why this trapping level is not observed in thermoluminescent measurements.

It is possible that because of the single substitutional nitrogen impurity lying at approximately 2 eV below the conduction band (Vermeulen and Farrer 1975, Tatarinov 1986), diamonds with high single substitutional nitrogen concentrations will most probably have a Fermi level lying at more than 2.2 eV above the valence band. This high Fermi level might make it impossible to observe the trapping level 2.2 eV above the valence band. Another possible reason why this 2.2 eV level is not observed in diamonds with high single substitutional nitrogen concentrations, is that the nitrogen may compensate this level, causing it not to act as a trapping level.

5.6 Conclusion

Shallow hole levels above the valence band have been postulated, and are believed to be responsible for space charge trapping, the initial increase in pulse counting response, and for the increase in response if the diamond is exposed to light of at least 1.55 eV.

A trapping level of energy 2.2 ± 0.1 eV has also been postulated, and is believed to be responsible for the increase in response when diamonds low in single substitutional nitrogen concentration are pre-irradiated. This trapping level is depopulated when the diamond is exposed to light, and then acts as a trap, reducing the pulse counting response.

Light has a significant effect on these trapping levels, and thus on the pulse counting properties. To reduce the effect of these traps, the pulse counting diamonds should not be exposed to light and should be primed by exposure to γ- or X-ray radiation and red light or by exposure to ultraviolet light. Light has been shown to be a useful tool to investigate the trapping levels in pulse counting diamonds, and should be used in further investigations of pulse counting diamonds.

Chapter 6. SCINTILLATION COUNTING

6.1 Introduction

Scintillation counting measurements do not fit into the scope of this thesis, but some results will be mentioned, because they are relevant to the understanding of processes occurring within the diamond and because they will also be used as motivation in the conclusions.

The method of scintillation counting is similar to that used for conventional scintillation detectors. Radiation incident on the diamond ionizes charge carriers, which are free to move within the crystal. The electrons and holes recombine at centers in the crystal giving off electromagnetic radiation, with an energy characteristic of the luminescent center. The light is usually in the visible and ultra violet regions and can be measured by a photomultiplier tube.

6.2 Method

The apparatus is shown schematically in figure 6.1. The diamonds were synthetics to be used for the pulse counting measurements, they had been mechanically polished on opposite (100) faces, chemically polished and cleaned in the three part acid solution. Radiation from a ^{241}Am 5.5 MeV α-particle foil source was incident on one of the polished faces through an aluminium collimator of diameter 0.58 $\pm$ 0.01 mm. Since the experiment was done in air, the foil source and the diamond were placed as close together as possible. The α-particles traveled through $\approx$ 1 mm of air before they reached the diamond, resulting in an energy reduction of $\approx$ 3 %.

The luminescent output was measured with a 9750A EMI photomultiplier tube. The pulses were amplified by an Ortec 113 preamplifier and an Ortec 485 amplifier, and then recorded on a Nucleus Spectrum 88 Multichannel Analyser.

The spectra recorded show the number of events as a function of the intensity of light, not the energy of the light. The light energy is dependent on the nature of the luminescent center and is not identifiable by the photomultiplier tube. The energy of the radiation should be proportional to the intensity of light and should appear as the x-axis scale of the spectrum. As no distinct peak appeared, it was not possible to calibrate the x-axis in terms of α-particle energy. Each spectrum is plotted as a function of channels and the scale is kept the same for all the spectra shown. It should be noted that the calibration from channels to α-particle energy is dependent on the diamond and would most likely vary from diamond to diamond.

Even though the optical coupling between the diamond and the photomultiplier tube was not ideal, measurements (e.g. figure 6.3) have shown that good radiation energy resolution is possible. It also indicates that the poor radiation energy resolution obtained for most samples is a result of processes within the diamonds and is not a fault of the apparatus.

The diamonds were not pre-irradiated and were exposed to ambient light before being placed in the scintillation apparatus. The actual measurements were obviously performed in the dark.

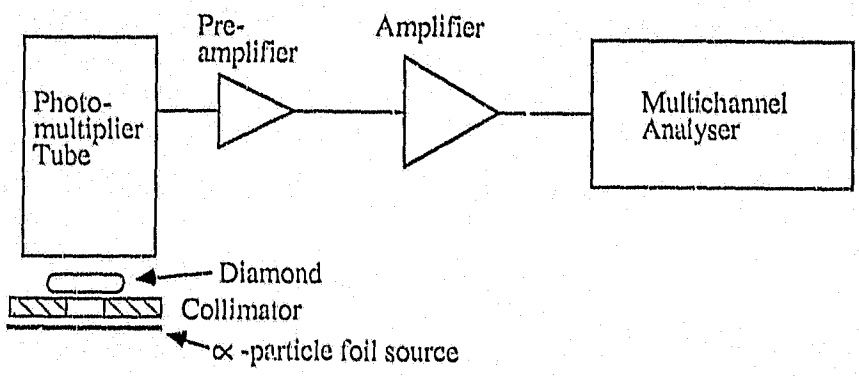


Figure 6.1. Schematic diagram of apparatus to measure scintillation spectra of diamond.

6.3 Results

Most spectra showed no peak corresponding to the α-particle energy, indicating little or no energy resolution. A typical spectrum is shown in figure 6.2. Many pulses occur with low light intensities, and few at high light intensities where the peak would be expected.

Nam et al (1989), using an iron free synthetic diamond, have shown that it is possible to obtain good energy resolution (cf. figure 6.3). Since their measurements were done on the same apparatus, it shows that the poor energy resolution is a result of the diamond and not of the apparatus. All the synthetic diamonds used here are iron based, showing the measurements to be in agreement with Nam et al, who have shown that iron based synthetic diamonds do not show good energy resolution.

The reason for little or no energy resolution is that most of the charge carriers in the diamond do not reach the luminescent centers. They either recombine at non-luminescent recombination centers or are trapped by trapping centers, a high percentage of which are probably created by the presence of iron. As a result only a small percentage of the ionized charge carriers reach the luminescent centers, producing light pulses which are less intense than expected.

Differing spectra were obtained for α-particles incident on different regions of the diamonds. Figure 6.4 shows two scintillation spectra from opposite faces of the same synthetic diamond. The spectra also varied for different regions of the same face, but did not differ as much as is shown in figure 6.4. Differences in spectra depending on the region of the diamond exposed to α-particles occurred in all diamonds tested, including natural diamonds. Since the α-particles were incident on a small area of the diamond (0.58 mm diameter) and have a small penetration depth ($\approx$ 60 μm), the differing spectra for the same diamond show that the recombination and/or luminescent and/or trapping centers are not evenly distributed throughout the diamond. Thus trapping and recombination are localized effects, and are caused by the inhomogeneous distribution of trapping and recombination centers during the synthesis process. The localized effect may also be influenced by the surface state of the diamond.

A synthetic diamond which showed some energy resolution, was irradiated with two different α-particle source strengths (same energy but different intensity of α-particles). The spectra are shown in figure 6.5. Measuring time of the spectra were different , to allow the number of low intensity light pulses to be approximately the same in each case. The weaker source had an intensity of 8 μCi.cm^{-2} and was recorded for 1250 seconds – this amounts to a quarter of the total radiation from the stronger source (400 μCi.cm^{-2} for 100 seconds). The peak from the stronger source is larger than the peak from the weaker source, even though the count rates for low intensities of light are the same. It is believed the difference in the shapes of the spectra is the result of trapping. Before many of the charge carriers reach the luminescent centers they are trapped and the resulting light pulse is less intense than expected. Some of the charge carriers in shallow traps (traps that can depopulate at room temperature) later escape from the traps and reach the luminescent centers, creating the very high number of low intensity light pulses seen in all the spectra. But when a stronger source is used, α-particles strike the diamond before many of the traps have depopulated. The charge carriers from this event will have a smaller probability of being trapped (as most of the traps are still occupied) and a more intense light pulse will result. Thus, for the stronger source, fewer low intensity and more high intensity light pulses are expected, as is shown in figure 6.5.

Phosphorescence decay curves measured by Nam et al (1989), and shown in figure 6.6, also indicate the presence of trapping. These curves measure the number of light pulses as a function of the time after the diamond has been irradiated. They show that many light pulses occur after the diamond has been irradiated, indicating the shallow traps are depopulating, and that the charge carriers reach the luminescent centers to produce light pulses. The pulses are of low light intensity and would create the high number of counts in the low light intensity region of the spectrum. The curves also show that the iron free synthetic diamonds have less phosphorescence, indicating less shallow trapping in these diamonds.

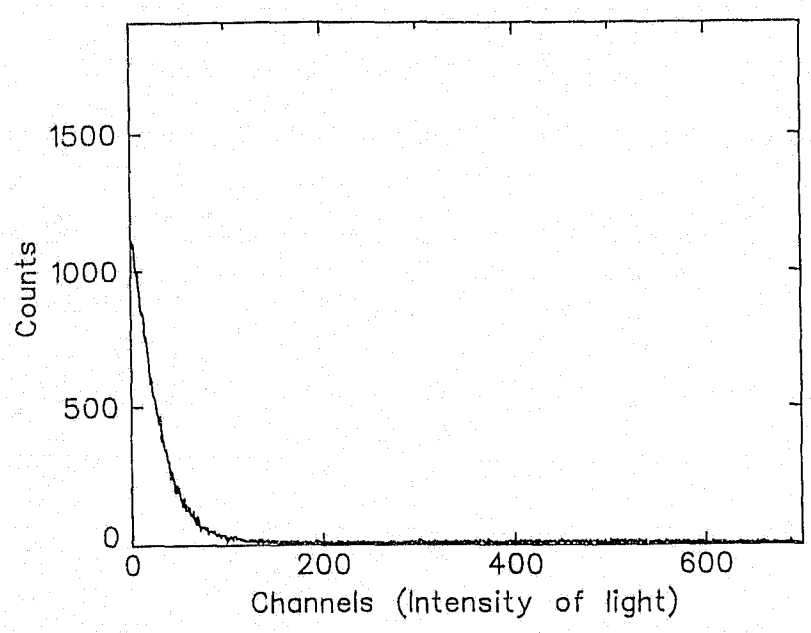


Figure 6.2. Typical scintillation spectrum from synthetic diamond used for pulse counting measurements. Diamond: Suite 2 no. 2.

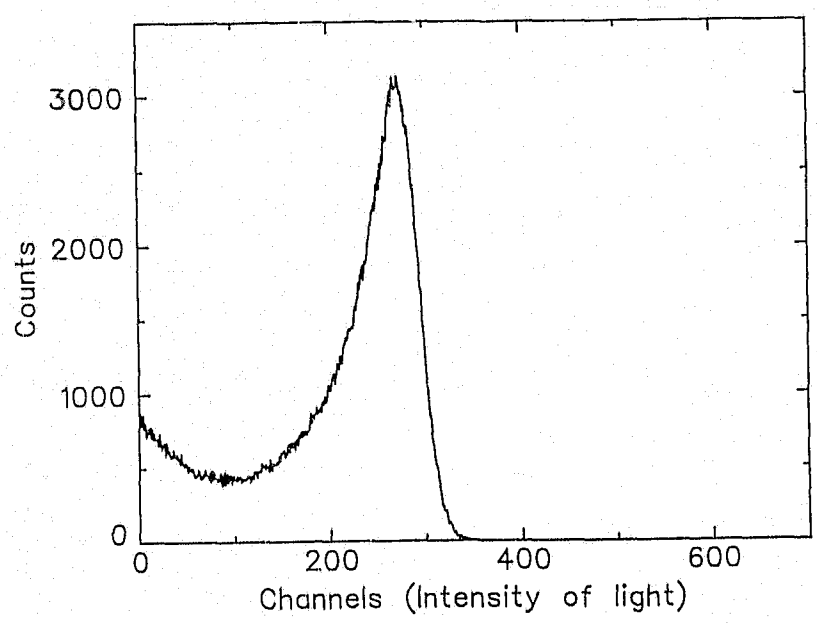


Figure 6.3. Scintillation spectrum of an iron free synthetic diamond. Measured by Nam et al (1989), using the same apparatus that is described in this chapter.

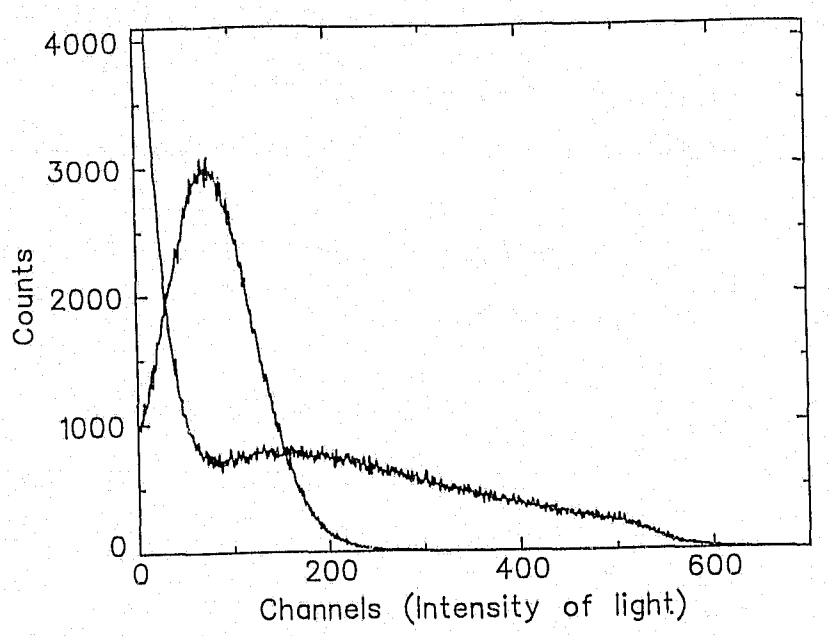


Figure 6.4. Scintillation spectra for two surfaces of the same synthetic diamond. Diamond: CoFe stone 6.

