

https://dspace.org/

Electronic conduction phenomena in various kinds of diamond

Farrer, Roger Geoffrey

2015-03-11
http://hdl.handle.net/10539/17249

Downloaded from a DSpace repository. https://dspace.org/

ELECTRONIC CONDUCTION PHENOMENA IN VARIOUS KINDS OF DIAMOND

Roger Geoffrey Farrer

A Thesis Submitted to the Faculty of Science,
University of the Witwatersrand, Johannesburg
for the Degree of Doctor of Philosophy

Johannesburg 1975

DECLARATION

I declare that this thesis is my own work, that no part of it has been or will be submitted for a degree at any other university and that no information in it has been obtained while I have been employed by, or working under the aegis of, any person or organisation other than this University.

R.G. FARRER

ABSTRACT

This thesis reports experimental measurements of photoconductivity, electrical resistance as a function of temperature and the thermoelectric effect, which give information about the electronic properties of three of the simplest defects in diamond. These are the vacancy which is characterised by the GR1 and GR2-8 optical absorption features, the isolated substitutional nitrogen donor which occurs predominantly in type Ib diamond, and a defect which gives rise to the ND1 optical absorption system and is probably the nitrogen interstitial.

Minima occur in the photoconduction spectrum of irradiated diamond at the positions of maxima in the GR1 absorption band; this observation is consistent with the model in which the GR1 transitions occur between bound states of the vacancy and with the fact that GR1 luminescence has been observed. Photoconduction maxima, which persist down to 8K, are observed at the positions of the GR2-8 and the ND1 optical absorption maxima; these observations explain the absence of ND1 luminescence which has been reported in the literature. The mechanism whereby these sharp photoconduction peaks are created even at very low temperatures cannot be established from these measurements, but it is suggested that autoionization takes place from the second and higher excited states of the vacancy and the first excited state of the ND1 centre which lie within the conduction or valence bands. These results are considered to be of considerable importance for future theoretical treatments of the electronic states of these centres.

Measurements of photoconduction in natural and synthetic type Ib diamond show that the 4 eV threshold which has been observed in the spectrum of type Ia diamond is not characteristic of the type Ib spectrum; the commonly held view that this is the photoionization threshold for the isolated substitutional nitrogen donor is therefore believed

to be incorrect. It is suggested from the results of measurements of photoconduction, electrical resistance as a function of temperature and the thermoelectric effect in type Ib diamond that the thermal activation energy of this donor is about 1.7 eV and that the optical ionization threshold is about 2.2 eV at 80K. The difference between these two activation energies is discussed in terms of the large Jahn-Teller distortion experienced by the centre. An additional photoconduction feature in natural type Ib diamonds, with a temperature independent threshold at 1.7 eV, is tentatively identified with the electron paramagnetic resonance 'Leivo' centre.

ACKNOWLEDGEMENTS

My sincere thanks are due to Prof. F.R.N. Nabarro, Prof. P.T. Wedepohl and Prof. J.H.N. Loubser, who supervised some or all of the work reported in this thesis. I am also extremely grateful to my colleagues in the Department of Physics, University of the Witwatersrand, for many interesting discussions, criticisms and comments, and especially to Dr L.A. Vermeulen for much stimulation, help and encouragement. Thanks are also due to Mr J. Watts, Mr R. Nel, Mr P.J. van der Schyff and other technical staff in the department for the construction of the apparatus used in these investigations.

I am particularly grateful to Miss B. Brown for typing the manuscript, to Mrs K. Peach for preparing the drawings and to the staff of the printing office of this university for reproducing this thesis.

I acknowledge with thanks the financial support of the Diamond Research Laboratories, Johannesburg, who also provided financial assistance which enabled me to attend the 1974 Diamond Conference.

CONTENTS

		Page
Abstract		ii
Acknowledgements		iv
Contents		v
List of figures		viii
CHAPTER 1 INTRODUCTION		1
CHAPTER 2 ELECTRONIC PROPERTIES OF DEFECTS IN DIAMONDS		3
2.1	General properties of defects in diamonds	3
	2.1.1 Type Ia diamond	3
	2.1.2 Type Ib diamond	7
	2.1.3 Type IIa diamond	13
	2.1.4 Type IIb diamond	14
2.2	Photoconductivity in diamond	15
	2.2.1 Type Ia diamond	15
	2.2.2 Type Ib diamond	17
	2.2.3 Type IIa diamond	17
	2.2.4 Type IIb diamond	17
2.3	Defects in irradiated diamond	20
	2.3.1 Introduction	20
	2,3.2 The GR1 band and associated features	21
	2.3.3 The ND1 band	24
	2.3.4 Other optical absorption bands	27
	2.3.5 Electron paramagnetic resonance centres	28
2.4	Discussion of previous work and aims of this investigation	29
CHAPTER 3 EXPERIMENTAL METHODS AND APPARATUS		33
3.1	Measurement of photoconductivity	33
	3.1.1 General description	33

3.1.2 The room temperature sample holder 35
3.1.3 The liquid helium cryostat 35
3.2 Measurement of thermal activation energies 44
3.2.1 The temperature dependence of electrical resistance 44
3.2.2 The general purpose apparatus 45
3.3 Determination of the sign of the charge carriers 47
3.3.1 The thermoelectric effect 47
3.3.2 The thermoelectric effect apparatus 49

CHAPTER 4 EXPERIMENTAL RESULTS 53

4.1 Electron-irradiated type Ia and type IIa diamonds 53
4.1.1 Introduction 53
4.1.2 Photoconduction 53
4.1.3 Summary of results 57
4.2 Natural type Ib diamonds 61
4.2.1 Introduction 61
4.2.2 Room temperature photoconduction and optical absorption 61
4.2.3 Electrical resistance and thermo-electric effect 63
4.2.4 Photoconduction and optical absorption after heating 63
4.2.5 Summary of results 67
4.3 Synthetic type Ib diamonds 70
4.3.1 Introduction 70
4.3.2 Photoconduction 70
4.3.3 Electrical resistance and thermo-electric effect 75
4.3.4 Sample of S12 75
4.3.5 Summary of results 79