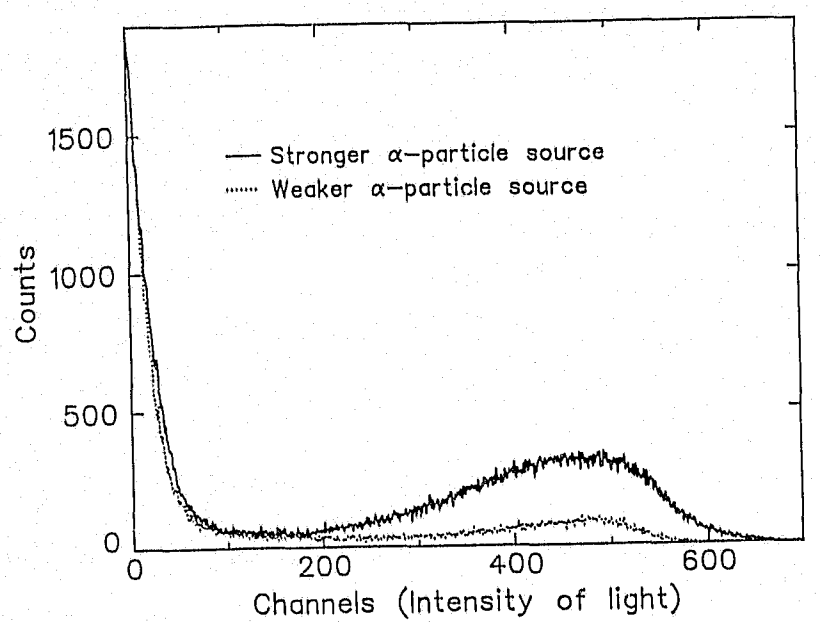


Figure 6.5. Scintillation spectra for two different intensities of 5.5 MeV α-particle sources, both incident on the same position of a synthetic diamond. Diamond: CoFe stone 6.

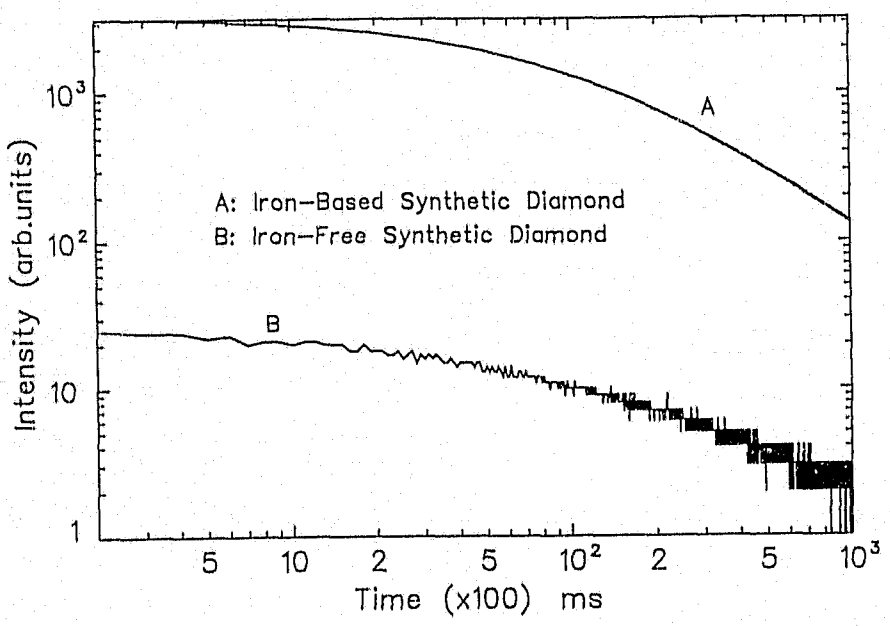


Figure 6.6. Phosphorescence decay curves from Nam et al 1989.

6.4 Conclusion

It was noted that synthetic diamonds with low single substitutional nitrogen concentration (less than 60 ppm) showed no energy resolution at all, but synthetic diamonds with single substitutional nitrogen concentration greater than 60 ppm showed some energy resolution. It is believed that the gettering agents added during the synthesis process to reduce the nitrogen concentration, create traps and possibly recombination centers, thus causing a reduced energy resolution.

The model of trapping and luminescent recombination would be similar to that proposed by Nam (1989) for thermoluminescence, the only difference being that the traps described here are shallow enough to be depopulated at room temperature. Other traps do exist but would not contribute to the phosphorescence unless the diamond was heated. These other traps do however still trap the charge carriers causing a reduced scintillation response.

Scintillation measurements of the diamonds that were used for pulse counting, indicate that these diamonds contain luminescent centers which will cause recombination of charge carriers during the pulse counting measurements, resulting in a decreased pulse counting response. As has been mentioned, trapping also occurs, and other recombination centers may exist; these reduce the scintillation response and will also be the cause of reduced pulse counting response.

In order to produce an improved scintillation or pulse counting device these centers have to be removed or their effect must be greatly reduced. Using iron free synthetic diamonds would be a starting point towards getting an improved response. No pulse counting measurements were, however, done with iron free synthetic diamond, as the only samples that could be synthesized were too small to be mechanically polished and to have contacts applied.

Chapter 7. THE NITROGEN IMPURITY

7.1 Introduction

Nitrogen is the major impurity in diamond (Berman 1979), and has been detected in concentrations of up to 0.3 % (Kaiser and Bond 1959). The nitrogen atom is found interstitially or substitutionally in place of a carbon atom, in either single or in aggregate form or combined with another defect, such as a vacancy. In synthetic Ib diamonds, the nitrogen is found predominantly in the single substitutional form (Dyer et al 1965, Clark et al 1979 and Madiba et al 1988). The nitrogen atom has five valence electrons, and when in a substitutional position in the diamond lattice, bonds tetrahedrally to the four surrounding carbon atoms (figure 7.1). This leaves one unpaired electron from the nitrogen which forms an C-N antibonding orbital (Smith et al 1959) that is evenly distributed over the four bonds (van Wyk 1988), and causes the impurity to be paramagnetic. One result is strong absorption in the ultraviolet and low wavelength visible regions which is the cause of the characteristic yellow colour of diamonds with high concentrations of single substitutional nitrogen.

The unpaired electron can interact with an external magnetic field causing a splitting of the unpaired electron's energy levels which are then further split by interaction with the nuclear spin angular momentum. The splitting of these levels can be measured by Electron Spin Resonance (ESR) techniques, and this method has been used to determine the concentrations of the paramagnetic nitrogen impurity.

The nitrogen concentration of synthetic diamonds is influenced by the materials which are included in the synthesis process. In order to produce synthetic diamonds with low nitrogen concentrations, gettering agents (e.g. Al,Ti) are included with the synthesis materials. The metal gettering agents as well as the metal catalysts appear as impurities in synthetic diamonds, and in most low nitrogen synthetic diamonds small metal inclusions are visible. The metal inclusions affect the ESR magnetic field and so create additional errors in the ESR measurements of low nitrogen synthetic diamonds. The metal inclusions are also believed (Fallon et al 1989) to be responsible for some trapping levels, and thus for some of the effects which are observed.

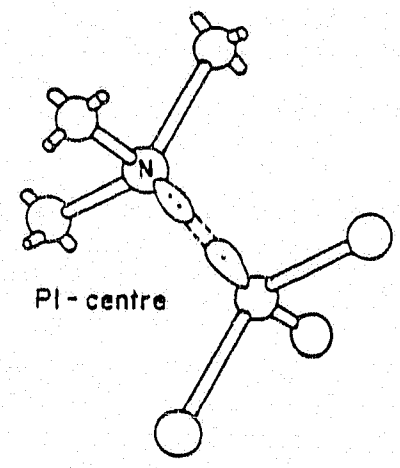


Figure 7.1. Schematic diagram of the single substitutional (paramagnetic) nitrogen impurity in the diamond lattice. Also referred to as the P1 centre.

7.2 ESR techniques and measurements

The ESR technique depends on the interaction between the spin angular momentum of an unpaired electron and an external magnetic field. This dependence causes the electron energy level degeneracy to be lifted and shifts the levels by approximately 10^{-4} eV. A hyperfine interaction also occurs between the electron spin angular momentum and the nuclear spin angular momentum, causing a further degeneracy and a shift in the electron energy levels by approximately 10^{-6}eV. These hyperfine interactions are described by the Hamiltonian

$$\mathcal{H} = \beta \hat{H} \cdot g \cdot \hat{S} + \hat{S} \cdot A \cdot \hat{I} \tag{7.1}$$

where β is the Bohr magneton $= \dfrac{e\hbar}{2mc}$

$\hat{H}$ is an external magnetic field operator,

g is the gyromagnetic ratio tensor,

$\hat{S}$ is the electron spin angular momentum operator,

A is the interaction tensor, and

$\hat{I}$ is the nuclear spin angular momentum operator.

The two interactions give rise to an electron energy level shift of

$$E_{m_S m_I} = g\,\beta\,H\,m_S + A\,m_S\,m_I\,, \tag{7.2}$$

where m_S and m_I are the electron spin and nuclear spin quantum numbers respectively. The selection rule ($\triangle m_I = 0$) allows only certain transitions between the energy levels to occur as is shown in figure 7.2.

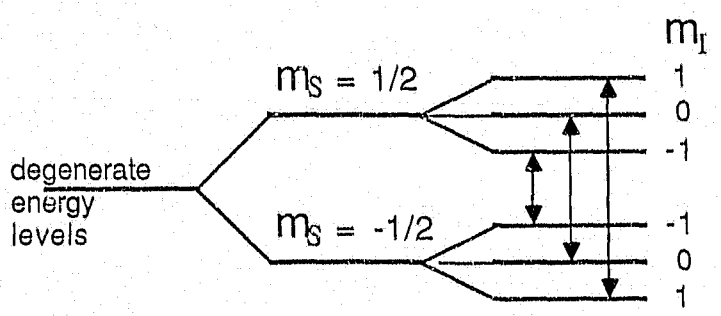


Figure 7.2. Electron energy level splitting for the single substitutional nitrogen impurity in diamond. The arrows show the allowed energy transitions. $\left(S = \frac{1}{2},\ (m_S = -\frac{1}{2}, +\frac{1}{2})\right.$ and $I = 1,\ \left.(m_I = -1, 0, +1)\right)$.

The ESR measurement is carried out by placing the sample in a magnetic field and using microwaves to excite the electrons to higher energy levels. When the microwaves are at the correct wavelength, they are absorbed by the electrons being excited. It is difficult to alter the microwave wavelength, so it is kept fixed and the magnetic field is changed linearly, thus changing the energy of the electron energy levels. The detection system of the ESR spectrometer produces a signal wnich is proportional to the slope of the absorption curve (for further details see Wertz and Bolton 1972). The ESR spectrum is thus a plot of the derivative of the absorption signal as a function of the magnetic field strength.

Typical ESR spectra for the single substitutional nitrogen impurity in diamond are shown in figure 7.3. The orientation of the diamond crystal will determine which of the of the spectra are seen or if a linear combination of the spectra is observed.

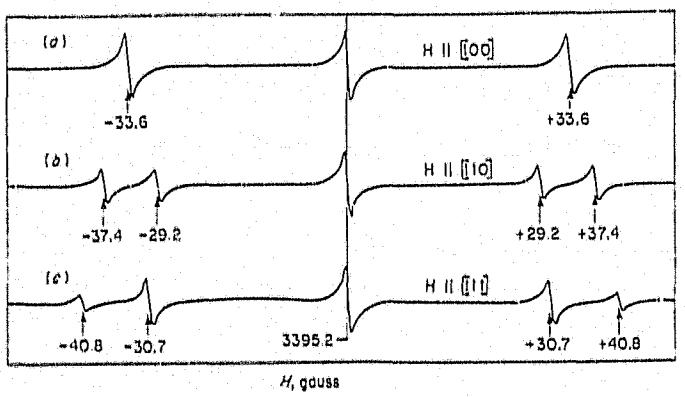


Figure 7.3. ESR spectra of single substitutional nitrogen in diamond at 22 °C. (a) $H \parallel [100]$, (b) $H \parallel [110]$, and (c) $H \parallel [111]$. (Taken from Smith et al 1959).

The area of the absorption signal represents the number of unpaired electrons, and thus, for this case, represents the single substitutional nitrogen concentration. The output curve was integrated twice to get the absorption curve area, and this area was compared with that of a diamond which had been measured under the same conditions and for which the single substitutional nitrogen concentration was known. From the comparison, the single substitutional nitrogen concentration of the unknown diamond was calculated. In figure 7.4 a typical ESR spectrum that was measured is shown and the spectrum after it was integrated twice is shown in figure 7.5.

Detection of single substitutional nitrogen concentrations of less than 20 ppm were difficult as these concentrations were at the detection limits of the ESR spectrometer. Because of this some ESR measurements were performed at temperatures of ≈ 400 °C. The unpaired electron has a shorter relaxation time at higher temperatures, causing larger microwave absorption and thus a larger ESR signal. The ESR measurements for the suite 1 and suite 2 diamonds were performed at ≈ 400 °C. All other ESR measurements were performed at room temperature. Errors also occurred in the ESR measurements of low nitrogen synthetic diamond because of high metal concentrations. The metal is introduced during synthesis to reduce the nitrogen concentration, and unfortunately results in small metal inclusions in the diamonds. Magnetic fields are induced in the metal inclusions and this alters the magnetic field around these inclusions.

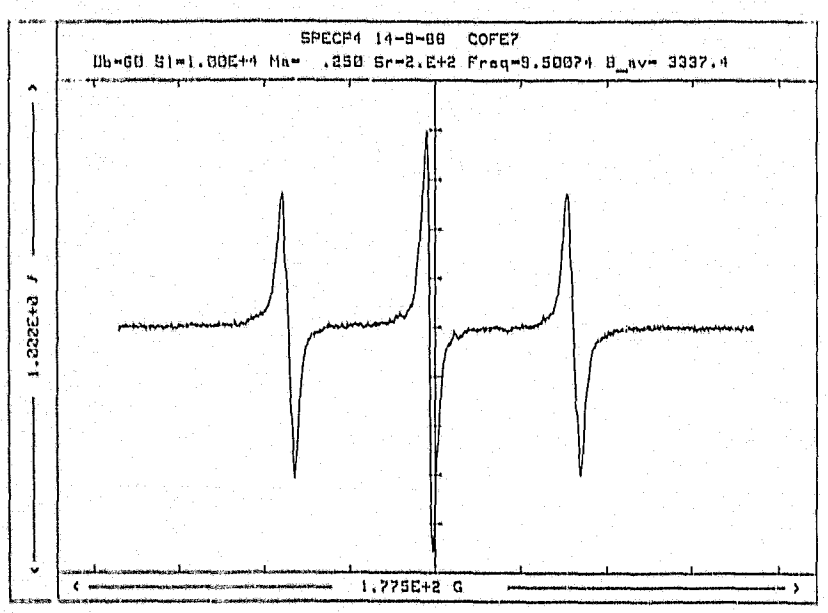


Figure 7.4. A typical ESR spectrum. Diamond: CoFe stone 6.

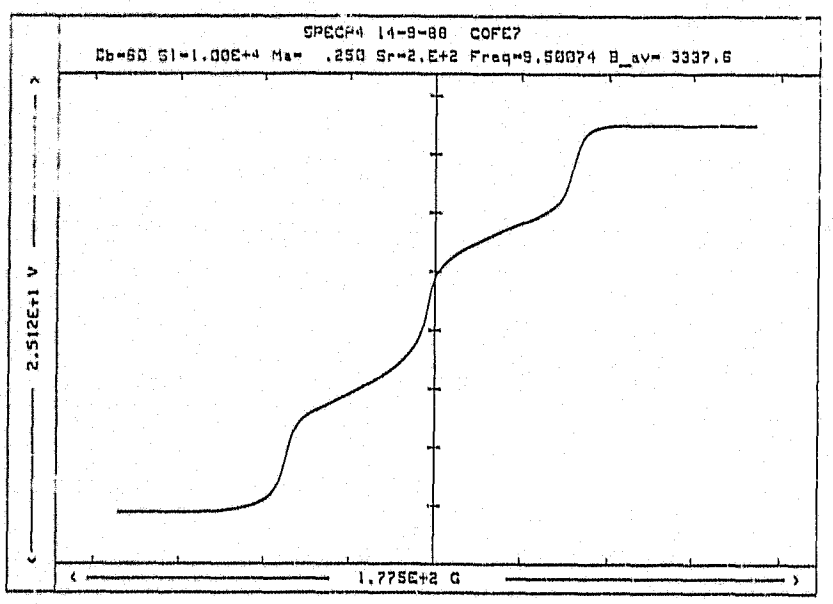


Figure 7.5. The ESR spectrum in figure 7.4 integrated twice.

7.3 Results

Differences in the single substitutional nitrogen concentration between diamonds of the same synthesis type were of the same order as errors from the ESR measurements. Thus the single substitutional nitrogen concentrations were calculated as an average for each diamond synthesis type. The average was taken over several diamonds and over several ESR measurements of each (see table 7.1).

Diamond synthesis	ESR Nitrogen concentration	Pulse counting (counts/s/mg/mGy·h^{-1})	Scintillation response ($\times 10^5$ counts per 100s)
WDD	122 ± 20 ppm	0.293 ± 0.047	0.21 ± 0.04
691	60 ± 10 ppm	0.375 ± 0.068	0.28 ± 0.06
R1069	11 ± 3 ppm	—	9.1 ± 2.7
Suite 2	7 ± 2 ppm	1.62 ± 0.13	0.39 ± 0.08
Suite 1	3 ± 1 ppm	1.97 ± 0.17	2.6 ± 0.5

Table 7.1. Average single substitutional nitrogen concentration for types of synthetic diamonds, their saturation pulse counting response and their scintillation counting response.

The pulse counting response was plotted as a function of the single substitutional nitrogen concentration (figure 7.6). The response was recorded as the number of counts per second per milligram of diamond per mGy·h^{-1}, and was recorded at a saturation voltage. Some diamonds had only carbon implanted surfaces and thus displayed the space charge effect. For diamonds that initially had carbon implants and that were later implanted with boron to make a *p*-doped surface for contact application, it was noted that the count rate recorded before the space charge took effect was the same as the normal count rate recorded after the diamond had received a boron *p*-doped contact. The count rate for diamonds with only carbon implants was thus measured before the space charge decrease started.

No response was obtained for the R1069 synthesis type of diamond, as they were found to have an impedance too low for them to be used in a pulse counting circuit. It is believed that the low resistance was due to a high metal concentration in these diamonds.

The pulse-counting response of synthetic diamonds to γ-ray dose rates increases with decreasing single substitutional nitrogen concentration (figure 7.6). This is consistent with other diamond pulse counting investigations, in which it has been shown that only diamonds with low nitrogen concentrations work as pulse counters (Konorova et al 1966, Konorova and Kozlov 1971, Kozlov et al 1975, De Blasi et al 1979, Nava et al 1979). In these investigations natural diamonds were used and reference was made to total nitrogen concentration, but no correlation between pulse counting response and nitrogen concentration was made. The concentration of single substitutional nitrogen is obviously one of the reasons why some diamonds work as pulse counters and others not. Diamonds with high single substitutional nitrogen concentrations will lose most of the radiation induced charge carriers because of recombination, and thus no detectable pulse will be observed. It is not the only reason, however, as other impurities also affect the response. The SIN 11 diamond for example, did not work as a pulse counter despite a low nitrogen concentration as it is of type IIa.

Other types of measurements have shown an increase in response as the single substitutional nitrogen concentration is reduced. Thermoluminescence measurements indicate an exponential type increase in thermoluminescence response as a function of decreasing single substitutional nitrogen concentrations (Nam et al 1987, and Eliseev et al 1988). The d.c. conduction response to radiation also increases for decreasing single substitutional nitrogen concentrations (Keddy et al 1988), and Burgemeister (1982). The latter author states specifically that synthetic diamonds must be low in nitrogen concentration to be able to work in this mode. Van Enckevort and Seal (1987) have plotted the d.c. conduction response as a function of the nitrogen concentration, and show the response increasing exponentially with decreasing nitrogen concentration.

Comparing the increase in response measured here, with that measured by thermoluminescence and by d.c. conduction, indicates that the pulse counting increase with decreasing single substitutional nitrogen concentration is less than expected. There are two possible reasons for this; the many traps in low nitrogen synthetic diamonds causing

a smaller than expected increase, but then this should have been observed in thermoluminescent measurements by Nam (1989) who used similar diamonds. Or it may have been caused by the applied voltage reducing the effect of the single substitutional nitrogen centre. With the present data it is not possible to deduce the size of the effect of the single substitutional nitrogen. All that can be said is that the pulse counting response increases with decreasing single substitutional nitrogen concentration.

The scintillation response was also plotted as a function of the single substitutional nitrogen concentration (figure 7.7). The response was taken as the total number of counts in the scintillation spectrum. The incident radiation in each case was from a ^{241}Am α-particle source, and incident through a small aperture. Since the α-particles have a penetration depth less than the thickness of any of the diamonds, the incident radiation was identical in all cases. All the spectra had many counts for low light intensities, but had no peak corresponding to the α-particle energy. The low light intensity pulses are believed to be due to trapping of charge carriers in diamond (cf. Chapter 6), and more than one pulse may have occurred for a single α-particle . Large differences in the scintillation response (of up to 50%) were observed by having the α-particles incident on different parts of the diamonds. In view of the errors in the scintillation response figure 7.7 should be viewed with some scepticism. The very high number of counts for the R1069 synthesis type diamonds is believed to have occurred because of shallow traps due to metal impurities creating many low intensity light pulses for a single α-particle . The general trend, however, indicates that scintillation response does increase with decreasing single substitutional nitrogen concentration.

The scintillation counting response also does not have the expected exponential increase with decreasing single substitutional nitrogen concentration. With the present data, it is not possible to accurately predict how the response changes with single substitutional nitrogen concentration. Because of the probable inaccuracies in the measured response, the response may in fact increase exponentially with decreasing single substitutional nitrogen concentration.

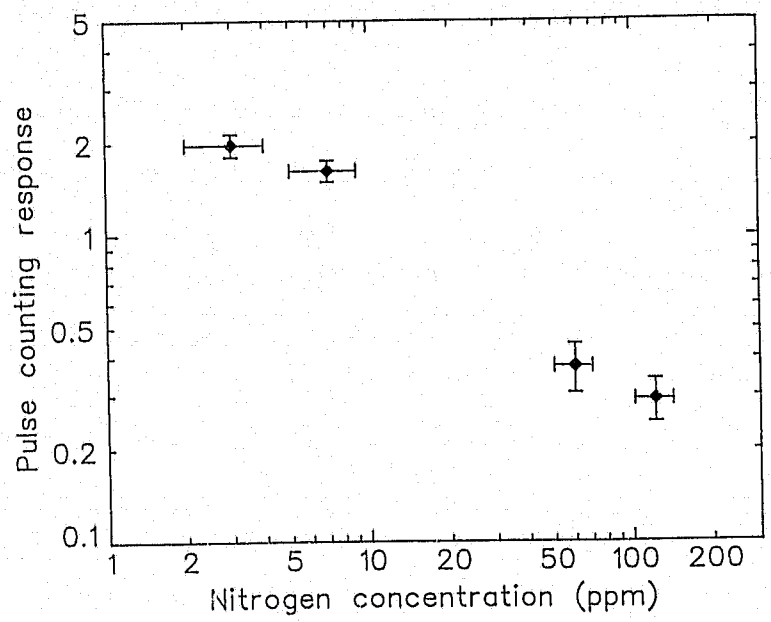


Figure 7.6. Pulse counting response as a function of single substitutional nitrogen concentration.

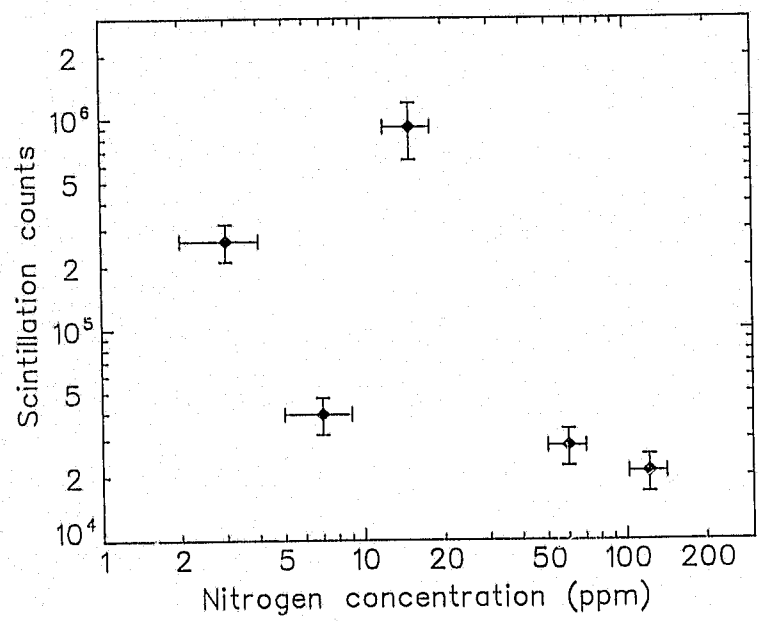


Figure 7.7. Scintillation counting response as a function of single substitutional nitrogen concentration.

7.4 Discussion

The results indicate an increase in response with decreasing single substitutional nitrogen concentration which can only be due a decrease in the conduction of charge carriers. The single substitutional nitrogen must thus act as a charge carrier recombination centre. It can not act as a electron or hole trap, as this would cause a change in response as a function of time which is not observed. This is consistent with the findings of van Enckevort and Seal (1987), who state that nitrogen acts as a charge carrier recombination centre. The recombination will shorten the lifetime of the charge carriers (Konorova et al 1966), and reduce the size of the electric pulse produced when the diamond is used in a pulse counting mode. Because of the discriminator cut off point, the reduction of the size of the recorded pulse will cause a reduction the number of counted pulses. The recombination would also reduce the d.c. conduction response and the number of charge carriers that reach luminescent centres in scintillation and thermoluminescent modes.