CHAPTER 5 DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1	Irradiated diamonds	84
5.2	Type Ib diamonds	88
5.3	Additional suggestions for further work	92

REFERENCES 95

LIST OF FIGURES

Figure		Page
2.1	One-phonon absorption spectra due to nitrogen in diamond	5
2.2	Optical absorption spectra of natural type Ib diamonds	10
2.3	Absorption spectra of synthetic type Ib diamonds	11
2.4	The photoconductivity spectrum of a type IIb diamond	19
2.5	The absorption spectrum of an electron irradiated type II diamond	22
2.6	The ND1 optical absorption system	25
3.1	A block diagram of the arrangement used to measure photoconductivity in diamond	34
3.2	The monochromator output using the tungsten lamp	36
3.3	The monochromator output using the deuterium lamp	37
3.4	The dispersion of the monochromator	38
3.5	The room temperature sample holder	39
3.6	The liquid helium cryostat	40
3.7	The sample holder in the helium cryostat	42
3.8	The variation of resistance with temperature of the Allen-Bradley resistor used for temperature measurement in the helium cryostat	43
3.9	The general purpose apparatus	46
3.10	The current-voltage characteristic of a synthetic diamond at 290^{o}C	48
3.11	The general purpose apparatus as modified for the observation of the thermoelectric effect	50
3.12	(a) The temperature of, and the temperature difference across a type IIb diamond during observation of the thermoelectric effect	

(b) The thermoelectric effect observed in a type IIb diamond 51

4.1 Photoconduction and optical absorption at 80K in the neighbourhood of the GR1 band in an electron-irradiated type IIa diamond 54

4.2 Photoconduction and optical absorption at 80K in the neighbourhood of the GR2 to GR8, R9 and R10 lines in an electron-irradiated type IIa diamond 55

4.3 The 80K photoconduction spectrum of an electron-irradiated type Ia diamond in the neighbourhood of the GR2 to GR8, R9 and R10 lines and the ND1 system 56

4.4 Photoconduction and optical absorption at 8K in the neighbourhood of the ND1 system 58

4.5 Photoconductivity in an electron irradiated type Ia diamond in the neighbourhood of the ND1 system (a) at 80K and (b) at 8K 59

4.6 The photoconductivity spectrum at 80K in an irradiated type Ia diamond which contains both the N3 and ND1 systems 60

4.7 Room temperature photoconduction spectra of natural Ib diamonds 62

4.8 A comparison of photoconduction and optical absorption in a natural type Ib diamond 64

4.9 The current through a natural diamond as a function of temperature, for a fixed applied voltage 65

4.10 The thermoelectric effect (a) in a p-type semiconducting diamond and (b) in a natural type Ib diamond 66

4.11 The optical absorption spectrum of a natural type Ib diamond after cooling from 400°C and after bleaching with 2.5 eV light 68

4.12 The unnormalized photoconduction spectrum of a natural type Ib diamond after heating to 400°C and after bleaching with 2.5 eV light 69
4.13 The infrared spectrum of a synthetic type Ib diamond 71
4.14 Tne visible-ultraviolet absorption spectrum of a synthetic type Ib diamond 72
4.15 The room temperature photoconduction spectrum of synthetic diamond S4 73
4.16 The room temperature photoconduction spectrum of synthetic diamond S6 74
4.17 The temperature dependence of the 2 eV threshold in synthetic diamond 76
4.18 The current through synthetic diamond S8 as a function of temperature with a fixed applied voltage 77
4.19 The thermoelectric effect in a synthetic type Ib diamond 78
4.20 The infrared photoconductivity spectrum of sample S12 at 80K 80
4.21 The photoconductivity spectrum of sample S12 at 80K 81
4.22 The current through sample S12 as a function of temperature for a fixed applied voltage 82

5.1 The photoconduction spectrum at 80K of a type Ia gem sand diamond 94

CHAPTER 1

INTRODUCTION

Diamond is a crystalline form of carbon, in which each carbon atom is covalently bonded to four neighbouring atoms and provides one of the two electrons in each bond. The crystal structure consists of two face-centred cubic lattices which interpenetrate and are displaced from each other by a quarter of the body diagonal. The resulting material is extremely hard and has a high coefficient of thermal conductivity - a combination which makes diamond very valuable industrially as a cutting, grinding and polishing material. Two of its optical properties which contribute to making diamond the most valued of all gem-stones are its high refractive index and the fact that it is (in pure form) transparent to the whole visible spectrum.

Diamond is the simplest of the covalently bonded materials which have the diamond structure, and the study of the electronic properties of defects in diamond is of considerable scientific interest. With the exception of the acceptor centre in semi-conducting diamond, defects in diamond give rise to deep-lying energy levels within the forbidden energy gap. While the electronic properties of shallow impurity levels are well understood, the theoretical description of deep electronic states of impurities and defects produced by radiation damage in covalently bonded solids has been described as one of the most important unsolved problems in modern theoretical solid state physics (Messmer and Watkins 1973; Larkins 1973).

Levels which lie within the forbidden energy gap of crystalline solids give rise to experimentally observable features such as increased electrical conductivity, electron paramagnetic resonance, and optical absorption, luminescence and photoconduction at energies considerably less than the

intrinsic band gap energy. Experimental studies of properties like these are of considerable interest since they provide valuable information about the position and nature of the levels concerned.

In this thesis, the electronic properties of defects in diamond are reviewed. Investigations are reported of (i) the photoconductive properties of defects which are induced in diamond by electron irradiation, and (ii) the photoconductive and allied properties of type Ib diamond, which contains nitrogen atoms in isolated substitutional form.