At present it is generally assumed that the single substitutional nitrogen level lies $\approx$ 1.7 eV below the conduction band (Vermeulen and Farrer 1975, Tatarinov 1986). To show conclusively that the single substitutional nitrogen acts as a recombination centre requires measuring the energy produced when the electron and hole recombine. This would either occur in the form of photons or the energy would be transferred to the crystal lattice (phonons). It seems unlikely that the recombination would produces photons since Nam et al (1987) have observed increasing thermoluminescence response with decreasing single substitutional nitrogen concentration. It is possible however, that the photon energy is outside the range of their photomultiplier tube. The recombination energy should be measured so that the question of the effect of the single substitutional nitrogen is answered more comprehensively. A method of measuring the energy transferred to the crystal lattice would be to use the diamond as a bolometer (Coron et al 1985). The thermal pulse produced per radiation interaction would be an indication of the energy transferred to the crystal lattice. It would be interesting to measure the bolometric response of diamond as a function of the single substitutional nitrogen concentration, assuming a suite of diamonds differing only in single substitutional nitrogen concentration could be obtained.

Chapter 8. DISCUSSION OF RESULTS

8.1 Number of pulses recorded

Only a small percentage of the incident γ-rays will interact with the diamond (figure 8.1). The number of interactions will depend on the interaction cross section for the particular energy and the thickness of diamond through which the γ-rays travel (cf. equation 2.2). The number of interactions decrease with increasing γ-ray energy, and for the ^{137}Cs γ-rays (661.2 keV), only 2.7 % will interact with a diamond 1 mm thick.

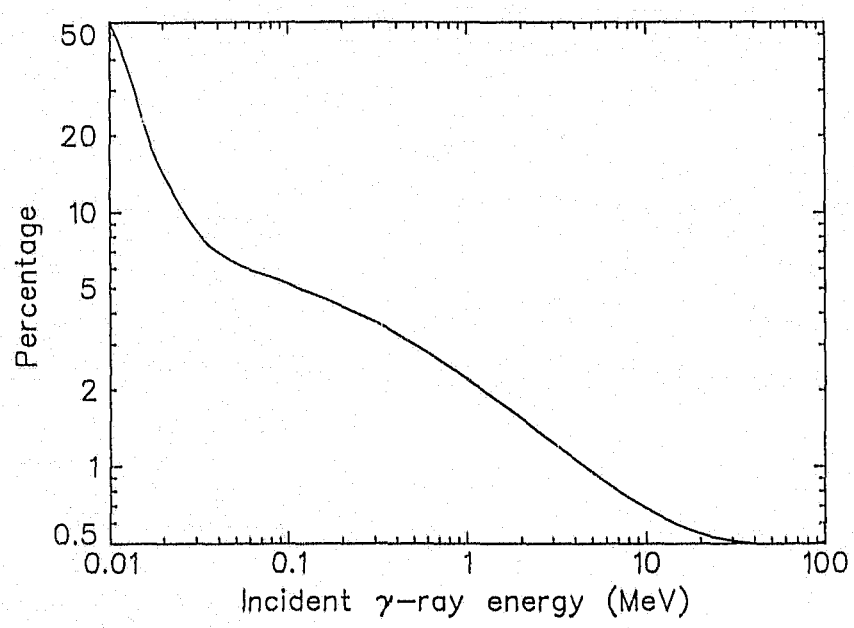


Figure 8.1. Percentage of incident γ-rays that will interact with a diamond 1 mm thick.

The Suite 2 diamond recorded ≈ 400 interactions per second at a distance 10.5 cm from the ^{137}Cs γ-ray source. The diamond is 1 mm thick and was assumed to have a 2 mm^2 surface area – the cross sectional area is larger than 2 mm^2 – but the diamond edges between the contacts are rough (not polished) reducing the volume producing a non-uniform electrical field and thus poor pulse counting response. The number of γ-rays incident per second on the diamond was calculated to be ≈ 35500 and should have resulted in ≈ 900 γ-ray interactions per second. Assuming an exponential pulse height distribution, then approximately $\frac{1}{3}$ of the number of pulses are rejected because of the discriminator setting. This indicates an experimentally observed ≈ 600 counts per second, which is in good (order of magnitude) agreement with the theoretically predicted ≈ 900 γ-ray interactions per second.

Differences may be the result of the estimated diamond surface area and of the assumed exponential shape of the pulse height distribution. The relatively good agreement indicates that the interacting γ-rays all produce recordable pulses. Thus in order to produce more sensitive diamond detectors able to measure down to normal background levels, larger diamonds are required so that a higher number of γ-ray interactions can be counted.

8.2 The space charge

The contacts have been shown to affect the development of space charge, and it has also been shown that a boron-doped surface layer used as the positive contact and a carbon ion implanted surface layer used as the negative contact were required to stop the development of space charge (cf. Chapter 4). Such contacts were first proposed by Konorova and Kozlov (1971) who describe the need for a 'hole injection' contact.

It was initially believed that the contacts formed Schottky barriers because of the metal-semiconductor junction nature of the contact (cf. Muller and Kamins 1977, chapter 2). The boron-doped surface layer is *p*-type semiconducting (Prins 1989a,b) and the carbon ion implanted surface layer is assumed to be *n*-type semiconducting (Prins 1982) – thus these contacts formed Schottky barriers biased in the same direction. For connection in a direction allowing current flow (forward biased), the metal lead from the boron doped surface layer was connected to the negative potential and the metal lead from the carbon ion implanted surface was connected to the positive potential.

When the diamond was connected in this manner, a space charge related decrease in the count rate was observed (cf. figure 4.6), but a constant count rate was observed if the diamond was connected with the opposite polarity, i.e. reverse biased (cf. section 4.3). The space charge is thus not due to the Schottky barrier nature of the contacts. It is believed that the contacts do form Schottky barriers, but their effect is negligible in comparison to the effect of the trapped space charge. The development of space charge is not stopped solely by the boron-doped surface layer, since a space charge related decrease was observed for two such contacts (cf. section 4.3).

The space charge is trapped by shallow hole traps which are able to populate and depopulate at room temperature (cf. section 5.4, Willardson and Danielson 1950). The space charge will depend on the concentration of shallow traps, will vary thus from diamond to diamond and will vary within a single diamond. It is interesting to note that a natural IIa diamond (SIN 12), without implantation, displayed only a small space charge decrease (figure 8.2), indicating that the space charge decrease does not result solely from the type of contacts. It is also interesting to note that the space charge decrease observed while using the SIN 12 diamond depended on the high voltage polarity (figure 8.2), indicating an unsymmetrical trapping of space charge. Even with the boron-doped and carbon ion implanted contacts, a space charge related decrease was observed for a high nitrogen diamond (figure 8.3). Mukhachev et al (1983,1984) have also reported varying count rates for diamonds with the contacts described by Konorova and Kozlov (1971). Thus contacts that suppress space charge do not work perfectly for all diamonds. It is therefore concluded that suppression of space charge depends on both the trapping centres and the contacts.

Konorova and Kozlov have reported that the 'hole injection' nature of these contacts is the reason for the suppression of the space charge. Space charge electrons are trapped close to the positive contact, and the injection of holes through the boron-doped contact is believed to cause the removal of the trapped electrons, resulting in no negative space charge accumulation. Models of polarization and hole injection have been proposed by Mukhachev et al (1983,1984). They propose different polarities of space charge occurring in different regions of the diamond, and depending on the type (their own classification) of diamond used. It is believed that differing trapping concentrations in different regions of the diamond will be the cause of different space charge distributions. Mukhachev et al (1983,1984) in conclusion agree with Konorova and Kozlov (1971) about the hole

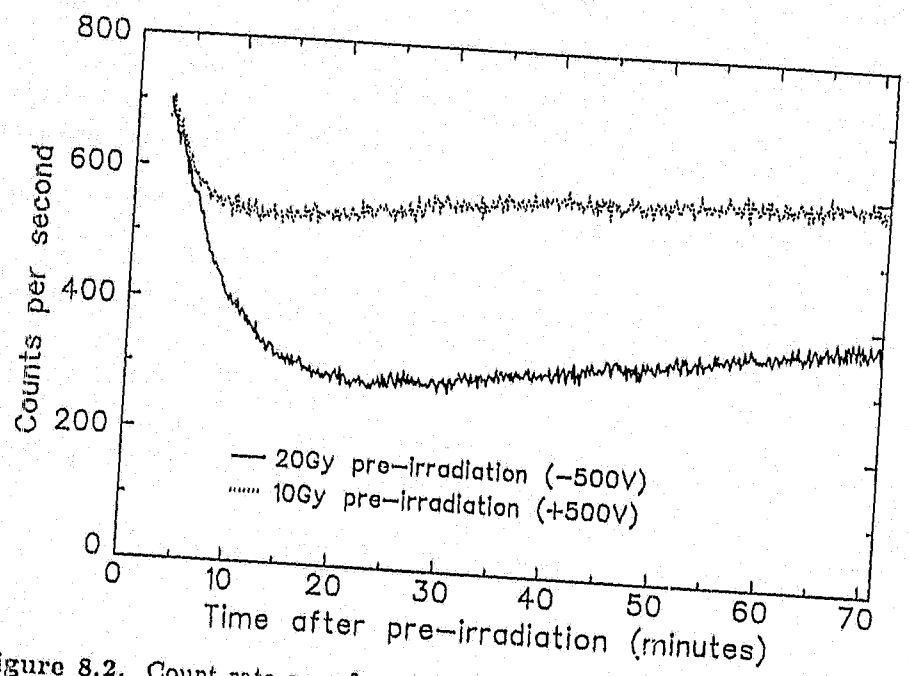


Figure 8.2. Count rate as a function of the time after pre-irradiation. Diamond: SIN 12.

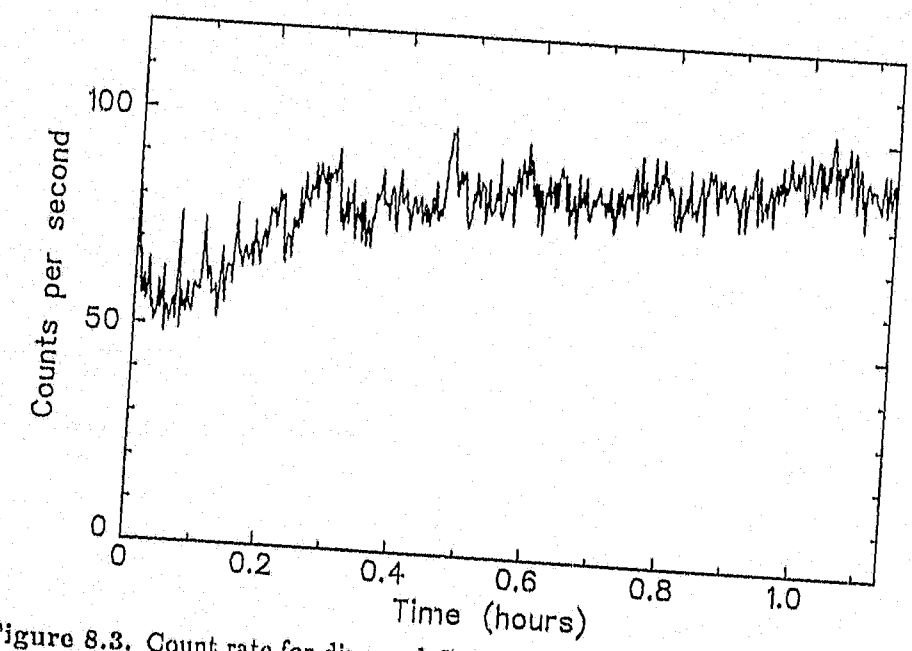


Figure 8.3. Count rate for diamond CoFe stone 6 with boron-doped and carbon ion implanted contacts.

injection mechanism but also mention that the correct combination of electron and hole traps are also required to establish the necessary space charge structure in diamond. It is believed that this conclusion is correct, i.e. that a hole injection contact and a necessary combination of trapping centres (or no trapping centres) are required to produce a space charge free pulse counting diamond.

The space charge trapping is not completely understood and, in order to do so, the space charge trapping centres should be investigated and if possible removed. Methods of investigating these centres involve Space Charge Limited Current and Thermally Stimulated Current techniques (de Blasi et al 1979 and Mukhachev et al 1984). The space charge trapping centres can also be probed using monochromatic light (cf. Chapter 5).

8.3 Effect of potential across diamond (Hecht function)

The Hecht function (equation 2.12) describes the charge collection efficiency for charge carriers produced in a crystal subject to an electric field. The charge collection efficiency depends on charge carrier mobilities and lifetimes, and on the magnitude of the electric field. The electric field in diamond pulse counters was produced by the high voltage applied across the contacts and was thus known. The count rate was used as a measure of the charge collected, and known values of the charge carrier mobilities and lifetimes were obtained from Canali et al (1979). The only fitting parameter used was an arbitrary constant, k, which describes the ratio between the charge produced and the number of incident γ-rays, i.e.

$$\begin{aligned} Count\,Rate = & k\{s - W_e[1 - exp(-s/W_e)]\} \\ & + k\{s - W_h[1 - exp(-s/W_h)]\} \end{aligned} \tag{8.1}$$

where s is the length between the diamond contacts, $W_e = \mu_e \tau_e V/s$ ($W_h = \mu_h \tau_h V$) is the electron (or hole) path length, μ_e (μ_h) is the electron (or hole) mobility, τ_e (τ_h) is the electron (or hole) lifetime and V the potential applied across the diamond contacts. The constant, k, should be the same for all the points plotted in figure 8.4, as the same diamond, dose rate and radiation source were used in each case. The suite 2 diamond was employed as it did not display a space charge related decrease. The electric field created by the potential across the contacts should thus be the only field affecting the charge carriers.

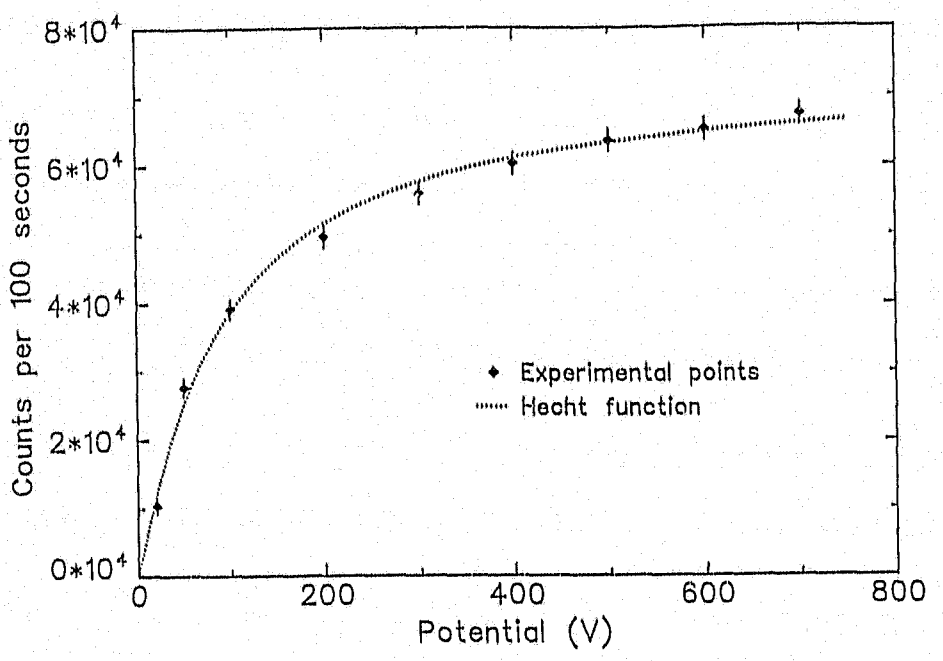


Figure 8.4. Hecht function fit for the pulse counting rate as a function of potential across the diamond contacts. Diamond: Suite 2.

The Hecht function fit (figure 8.4) for the suite 2 diamond with a boron *p*-doped and a carbon ion implanted contact measured after pre-irradiation and after the initial increase in count rate, is in excellent agreement with the experimental points. The excellent agreement indicates that the potential across the diamond was the same as the potential producing the electric field; i.e. the electric field was not reduced by the development of space charge and no significant voltage drop occurred across the contacts. Compare this to the shape of the count rate versus potential across the contacts for a diamond with no implantation used for the contacts (figure 3.5); this shape indicates that the effective electric field is smaller than the electric field produced by the potential applied across the contacts.

The only fitting parameter used was the constant k, and known values for the charge carrier mobilities ($\mu_e = 2400\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$ and $\mu_h = 2100\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$) and lifetimes in a region measured by Canali et al (1979) ($\tau_e = 15 - 50$ ns, best fit for $\tau_e = 22$ ns and $\tau_h = 10 - 30$ ns, best fit for $\tau_h = 15$ ns) were used. Thus the values used for the Hecht function are in agreement with the charge carrier mobilities and lifetimes measured by Canali et al (1979). The problem of charge carriers recombining or being trapped is accounted for by the charge carrier lifetimes. It would be interesting to observe how the

charge carrier lifetimes differ between different diamonds. It would be expected that poor pulse counting diamonds would have shorter charge carrier lifetimes as opposed to longer lifetimes for better pulse counting diamonds.

A possible discrepancy in the above analysis is that the count rate was used as a measure of the charge collected. It may have been more correct to use the dose rate response described by equation 4.2 as a measure of the charge collected, but it is believed that this is unnecessary as a single (^{137}Cs) γ-ray source was used (cf. section 4.7). It will not be possible to know how accurately the count rate represents the charge collection efficiency until the reason for the exponential pulse height distribution is known or until the expected Compton pulse height distribution is obtained.

8.4 The shape of the pulse height spectrum

There are two possible reasons for the observed pulse height distribution. One possible reason is that the Compton electron, highly energetic because of energy transferred from the scattered γ-ray, has sufficient kinetic energy to escape the diamond crystal. Only a part of the energy transferred to the electron will go into exciting other electrons from the valence band to the conduction band, and the remaining energy will be lost with the electron. The recorded pulse will be smaller than the pulse expected if all the energy was absorbed by the diamond. This process will depend on the size of the diamond (the larger the diamond the smaller the probability of the electron escaping), and for each interaction will depend on the position in the diamond of the interaction and on the energy and momentum transferred to the Compton electron. It is believed, however, that this is not the reason for the pulse height distribution, since Konorova and Kozlov (1971) and Kozlov et al (1975) have observed good resolution for α-particle detection. Their diamonds were generally smaller than the diamonds described in this thesis, for which no energy resolution was obtained for α-particle detection but instead exponential pulse height distributions were obtained (cf. section 4.6). If the exponential α-particle pulse height distribution results from the loss of energetic electrons, it would not be expected that Konorova and Kozlov (1971) and Kozlov et al (1975) would have been able to obtain α-particle resolution with diamonds smaller than those described here. It is believed that Compton electrons do escape from the diamond crystal but that this is not the major effect responsible for the exponential pulse height distribution.

Kennedy (1959) has placed a scintillation material around a pulse counting diamond and investigated coincident pulses from the diamond and the scintillator, he has shown that the energy adds to the energy of the incident β-particles. The range of an energetic electron in diamond is approximately

$$R(\text{cm}) = 0.116E^{1.38} \quad \text{for } E < 0.8 \text{ MeV} \tag{8.2}$$

$$R(\text{cm}) = 0.154E - 0.038 \quad \text{for } E > 0.8 \text{ MeV} \tag{8.3}$$

for an electron of energy E (Berman 1965, p. 413). Thus electrons absorbing energy due to Compton scattering of ^{137}Cs γ-rays ($E < 477$ keV) will have a range of up to 0.04 cm – approximately half the average thickness of the diamond used.

The other possible reason is trapping and recombination of charge carriers from radiation induced pulses resulting in smaller pulses, a reason also proposed by Kennedy (1959), Champion and Wright (1959) and Afanas'eva and Konorova (1964). It is known that the number of charge carriers in the radiation induced pulses are reduced because of charge carrier recombination at recombination centres (cf. Chapter 7) and luminescent centres (cf. Chapter 6). It is believed that trapping of charge carriers occurs at traps which populate and depopulate at room temperature. The charge carriers are believed to be released from the traps at later stages, leaving traps unoccupied to trap further charge carriers, and that the charge carriers are released too late to form part of the radiation induced pulse from which they were trapped. The inhomogeneous distribution of trapping and recombination centres (cf. section 6.3) will cause different percentages of charge carriers to be trapped, depending on where in the diamond the radiation induced pulse originated. This is believed to lead to the exponentially shaped pulse height spectrum.

A change in the shape of the pulse height spectrum was observed for the SIN 12 diamond after pre-irradiation (figure 8.5). With no pre-irradiation, trapping by the 2.2 eV trapping level occurred (cf. Chapter 5) and the pulse height spectrum was exponential in shape. After pre-irradiation, trapping by the 2.2 eV level did not occur, and pulse height spectrum was more rectangular in shape (figure 8.5). The SIN 12 diamond showed this effect to the greatest extent, and had the smallest trapping level concentration of all the diamonds tested (SIN 12 displayed the smallest space charge decrease of all the diamonds tested without implantation and had a large pulse counting

response). This observation gives substance to the argument that trapping of charge carriers is responsible for the exponential pulse height distribution and that the removal of trapping and recombination centres will result in the expected Compton pulse height distribution. The pulse height distribution of the SIN 12 diamond after pre-irradiation is not the expected Compton distribution, because other levels exist which cause trapping and recombination of charge carriers.

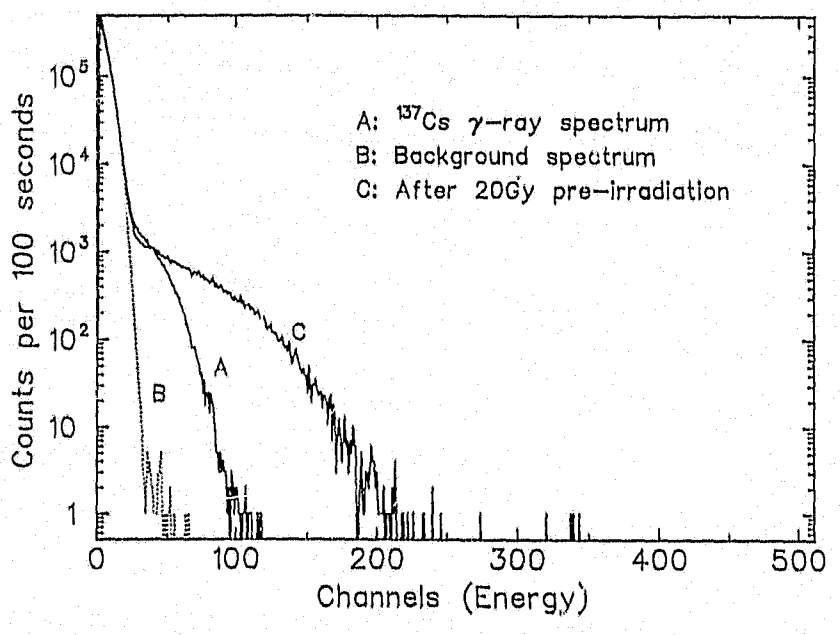


Figure 8.5. Pulse height spectra for the SIN 12 diamond.

All pulse counting measurements thus depend on the concentration of traps and recombination centres, the relative trap densities and locations and the recombination centre distributions. Since recombination and trapping densities vary between diamonds, the pulse counting response should vary from diamond to diamond – as it indeed does. The advantage of using synthetic diamonds is that they are reproducible and so allow for more consistent results when using different diamonds of the same type. Hopefully, this should allow more agreement and understanding of the defects present in diamond.

Kozlov and Konorova (1972) have specified that diamonds required for pulse counting should have a distance betweer the contacts less than the drift length of the charge carriers (i.e. about 0.1 to 0.3 mm). The diamonds used had a thickness of about

1 mm. The effect of the thickness should be investigated since it may affect the recorded pulse height distribution.

The dose rate response (cf. section 4.7, equation 4.2) indicates that the dose rate recorded is proportional to the size of the recorded pulses. This should not be so if part of the charge is lost due to recombination and trapping of charge carriers. There is thus a contradiction between the dose rate response and the model of trapping and recombination causing the observed pulse height distribution. This might be explained by the number of charge carriers being trapped or recombined being somehow proportional to the number that are produced. The apparent contradiction should however be the subject of further investigations.

8.5 Energy dependance of the pulse height distribution

It was observed that the slope of the semi-log representation of the pulse height distribution decreased with increasing radiation energy (cf. section 4.5).

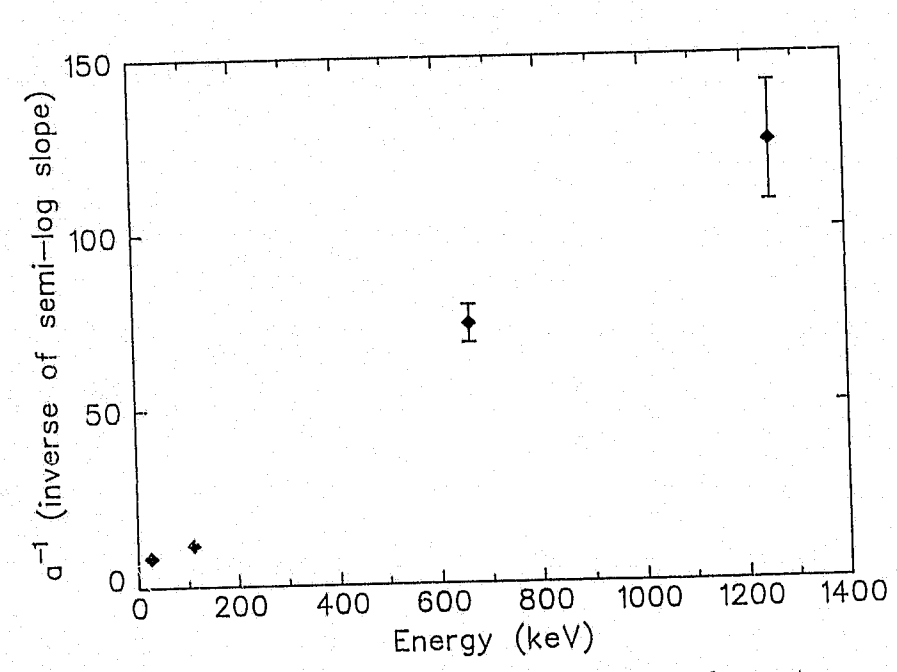


Figure 8.6. Inverse of the semi-log slope of the pulse height spectrum as a function of radiation energy.

A plot was made of the inverse slope of the semi-log pulse height representation as a function of the radiation energy, i.e. $1/a$ from the fitted function

$$p = ke^{-ac} \tag{8.4}$$

where p is the probability of an event occurring in channel c, and k and a are constants of proportionality. Figure 8.6 indicates linearity. This is encouraging as it indicates an energy dependence of the pulse height spectrum, and gives insight into the energy dependence of the process or processes that cause the observed exponential pulse height distribution.