Some of the results reported in this thesis are published in the following papers:

'On the Substitutional Nitrogen Donor in Diamond'
Farrer RG 1969 Solid State Comm. 7 685

'Photoconductivity in Irradiated Diamond'
Farrer RG and Vermeulen LA 1972 J. Phys. C: Solid State Phys. 5 2762

'Charge Carriers in Diamond'
Vermeulen LA and Farrer RG 1975 Diamond Research 1975 (Industrial Diamond Information Bureau, London) (to be published)

CHAPTER 2

ELECTRONIC PROPERTIES OF DEFECTS IN DIAMONDS

2.1 General properties of defects in diamonds

2.1.1 Type Ia diamond

Natural diamonds were originally classified into two types depending on their optical absorption in the infrared, visible and ultraviolet regions of the spectrum (Robertson, Fox and Martin 1934; Sutherland, Blackwell and Simeral 1954; Clark, Ditchburn and Dyer 1956a). Type I diamonds (now known as type Ia following the subdivision of type I diamonds into two types by Dyer, Raal, du Preez and Loubser (1965)) show absorption starting at about 330 nm which increases fairly rapidly at shorter wavelengths (the so-called 'secondary absorption edge'), whereas type II diamonds are transparent down to the fundamental absorption edge at 225 nm. Type Ia diamonds also show absorption in the infrared at wavelengths longer than 7 μm, which is not present in type II diamonds; this is due to single-phonon absorption, which is forbidden in perfect diamond (Lax and Burstein 1955) and indicates the presence of defects which lower the symmetry of the crystal structure in their neighbourhood.

Frank (1956) suggested that anomolous spikes which had been observed in the X-ray diffraction patterns of type Ia diamonds (Raman and Nilakantan 1940; Hoerni and Wooster 1955) might be due to the precipitation of an impurity in the {100} planes. The major impurity in type Ia diamond was identified by Kaiser and Bond (1959), who showed that the strongest absorption band in the infrared (at 7.8μm) and the ultraviolet absorption at 306.5 nm were proportional to the amount of nitrogen in the diamonds (which was present

in concentrations of up to 0.25 atomic percent). Elliott (1960) suggested that the nitrogen might be in platelet form and in 1962 Evans and Phaal observed the presence of platelets in type Ia diamond by transmission electron microscopy.

Recent experimental work has cast doubt on the belief that most of the nitrogen in type Ia diamond is in platelet form. Sobolev, Lisoivan and Lenskaya (1968) have showed that the X-ray spike intensity does not correlate with the absorption at 7.8 μm, but does correlate well with an absorption peak at 7.3 μm. Evans and Wright (1971) have confirmed that a direct correlation exists between the integrated spike intensity and the total platelet area per unit volume, while Davies (1971) has found that the 7.3 μm peak is connected with little, if any, of the nitrogen in type Ia diamonds. Evans (1972, 1973) has suggested that the platelets are composed of an extra plane of carbon atoms due to the precipitation of interstitial carbon atoms, which are created when interstitial nitrogen atoms (incorporated during growth) diffuse to substitutional nitrogen atoms and exchange with a neighbouring substitutional carbon atom to form a pair of substitutional nitrogen atoms. This process of exchange continues and small aggregates of nitrogen on substitutional sites are formed.

Sutherland, Blackwell and Simeral (1954) subdivided the infrared absorption peaks which occur in the one-phonon region in type Ia diamond into two groups - A and B. Davies (1971, 1972a) has separated the spectra characteristic of the A and the B features on a quantitative basis; typical A and B spectra are shown in Fig. 2.1. The group A bands are characteristic of the nitrogen identified by Kaiser and Bond (1959) and the group B bands appear to be due to a different type of small nitrogen aggregate (Davies 1971; Sobolev and Lisoyvan 1972). The B' peak at 7.3 μm was originally thought to be associated with the B group, but has been shown to be independent of it (Clark 1965a,