Chapter 9. CONCLUSIONS

9.1 Summary of results

A pulse counting diamond detector has been developed which has a linear γ-ray dose rate response over six orders of magnitude – in the region of 1 μGy·h^{-1} to 1 Gy·h^{-1}. The response has also been shown to be γ-ray energy independent. The space charge effect, which has hindered many previous attempts to develop pulse counting diamond detectors, has been eliminated by the construction of special electrical contacts. The diamond surface connected to the positive potential is ion implanted with boron, annealed and etched to create a *p*-doped conducting surface layer. The surface used as the negative contact is ion implanted with carbon. The pulse counting response was shown to increase by priming the diamond with a large γ-ray, X-ray or ultraviolet radiation dose. Exposure of a primed diamond to light returned it to an unprimed state, and the pulse counting diamonds were thus not exposed to light once primed, or if used for a pulse counting measurement.

A trapping level of energy 2.2 $\pm$ 0.1 eV has been measured. The level was 'filled' by trapping of charge carriers during priming and 'depopulated' by exposure to ambient light. The level was not observed in synthetic diamonds with a single substitutional nitrogen concentration greater than 60 ppm. Shallow hole trapping levels (less than 1.55 eV above the valence band) were postulated and are believed to be responsible for the trapping of the space charge and the initial increase in the pulse counting rate after pre-irradiation. The method for characterizing these trapping levels was developed and can be used to characterize other trapping levels in pulse counting diamonds.

The pulse counting and scintillation response of synthetic diamonds were both found to increase with decreasing single substitutional nitrogen concentration, and it was thus concluded that the single substitutional nitrogen impurity acts as a charge carrier recombination centre. It has also been shown that the trapping and recombination centre density is inhomogeneous, and thus the radiation response in any of the possible modes varies as a function of position in the diamond, and varies from diamond to diamond.

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No γ-ray or α-particle energy resolution was possible using these pulse counting diamond detectors, and it is believed that this was due to the presence of charge carrier trapping and recombination centres within the diamonds.

9.2 Ideas for further research

It is believed that the pulse counting response of diamond radiation detectors can be improved, and several ideas are proposed for further research. The ultimate goal would be to produce a diamond free of impurities and defects which cause a decrease in the pulse counting response due to trapping and recombination centres reducing the number of charge carriers. Using the diamond in a scintillation mode requires luminescent centres, and luminescent and trapping centres are required for a thermoluminescent diamond. Thus different types of diamonds are required for the different modes of radiation detection. Synthetic diamonds will have to be used, so that sufficient diamonds of the correct type can be obtained.

The relationship between the various synthesis materials and their effect on the pulse counting response should be investigated. It is believed that some of the synthetic materials cause the creation of charge carrier trapping and recombination centres. Methods of characterizing trapping levels and identifying recombination centres have been established and are discussed in this thesis. These methods should be employed along with the testing of diamonds with differing concentrations of individual synthesis materials to establish the effect of the individual synthesis material on the pulse counting response. Once a material which causes trapping or recombination centres in the diamond is identified, the synthesis conditions and/or materials must be altered so that the effect or material is reduced and if possible eliminated. It is believed that this will be a long and difficult procedure and will involve the testing of many diamonds. For example, the single substitutional nitrogen impurity acts as a recombination centre (cf. Chapter 7), and thus the concentration of nitrogen must be reduced. This is done at present by adding gettering agents to the synthesis materials – which are believed to effect the pulse counting response. The process becomes complicated as compromises between the nitrogen and gettering agent concentrations will have to be found.

The effect of iron should be investigated. Scintillation response from iron free synthetic diamonds was very encouraging, because these were the only scintillation

synthetic diamonds to show reasonable energy resolution (cf. Chapter 6). It was not possible to use the iron free synthetic diamonds in a pulse counting mode, because they were too small for contact application. It is hoped that it will become possible to synthesize iron free diamonds, large enough to be tested as pulse counting detectors.

The effect of the size and shape of the diamonds should be investigated. Kozlov and Konorova (1972), specified that the diamonds required for pulse counting should have a distance between the contacts less than the drift length of the charge carriers, i.e. about 0.1 to 0.3 mm. The effect of distance between the contacts on the pulse counting response should be measured. No such measurements were carried out and all the diamonds tested had a thickness of larger than 1 mm. The measurement should be carried out by starting with a diamond $\approx$ 1 mm thick, then repeatedly carrying out a pulse counting measurement and then polishing the diamond $\approx$ 0.1 mm thinner, until only 0.1 to 0.2 mm remain. The effect of the volume of the diamond should be investigated, as energy transferred from the interacting radiation to an electron may be lost if the highly energetic electron escapes the diamond crystal (cf. section 8.4). It is believed that to measure lower dose rates larger volume diamonds are required (cf. section 8.1). The shape of the diamond may also be a cause of poor response because of weak electric fields at the rough diamond edges between the contacts. Thus the effect of the shape should be investigated, i.e. pulse counting diamonds with polished faces between the polished contact faces should be tested.

Scintillation radiation detection using diamond should be investigated to a greater extent, as it is believed that scintillation diamond detectors are better suited to in vivo measurements than are pulse counting diamond detectors. The scintillation diamond can be connected to a photomultiplier tube by means of a fibre optic cable (Nam et al 1989), making an extremely small and non-toxic radiation detection probe. The pulse counting diamond detectors require a high voltage and are thus a potential danger when used for in vivo measurements. A preamplifier is also required close to the pulse counting diamond, it would require space and would not be tissue equivalent. It has already been shown that good energy resolution is possible with scintillation diamonds, and testing procedures for scintillation diamond detectors are fairly simple in comparison to testing pulse counting diamonds (electrical contacts are not required). For health physics applications it is believed that pulse counting diamond detectors have an advantage, because a small portable detector can be produced. The radiation

detector which could be carried by a radiation worker, would be able give an instant reading of the radiation dose rate and/or accumulated dose and could give a warning if specific limits were exceeded.

Appendix A : LIST AND DESCRIPTION OF DIAMONDS

The diamonds are listed by name in alphabetical order:

('Thickness' refers to the distance between the polished faces used as the electrical contacts, and 'Nitrogen' refers to the single substitutional nitrogen concentration).

Name: 691 stone 4
Type: Synthetic, NiFe solvent/catalyst
Mass: 18.04 ± 0.01 mg
Thickness: 1.301 ± 0.0005 mm
Nitrogen: 60 ± 10 ppm
Contacts: Silver epoxy to carbon implanted and first attempted boron implant.
Comments: Behaved like diamond with two carbon implants.

Name: 691 stone 6
Type: Synthetic, NiFe solvent/catalyst
Mass: 18.12 ± 0.01 mg
Nitrogen: 54 ± 10 ppm
Contacts: None.
Comments: Not used in pulse counting mode.

Name: 691 stone 7
Type: Synthetic, NiFe solvent/catalyst
Mass: 15.27 ± 0.01 mg
Nitrogen: 50 ± 15 ppm
Contacts: None.
Comments: Not used in pulse counting mode.

Name: **CoFe stone 4**
Type: Synthetic WDD, CoFe solvent/catalyst
Nitrogen: 128 ± 25 ppm
Contacts: Silver epoxy to boron and carbon implanted faces.
Comments: Problems with space charge effect, similar to carbon implanted faces.

Name: **CoFe stone 5**
Type: Synthetic WDD, CoFe solvent/catalyst
Thickness: 0.90 ± 0.05 mm
Nitrogen: 122 ± 20 ppm
Contacts: Originally silver epoxy to polished faces, then silver epoxy to carbon implanted surfaces.
Comments: Problems because of space charge, pre-irradiation has almost no effect.

Name: **CoFe stone 6**
Type: Synthetic WDD, CoFe solvent/catalyst
Mass: 18.00 ± 0.02 mg
Thickness: 1.074 ± 0.0005 mm
Nitrogen: 122 ± 20 ppm
Contacts: Silver epoxy to boron *p*-doped and carbon implanted surfaces.
Comments: Good counter takes approximately one hour to increase to saturation value, pre-irradiation has almost no effect.

Name: **CoFe stone 7**
Type: Synthetic WDD, CoFe solvent/catalyst
Mass: 15.27 ± 0.01 mg
Nitrogen: 130 ± 25 ppm
Comments: No contacts, not used in pulse counting mode.

Name: **CoFe stone 10**
Type: Synthetic WDD, CoFe solvent/catalyst
Contacts: Silver epoxy to boron *p*-doped and carbon ion implanted.
Comments: Polished face between two polished contact faces, for α-particle detection (cf. section 4.6).

Name: **D11**
Type: Synthetic WDD, CoFe solvent/catalyst
Contacts: Drukker contacts to carbon implanted surfaces.
Comments: Problems with space charge effect.

Name: **D11**
Type: Synthetic WDD, CoFe solvent/catalyst
Contacts: Drukker contacts to carbon implanted surfaces.
Comments: Problems with space charge effect.

Name: **D21**
Type: Synthetic WDD, CoFe solvent/catalyst
Contacts: Drukker contacts to polished surfaces.
Comments: Problems with space charge effect.

Name: **D22**
Type: Synthetic WDD, CoFe solvent/catalyst
Contacts: Drukker contacts to polished surfaces.
Comments: Good counter, problems with space charge effect.

Name: **D31**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to carbon implanted surfaces.
Comments: Problems with space charge effect.

Name: **D32**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to carbon implanted surfaces.
Comments: Problems with space charge effect.

Name: **D33**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to carbon implanted surfaces.
Comments: Problems with space charge effect.

Name: **D41**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to polished surfaces.
Comments: Short circuits, does not work as a counter.

Name: **D42**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to polished surfaces.
Comments: Short circuits, does not work as a counter.

Name: **D43**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to polished surfaces.
Comments: Poor counter, severe space charge.

Name: **D61**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to laser scribed surfaces.
Comments: Short circuits, does not work as a counter.

Name: **D62**
Type: Synthetic 691, NiFe solvent/catalyst
Contacts: Drukker contacts to laser scribed surfaces.
Comments: Short circuits, does not work as a counter.

Name: **Original 691**
Type: Synthetic, NiFe solvent/catalyst
Mass: 71.0 ± 0.1 mg
Thickness: 1.61 ± 0.01 mm
Nitrogen: 61 ± 10 ppm
Contacts: Silver epoxy to carbon ion implanted 100 faces.
Comments: High count rate because of large size, displayed large space charge decrease.

Name:	**R1069 stone 1**
Type:	Synthetic, CoFe solvent/catalyst, Al gettering agent
Mass:	12.08 ± 0.01 mg
Thickness:	1.0387 ± 0.0002 mm
Nitrogen:	15 ± 5 ppm
Contacts:	None.
Comments:	Not used for pulse counting.

Name:	**R1069 stone 2**
Type:	Synthetic, CoFe solvent/catalyst, Al gettering agent
Mass:	10.01 ± 0.01 mg
Thickness:	0.9585 ± 0.0002 mm
Nitrogen:	16.5 ± 5 ppm
Contacts:	Silver epoxy to the polished faces.
Comments:	Shorting, not able to use as a pulse counter, i.e. impedance is too low.

Name:	**R1069 stone 3**
Type:	Synthetic, CoFe solvent/catalyst, Al gettering agent
Mass:	4.91 ± 0.01 mg
Thickness:	0.3817 ± 0.0002 mm
Nitrogen:	15 ± 5 ppm
Contacts:	None.
›mments:	Not used for pulse counting.

ᴺ ᵐe:	**R1069 stone 4**
ɹype:	Synthetic, CoFe solvent/catalyst, Al gettering agent
Mass:	4.10 ± 0.01 mg
Thickness:	0.3788 ± 0.0002 mm
Nitrogen:	11 ± 5 ppm
Contacts:	Silver epoxy to the polished faces.
Comments:	Shorting, not able to use as a pulse counter, i.e. impedance is too low.

Name: **SIN 3**

Type: Natural IIa

Mass: 91.00 ± 0.02 mg

Thickness: 0.5800 ± 0.0002 mm

Contacts: Silver epoxy to polished surfaces.

Comments: Good counter, needs pre-irradiation, problems with space charge.

Name: **SIN 11**

Type: Natural IIa

Contacts: Silver epoxy to polished surfaces.

Comments: Very bad counter, just works when exposed to white light.

Name: **SIN 12**

Type: Natural IIa

Mass: 22.08 ± 0.02 mg

Thickness: 0.22 ± 0.02 mm

Contacts: Silver epoxy to polished surfaces.

Comments: Good counter, needs pre-irradiation, small problem with space charge.

Name: **Suite 1**

Type: Synthetic, NiFe solvent/catalyst and Al, Ti gettering agents and Ni_2B

Mass: 37.56 ± 0.05 mg

Thickness: 1.60 ± 0.01 mm

Nitrogen: 3 ± 1 ppm

Contacts: Worked with silver epoxy to polished diamond faces, but caused a short circuit once implanted with carbon.

Comments: Displayed a very high count rate, but large space charge decrease. Shorting is believed to be due to the presence of boron.

Name: **Suite 1 no. 3**

Type: Synthetic, NiFe solvent/catalyst and Al, Ti gettering agents and Ni_2B

Mass: 31.93 ± 0.02 mg

Thickness: 1.6740 ± 0.0002 mm

Nitrogen: 3 ± 1 ppm

Contacts: Silver epoxy to polished (100) faces.

Comments: Shorting, would not work as pulse counter.