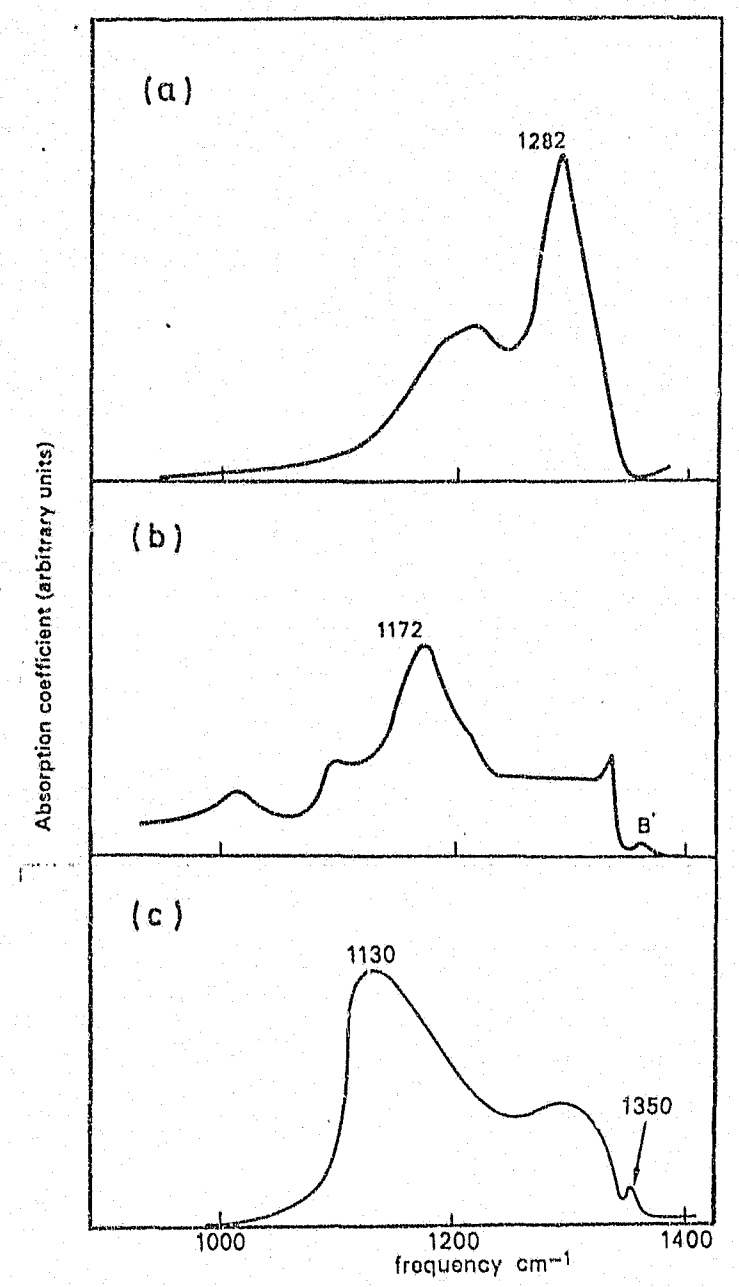


FIG. 2.1 The one-phonon absorption spectra due to (a) the A form and (b) the B form of nitrogen in type Ia diamond (from Davies and Summersgill 1973). The B' peak in (b) is independent of the B form of nitrogen.
(c) shows the spectrum due to single substitutional nitrogen in type Ib diamond (from Davies 1972a and Dyer et al 1965)

Davies 1971); it is the feature which is now correlated with the platelets. It was also believed that the B group was associated with the N3 absorption system which occurs in many type Ia diamonds (Sutherland, Blackwell and Simeral 1954) and with the N9 absorption band (Clark, Ditchburn and Dyer 1956a); both of these associations have been shown to be incorrect (Davies and Summersgill 1973), and the N3, N9, A and B absorption features are now thought to be independent.

The N3 absorption system (Mani 1944; Clark, Ditchburn and Dyer 1956a) consists of a principal line (which Davies and Summersgill (1973) have recently reported to be a doublet) at 2.989 eV (415.0 nm) accompanied on the high energy side by a number of ancillary lines which are spaced about 0.08 eV apart. Fluorescence is observed from the N3 centre (Nayar 1941; Dyer and Matthews 1957), the emission spectrum being a mirror image of the absorption spectrum - a principal line at approximately the same position with ancillary lines at lower energies. The nature of these spectra is understood in terms of electronic transitions which take place between the ground state and the excited state of the N3 centre - the principal line being due to 'zero-phonon' electronic transitions, and the ancillary lines arising out of an interaction between the electronic states and the lattice vibrations (Elliott 1956, Clark 1965b).

It has been shown that the N3 centre has trigonal symmetry and that the 2.989 eV transition takes place between a non-degenerate ground state and a doubly degenerate excited state (Elliott, Matthews and Mitchell 1958; Runciman 1965; Crowther and Dean 1967; Clark and Norris 1970). The N3 absorption has been found to correlate (du Preez 1965) with the so-called '14-line' electron paramagnetic resonance system first observed by Smith, Gelles and Sorokin (1959), although there is some doubt whether the correlation is between the 14 line spectrum itself or with a broad underlying resonance line (Loubser and Wright 1973)

The nature of the N3 centre is still uncertain. Smith, Gelles and Sorokin (1959) suggested that the 14-line spectrum might be due to a single substitutional aluminium atom, but Every (1963) showed that this is highly unlikely. Dean (1965) proposed that the N3 defect might be a nearest neighbour donor-acceptor (nitrogen-aluminium) pair; his suggestion was supported by Sobolev, Il'in, Gil'bert and Lenskaya (1969a). Loubser and Wright (1973) have reported electron nuclear double resonance spectra of the 14-line system, and reject the donor-acceptor pair model in favour of a model first suggested by Mitchell (1964) which consists of three nitrogen atoms in next nearest neighbour positions on a {111} plane.

Another optical absorption system which has been investigated in some detail is the N9 system, which has a pair of zero phonon lines at 5.257 and 5.261 eV (at 100 K). This system was observed by Clark, Ditchburn and Dyer (1956a) to occur in intermediate diamonds which showed some of the absorption systems characteristic of type Ia diamonds (notably the N3 system) but in which the secondary absorption edge was absent. The luminescence from this system has been studied in detail by Wight and Dean (1967) who attributed their observations to the recombination of excitons bound to nearest neighbour donor-acceptor pairs - the same centre as was originally thought to be responsible for the N3 absorption and emission system.

2.1.2 Type Ib diamond

The discovery of single substitutional nitrogen atoms in diamond was made by Smith, Sorokin, Gelles and Lasher (1959), who observed the electron paramagnetic resonance signal due to the extra unpaired electron introduced by the nitrogen atom compared to the carbon atom it replaces.

Dyer, Raal, du Preez and Loubser (1965) suggested that diamonds containing nitrogen predominantly in this form be classified as type Ib, whereas diamonds containing nitrogen most of which is in aggregate form be classed as type Ia. When synthetic diamond contains nitrogen it is present in the single substitutional form (Charette 1961; Huggins and Cannon 1962; Sobolev et al 1969b; Chrenko, Strong and Tuft 1971) and is therefore classified as type Ib.

Much of the information which is known about the substitutional nitrogen atoms has been deduced from electron paramagnetic resonance studies. Smith, Sorokin, Gelles and Lasher (1959) determined that the extra electron is localised in an antibonding orbital along one of the carbon-nitrogen bonds, which experiences a Jahn-Teller distortion which is static at room temperature. Thermal reorientation of this distortion has been observed by Shul'man, Zaritskii and Podzyarei (1967) and Loubser and van Ryneveld (1967), who estimate the activation energy for reorientation to be 0.7 eV and 0.76 eV respectively. The presence of the isotope ^{15}N (which has a natural abundance of 0.365 percent) has been detected (Loubser and du Preez 1965) and Loubser, van Ryneveld and du Preez (1965) have found that exchange interaction between centres sufficiently close for their electron spins to be coupled can be observed in samples containing about 10^{18} (or more) nitrogen atoms per cm^3.

Dyer, Raal, du Preez and Loubser (1965) found that type Ib diamonds have characteristic optical absorption features in the infrared and in the visible-ultraviolet regions of the spectrum. The infrared absorption (see Fig. 2.1), which occurs in the single phonon region, consists of a sharp peak at 0.167 eV (1350 cm^{-1}), a broad main band at about 0.140 eV (1130 cm^{-1}) and a saddle between these two features (at about 0.16 eV). Absorption in the

visible-ultraviolet (shown in Fig. 2.2) starts at about 2 eV and increases steadily to about 4 eV, then rises rapidly to a peak at about 4.6 eV and continues to the fundamental absorption edge. At liquid nitrogen temperature small absorption lines were observed at 4.07, 4.15, 4.24, 4.58 and 4.64 eV. Dyer et al (1965) found good correlation between the strength of the electron paramagnetic resonance signal, the infrared absorption system (as measured by the area under the absorption curve) and the slope of the absorption curve at 2.6 eV. They proposed that the visible-ultraviolet absorption arose from ionization of the donor level formed by the substitutional nitrogen, and they placed this level 2.4 eV below the conduction band.

Subsequent authors (Sobolev et al 1969b; Chrenko, Strong and Tuft 1971) have found very similar optical absorption features in synthetic type Ib diamonds (see Fig. 2.3) and have confirmed that these correlate well with the amount of substitutional nitrogen present, although their methods of measurement were not identical with those of Dyer et al (1965). Both used the absorption coefficient at 0.140 eV as a measure of the infrared absorption, but for the visible-ultraviolet absorption Sobolev et al used the absorption coefficient at 2.6 eV, and Chrenko et al the absorption coefficient at 4.6 eV (the position of the peak in the ultraviolet). These two sets of authors also disagree on the quantitative correlation between the absorption coefficient at 0.140 eV and the amount of substitutional nitrogen present.

Attempts have been made to calculate the electronic properties of the substitutional nitrogen donor in diamond. Every (1970) obtained a reasonable fit to the Ib infrared spectrum (although his calculations did not predict the sharp peak at 0.167 eV), and to the visible spectrum. However, he assumed that there is no photoconduction corresponding to the visible absorption tail, despite clear

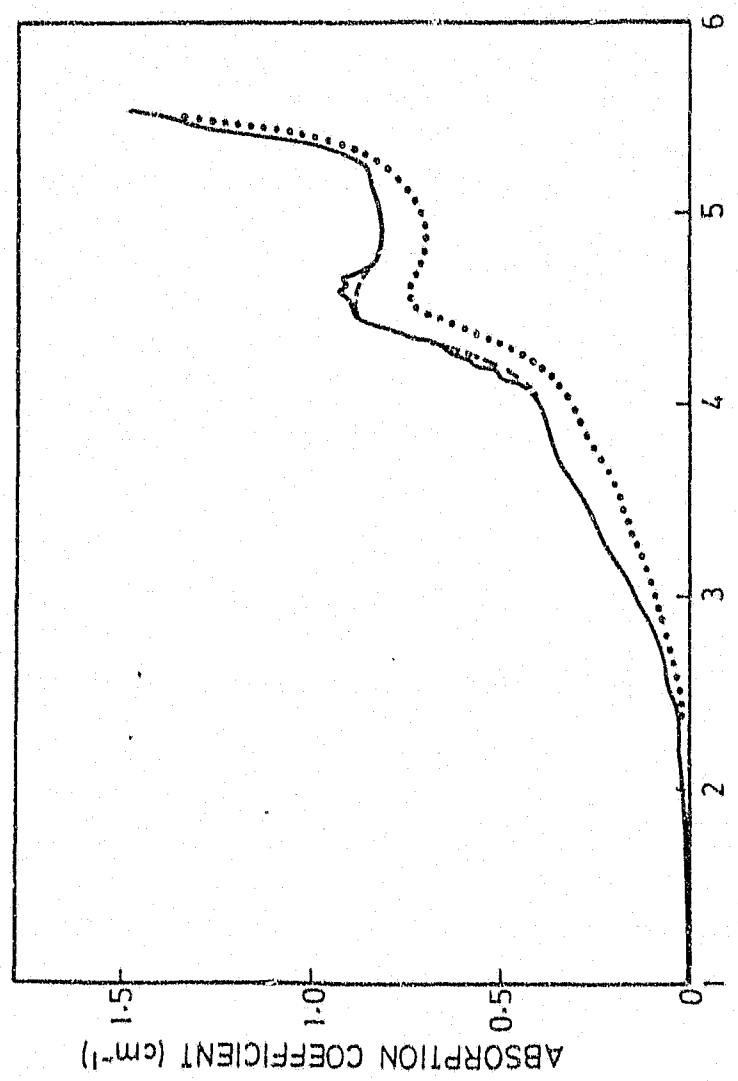


FIG. 2.2 The optical absorption spectra of two natural type Ib diamonds. The broken curves were observed at room temperature and the solid curve at 80K. From Dyer, Raal, du Preez and Loubser (1965).