Name: **Suite 2**

Type: Synthetic, NiFe solvent/catalyst, Al gettering agent

Mass: 9.37 ± 0.01 mg

Thickness: 0.977 ± 0.001 mm

Nitrogen: 7 ± 2 ppm

Contacts: Originally silver epoxy to polished faces, then silver epoxy to boron *p*-doped and carbon implanted surfaces.

Comments: Best counter, no space charge, needs pre-irradiation.

Name: **Suite 2 no. 2**

Type: Synthetic, NiFe solvent/catalyst, Al gettering agent

Mass: 15.61 ± 0.02 mg

Thickness: 1.0464 ± 0.0004 mm

Nitrogen: 7 ± 2 ppm

Contacts: Silver epoxy to polished (100) faces.

Comments: Displayed space charge related decrease in pulse counting rate.

Name: **Suite 2 no. 3**

Type: Synthetic, NiFe solvent/catalyst, Al gettering agent

Mass: 13.81 ± 0.02 mg

Thickness: Tapered 0.866 to 0.820 mm

Nitrogen: 7 ± 2 ppm

Contacts: Silver epoxy to both boron *p*-doped (111) faces.

Comments: Displayed small space charge decrease.

Name: **Suite 2 no. 4**

Type: Synthetic, NiFe solvent/catalyst, Al gettering agent

Thickness: 0.911 ± 0.002 mm

Nitrogen: 7 ± 2 ppm

Contacts: Silver epoxy to boron p-doped and carbon implanted surfaces.

Comments: Polished face between polished contact faces for detection of α-particles (cf. section 4.6).

Thermoluminescent spectra of the different diamonds

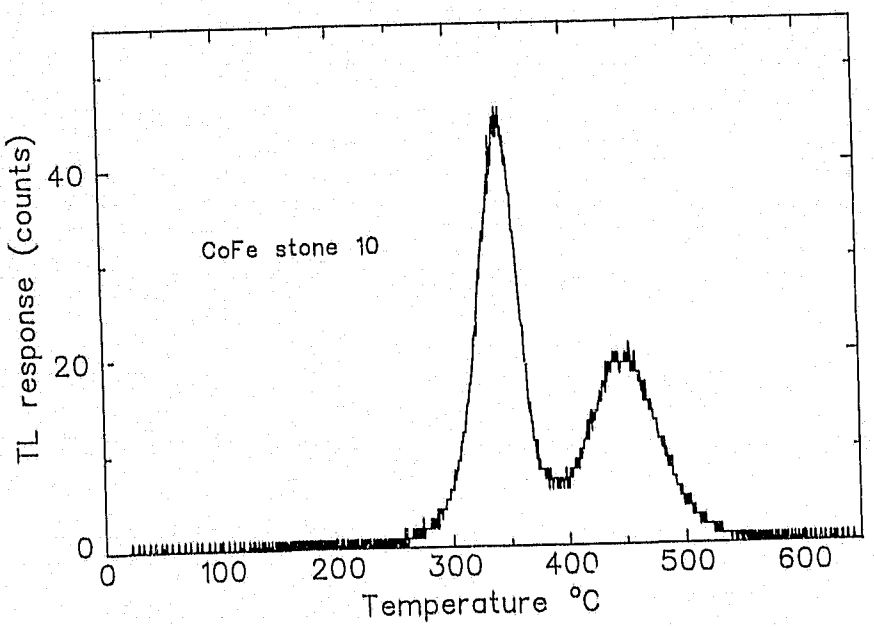


Figure A.1. Thermoluminescent spectrum of CoFe stone 10.

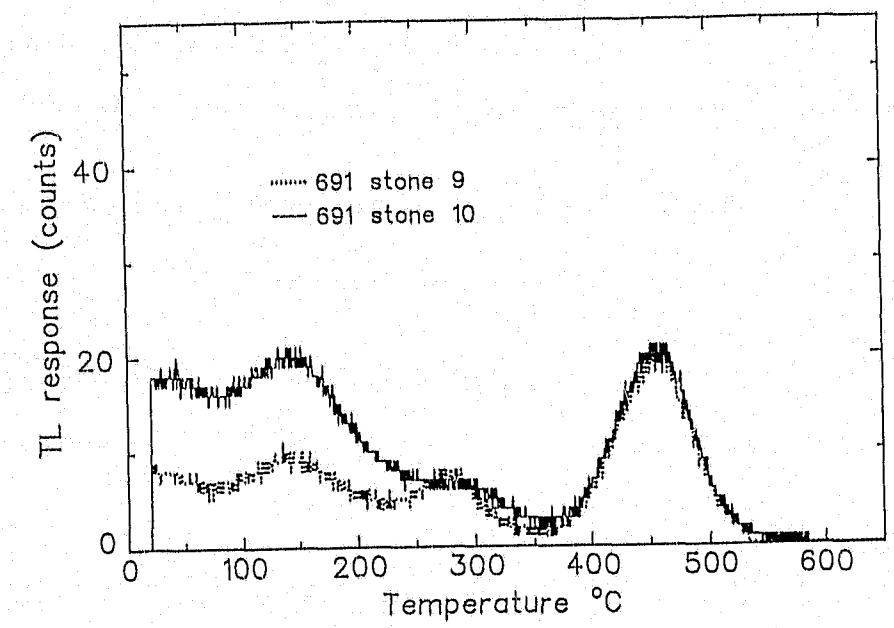


Figure A.2. Thermoluminescent spectrum of 691 stones 9 and 10.

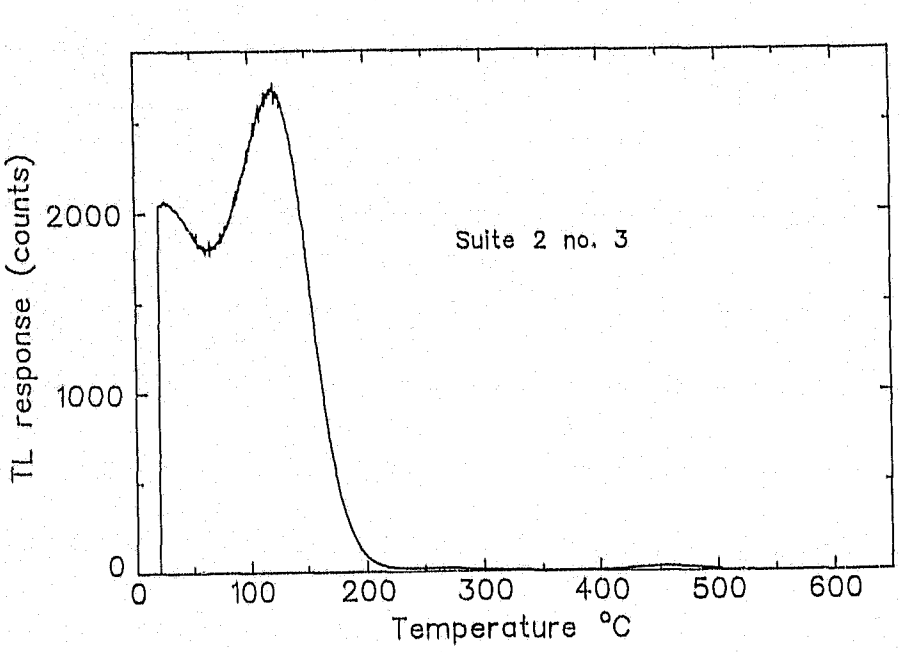


Figure A.3. Thermoluminescent spectrum of Suite 2 no. 3.

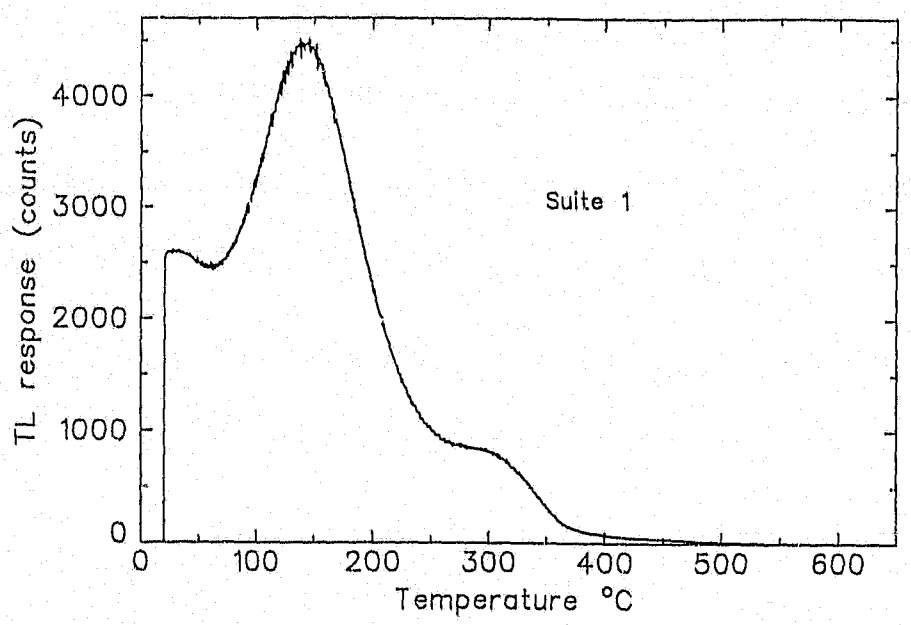


Figure A.4. Thermoluminescent spectrum of Suite 1.

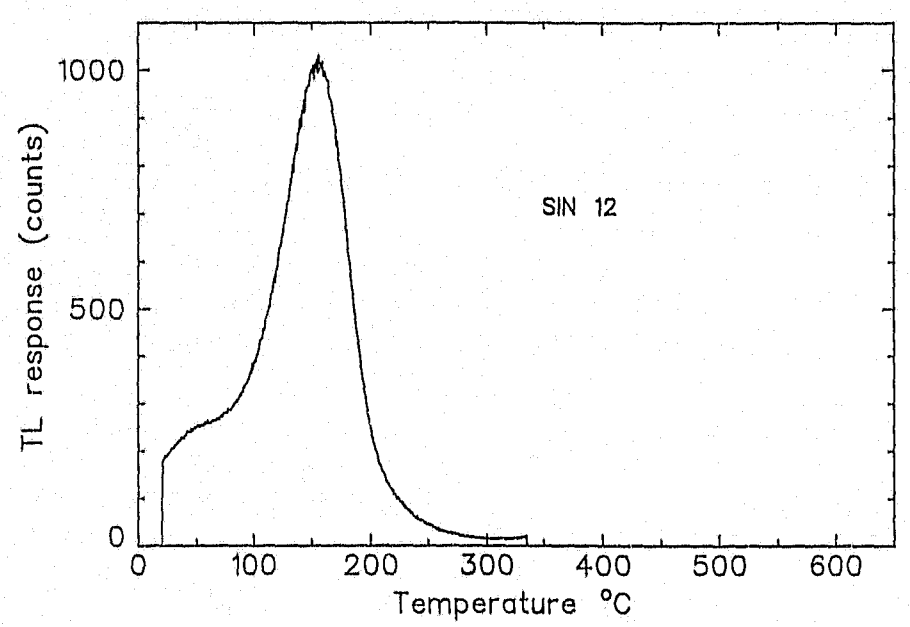


Figure A.5. Thermoluminescent spectrum of SIN 12.

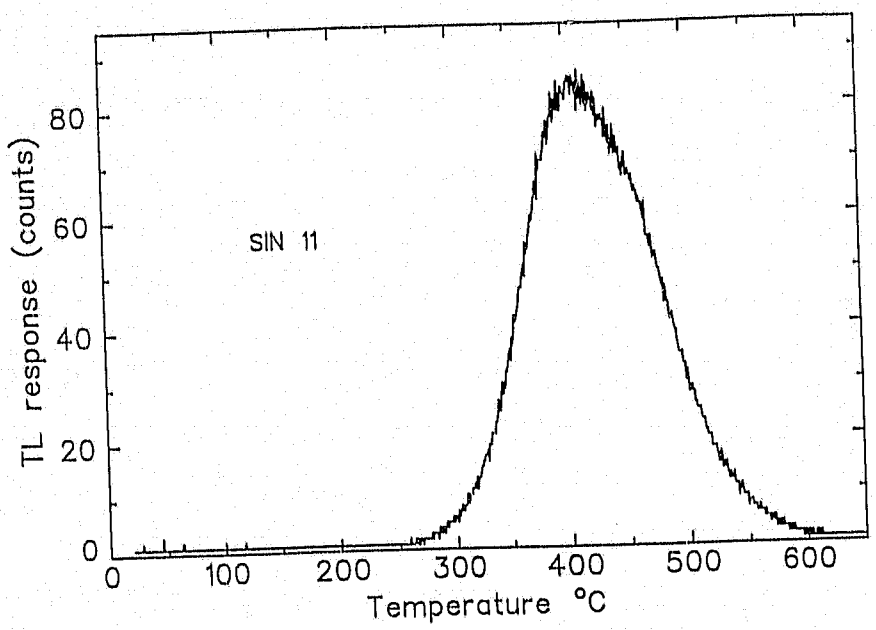


Figure A.6. Thermoluminescent spectrum of SIN 11.

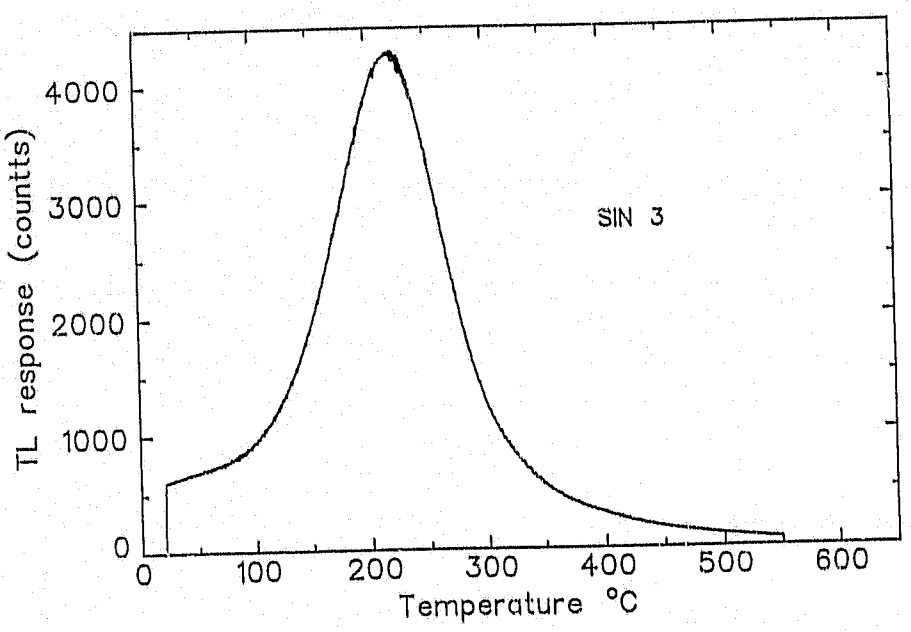


Figure A.7. Thermoluminescent spectrum of SIN 3.

Appendix B : CIRCUIT DIAGRAMS

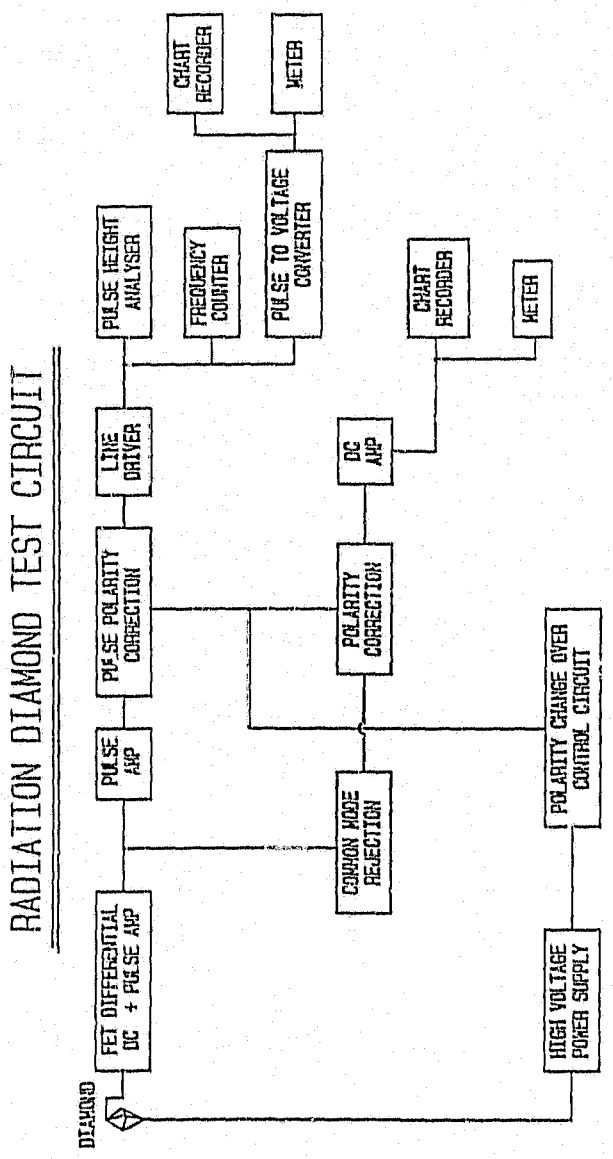


Figure B.1. Schematic diagram of custom built pulse counting circuit.

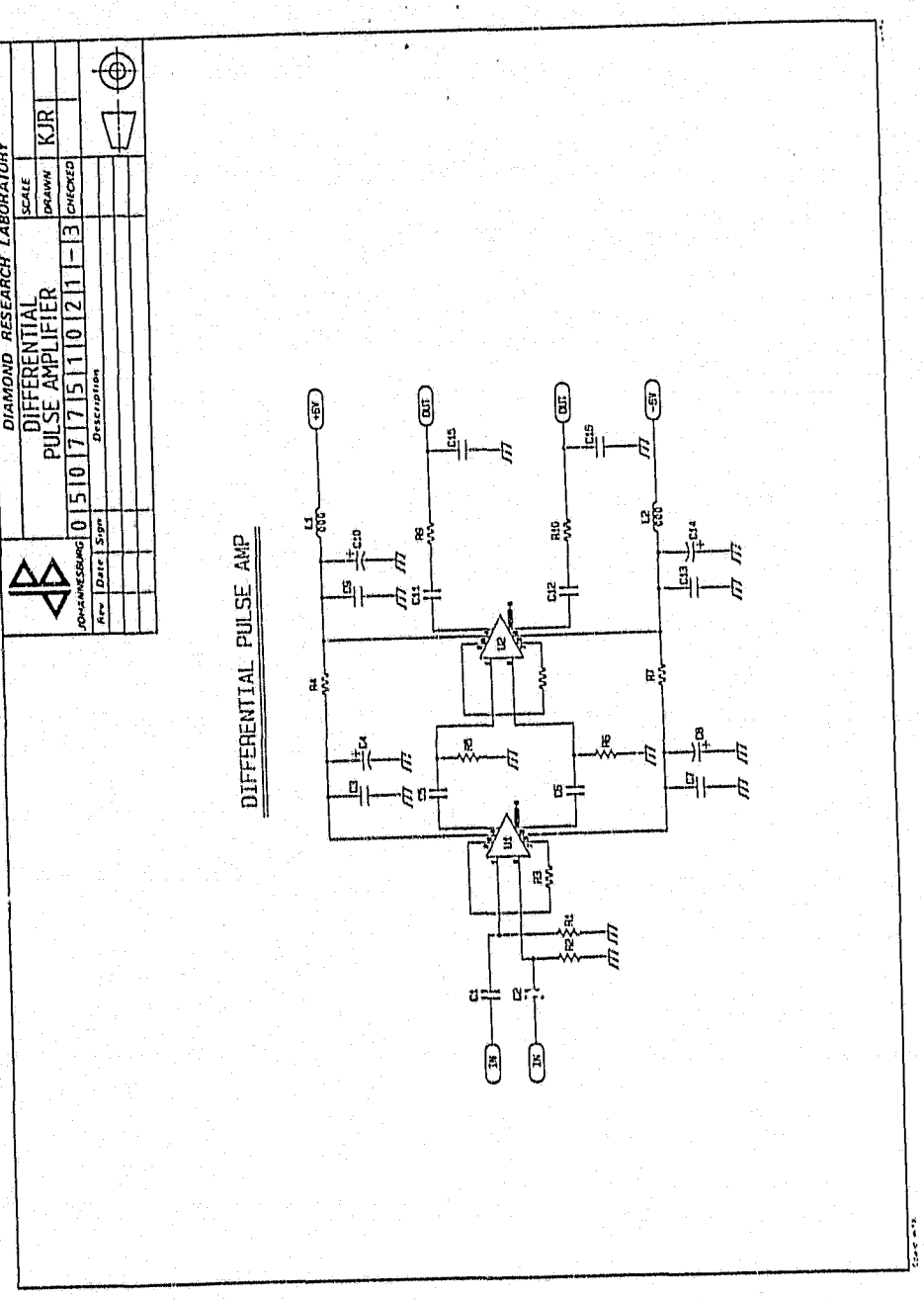


Figure B.2. Circuit diagram of custom built differential pulse amplifier.

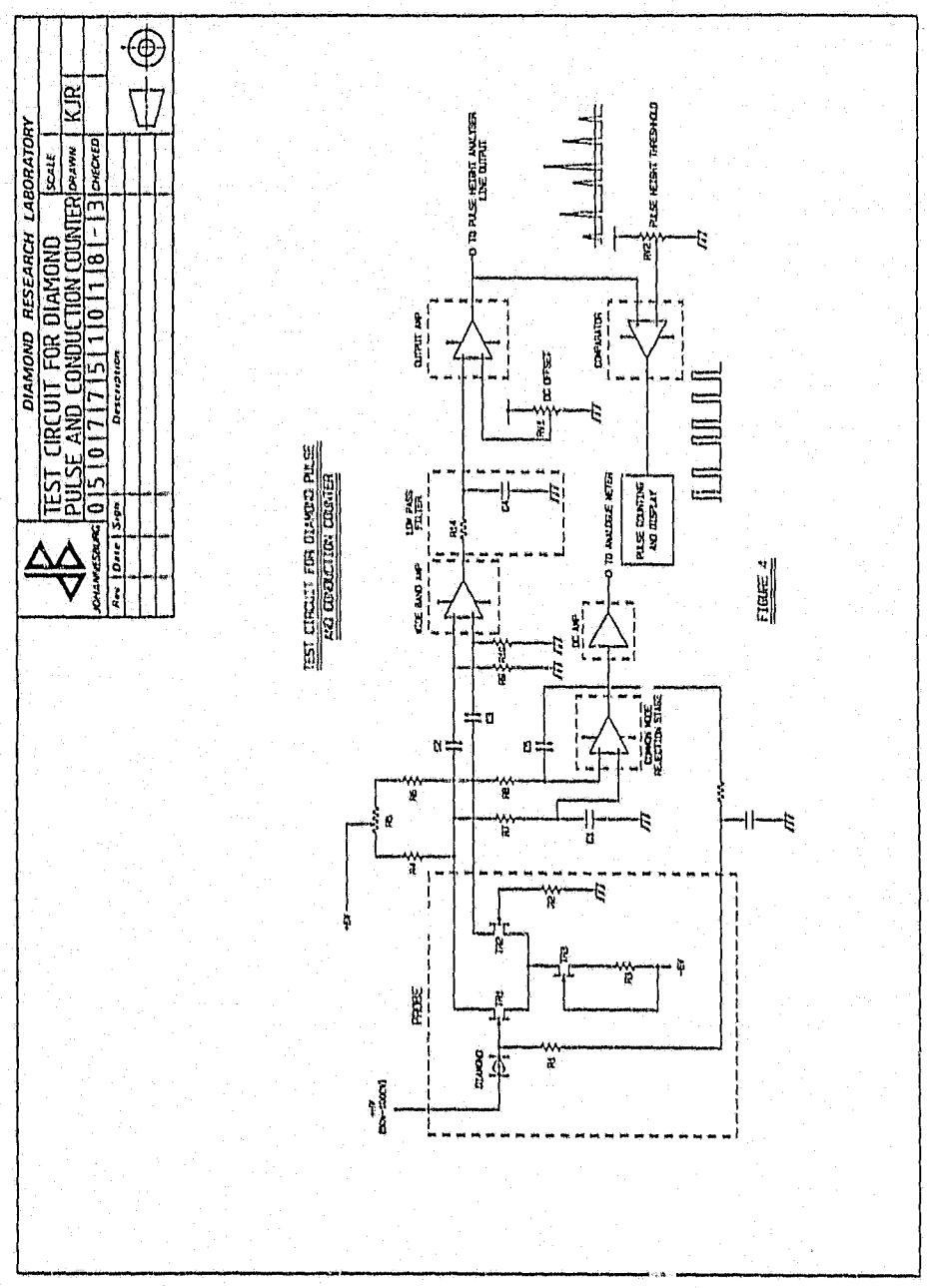


Figure B.3. Custom built test circuit for diamond pulse and conduction counter.

Appendix C : PAPERS, PATENTS and CONFERENCES

Papers

Nam T. L., Fallon P. J., Keddy R. J., van Rijn H. J. and Andrews J. F. (1989), "Detection of Nuclear Radiation by Scintillation Counting using Synthetic Diamond", Int. J. Appl. Radiat. Isotopes in print

Fallon P. J., Nam T. L., Keddy R. J., Burns R. C. and Grobbelaar J. G. (1989), "Synthetic diamonds used as pulse-counting γ-ray detectors", Int. J. Appl. Radiat. Isotopes in print

Patents

Nam T. L., van Rijn H. J., Keddy R. J., Fallon P. J. and Andrews J. F. (1989), "Diamond Scintillation Detector", South Africa (ZA): 88/9676 - 28.12.1988

Conferences

Fallon P. J. and Keddy R. J., "Synthetic diamonds used as *in-vivo* radiation detectors", SAIP Conference, Grahamstown, July 1988

Fallon P. J., Nam T. L., Keddy R. J., Burns R. C. and Grobbelaar J. G., "Synthetic Diamonds as Ionizing Radiation Detectors using pulse circuitry", Diamond Conference, Bristol, July 1989

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Nam T. L., Fallon P. J. and Keddy R. J., "Impurities and the TLD Diamond", SAIP Conference, Pretoria, July 1989

Keddy R. J., Fallon P. J., Nam T. L. and van der Merwe D. G., "Custom synthesized diamond crystals and their application as state of the art dosimeters", International Symposium on Radiological Protection, November 20-22, 1989, Beijing, China

Author Fallon P J
Name of thesis Synthetic diamonds as Pluse Counting Radiation Detectors 1989

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