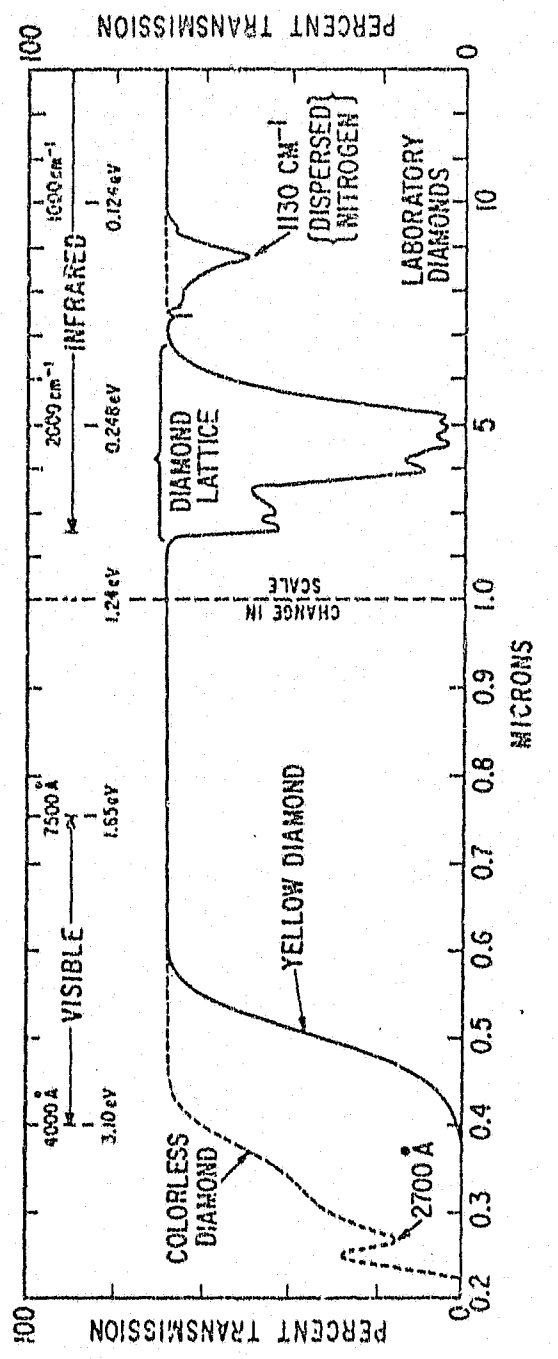


FIG. 2.3 Absorption spectra of synthetic type Ib diamonds (from Chrenko, Strong and Tuft 1971).

evidence to the contrary (Farrer 1969), and in his model this absorption was attributed to non-ionizing transitions at the nitrogen donor.

Messmer and Watkins (1970, 1973) and Larkins (1971a,b) have applied extended Huckel theory to a model consisting of a cluster of carbon atoms surrounding the substitutional nitrogen atom. Messmer and Watkins used a 35 atom cluster which predicts a band gap energy of 9.5 eV. They calculate the nitrogen donor to be about 1.5 eV below the conduction band before the distortion and they estimate a Jahn-Teller stabilization energy of about 5.0 eV, which by their arithmetic places the distorted donor about 2.2 eV above the valence band. Larkins (1971b), using a 41 atom cluster, calculates the undistorted donor to be 2.9 eV below the conduction band; this changes to 2.7 eV for a 47 atom cluster.

The use of extended Huckel theory and the cluster model to calculate the electronic properties of defect states in diamond has received much discussion and criticism (Moore and Carlson 1971; Lidiard 1972; Coulson 1972). It is generally agreed that this method constitutes an interesting approach to the problem of defect states in diamond, but there is considerable doubt about its quantitative validity. The width of the forbidden energy gap and the position of levels within it depend markedly on the size of the cluster and on the boundary conditions. Moore and Carlson (1971) and Larkins (1971a) indicate that calculation of distortion energies, and in particular the Jahn-Teller distortion energy calculated by Messmer and Watkins (1970, 1973), cannot be regarded as reliable. In addition, Messmer and Watkins expect their calculations to be more reliable for states associated with the valence band than for those associated with the conduction band. It is clear that the results of their nitrogen donor calculations should be treated with caution.

The electron paramagnetic resonance signals due to other defects involving nitrogen have been observed in type Ib diamonds. Ionized nitrogen pairs have been detected by Shcherbakova et al (1969); these can also be produced

in type I diamonds by irradiation followed by annealing. Loubser and Wright (1973) have observed singly ionized N-C-N centres, with the nitrogen atoms in next-neighbour positions. Klingsporn, Bell and Leivo (1970) have detected the presence of another centre (the Leivo centre) involving nitrogen, which Wedlake (1972) and Shcherbakova, Sobolev and Nadolinnyi (1972) have suggested might be a nitrogen-vacancy pair. If this is true, it should be possible to produce the centre in type Ib diamond by irradiation followed by annealing; attempts to do so (Loubser 1973) have been unsuccessful. Type Ib diamonds containing the Leivo centre show an increased optical absorption with maxima at about 2.4 eV and 2.9 eV after heating, which is accompanied by decreases in the electron paramagnetic spectra of both the isolated nitrogen and the Leivo centre (Loubser 1973). These effects can be reversed by illumination with visible light. They have been interpreted (Loubser 1973) in terms of a transfer of electrons from the single nitrogen to the Leivo centre during heating and a restoration of the electrons to the single nitrogen during optical bleaching.

2.1.3 Type IIa diamond

Type IIa diamonds are insulating diamonds which do not exhibit a secondary absorption edge and do not absorb at wavelengths longer than 7μm in the infrared. They contain very little of the nitrogen which is characteristic of type Ia and type Ib diamonds (Clark 1965a). Most type IIa diamonds have an absorption tail which starts at about 1.5 eV and gradually increases through the visible and ultraviolet until the fundamental absorption edge is reached; this tail is believed to be due to amorphous or graphitic regions of carbon (Clark, Ditchburn and Dyer 1956a and b).

Du Preez (1965) reported that type IIa diamonds exhibit

a single broad isotropic paramagnetic resonance line which correlates with the absorption tail. Loubser (1975) has recently observed two additional electron paramagnetic resonance systems in type IIa diamonds; these have ⟨110⟩ and ⟨111⟩ symmetry and both are spin 1 systems.

2.1.4 Type IIb diamond

Custers (1952, 1955) reported the discovery that a small fraction of type II diamonds are semi-conducting at room temperature and proposed that these be classified as type IIb. The electrical and optical properties of these diamonds were extensively studied during the ten years following their discovery and have been reviewed by Kemmey and Wedepohl (1965). They are found to be p-type semi-conductors with an acceptor level 0.35 eV above the valence band (Leivo and Smoluchowski 1955; Austin and Wolfe 1956; Wedepohl 1957). The acceptor centres give rise to a broad optical absorption band which extends from about 0.35 eV to about 2.5 eV. Seven groups of peaks in the infrared between 0.305 and 0.670 eV have been associated with the excitation of bound holes (some with the participation of optical phonons) (Wedepohl 1957, Hardy 1962). The acceptor impurities also cause absorption in the single phonon region beyond 7 μm (Hardy 1962).

For some time it was believed that single substitutional aluminium atoms were responsible for the semi-conducting properties of type IIb diamonds (Brophy 1956; Lightowlers 1962; Dean, Lightowlers and Wight 1965; Collins, Dean, Lightowlers and Sherman 1965; Crowther, Dean and Sherman 1967). However, Collins and Williams (1971) showed that this belief was incorrect, and Chrenko (1973) has proved conclusively from work on synthetic semi-conducting diamond that boron is responsible.

Bell and Leivo (1967) reported the observation of a sharp electron paramagnetic line in several natural semi-conducting diamonds, which they attributed to the acceptor centres. However, Bourgoin et al (1972) have observed two lines (neither of which is the Bell and Leivo line) in boron doped synthetic diamond; they believe these to be due to holes bound to boron atoms and free holes in the valence band.

2.2. Photoconductivity in diamond

2.2.1 Type Ia diamond

Photoconductivity was first observed in diamond by Gudden and Pohl (1920), and Robertson, Fox and Martin (1934) confirmed their observation of a marked increase in the photoconduction spectra at wavelengths shorter than about 300 nm in diamonds which the latter classed as type I. Others authors who reported a similar effect are Levi (1922), Taylor (1956) and Urlau, Logie and Nabarro (1961).

Vermeulen and Nabarro (1967) investigated the photo-conductive properties of these diamonds extensively, and found that their results could be explained on the basis of a model which proposed the existence of three energy levels within the forbidden gap. They found characteristic photoconduction thresholds at 0.85, 1.46, 2.2, 3.3, 4.05, 4.8, 5.25 and 5.52 eV, the first six of which they ascribed to extrinsic photoconduction, and the last two to the thermal decomposition of excitons and to intrinsic band gap transitions respectively. They attributed the large peak in the ultraviolet (with its threshold at 4.05 eV) to the presence of nitrogen in aggregate form, in agreement with Konorova, Sorokina and Shevchenko (1965).

Denham, Lightowlers and Dean (1967) observed oscillatory

structure beyond the intrinsic absorption edge in the photoconductivity of natural diamonds containing the N9 absorption/luminescence system, which they explained in terms of the preferential trapping at the N9 centre of excitons which have low residual kinetic energy after excess energy loss by the cascade emission of optical phonons. They also observed that photoconductivity maxima at the positions of the N9 absorption maxima changed to minima at low temperature, and interpreted these results in terms of the thermal liberation of an electron after the creation of an indirect exciton bound to the N9 centre; this effect had been observed previously by Nahum and Halperin (1962) who explained it in a very similar way. Denham et al (1967) also reported that the photoconductivity threshold at 4.05 eV was observed in all insulating diamonds, and supported the view of Dean (1965) that this is the photoionization limit for the isolated substitutional nitrogen donor.

Halperin and Nahum (1962) studied photoconduction, optical absorption and luminescence in type Ia and intermediate diamonds, and reported an inverse correlation in the region of the N3 system between the photoconductivity and both the optical absorption and the luminescence; minima occurred in the photoconduction spectra at the positions of maxima in the optical absorption and luminescence excitation spectra, at temperatures up to 350 K. The photoconductivity minima were explained in terms of competitive absorption by the N3 system against a broad background of photoconduction, the temperatures not being high enough for thermal ionization to occur from the excited state of the N3 centre.

2.2.2 Type Ib diamond

Vermeulen (1965) investigated photoconductivity in two natural type Ib diamonds and found that they had similar spectra. The photoconductive response commenced at about 1 μm and increased fairly rapidly around 700 nm. There was no evidence of the ultraviolet peak which has its threshold at 4.05 eV. No other measurements of photoconductivity have been made in diamonds which are unambiguously type Ib, apart from the work which is reported in this thesis (some of which has been published (Farrer 1969; Vermeulen and Farrer 1975)).

2.2.3 Type IIa diamond

Vermeulen (1965) has reported that two features occur in the photoconduction spectra of type IIa diamonds (apart from the exciton and band gap peaks which he observed in type Ia diamonds as well). A single peak in the infrared, with its long wavelength limit at about 1.3 μm is followed by a broad photoconductive development which starts at about 800 nm and extends to the intrinsic absorption edge; the latter feature appears to be related to the optical absorption tail which is observed in type IIa diamonds.

2.2.4 Type IIb diamond

Hardy, Smith and Taylor (1962) reported that the photoconductive spectrum of type IIb diamonds between 0.35 and 0.9 eV showed a considerable amount of detailed structure; minima in the spectrum were explained in terms of a reduced lifetime for free holes whose energy allowed them to be captured by excited bound states of the acceptor

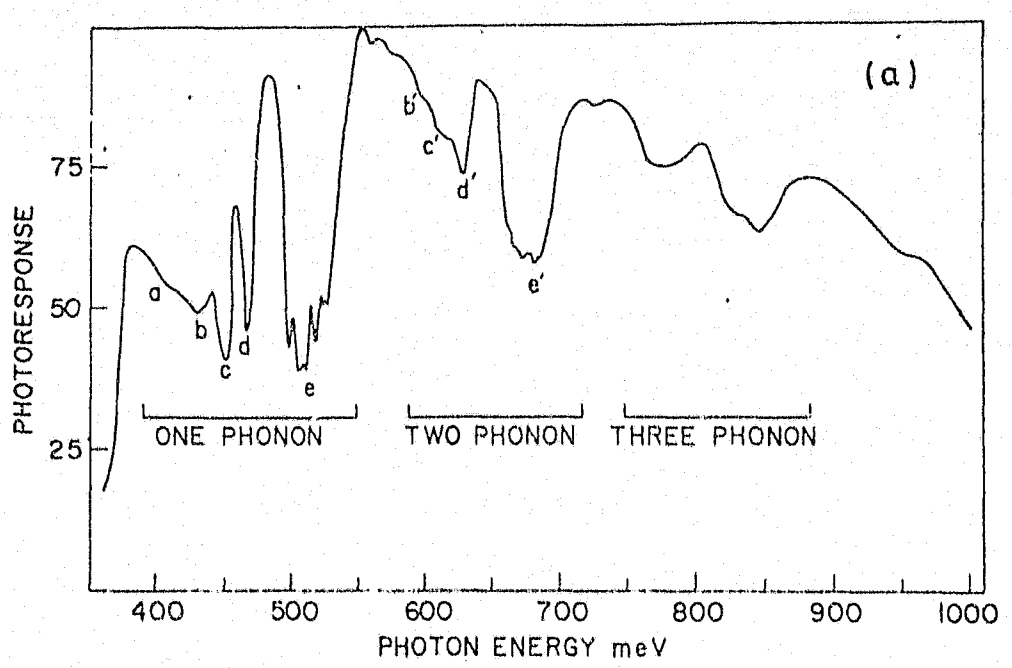
centre with the emission of an integral number of optical phonons. Collins and Lightowlers (1968) observed temperature-dependent maxima in the spectrum at energies below the ionization threshold of the acceptors, which they attributed to photothermal ionization, i.e. optical excitation of holes to excited states, followed by thermal excitation into the valence band.

Photoconduction spectra observed by Collins, Lightowlers and Dean (1969) are shown in Fig. 2.4. Minima involving free hole capture with the emission of up to 14 phonons were detected. They observed a gradual decrease in the spacing of these minima at higher energies, which they showed to be consistent with the curvature of the valence band and the dispersion curves for longitudinal optical phonons. They also observed minima in the spectrum which they attributed to phonon-assisted hole capture to excited states of the acceptor for which transitions from the ground state are forbidden and which are therefore not observed in absorption.

2.2.5 Photo-Hall effect measurements

Lenz (1927) observed the photo-Hall effect in an insulating diamond under ultraviolet illumination; his results yield a room temperature electron mobility of 200 $cm^2V^{-1}s^{-1}$. Klick and Maurer (1951) found that a type Ia diamond was n-type under illumination by broad-band light between 620 and 300 nm, and calculated a value of 900 $cm^2\ V^{-1}s^{-1}$ for the room temperature electron mobility.

Redfield (1954) found both p- and n- type conductivity in his study of the temperature dependence of the Hall mobility in diamonds under illumination. The two samples which he found to be p-type both transmitted ultraviolet light of wavelength 254 nm, and could have been type IIa



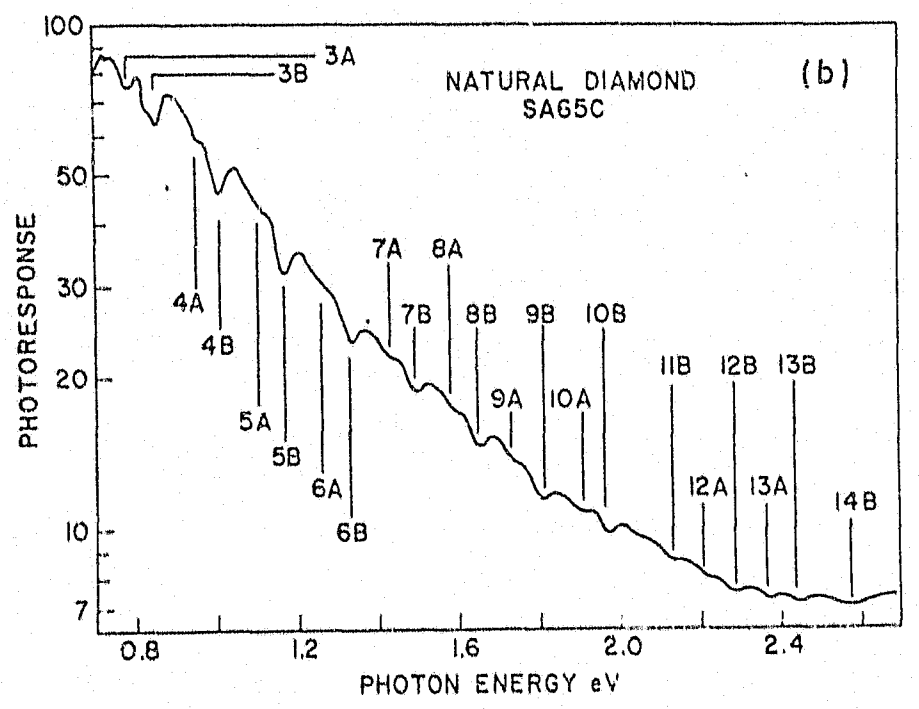


FIG. 2.4 The photoconductivity spectrum of a type IIb diamond (a) in the one-, two-, and three-phonon region above the acceptor ionization threshold, and (b) at higher energies, showing the minima associated with the multiphonon cascade process. Both spectra are from Collins, Lightowlers and Dean (1969).

diamonds; the diamonds which were opaque to this light were (with one rather doubtful exception) n-type. Details of the illumination used are not very clear, but the source appears to have been a tungsten spotlight, and infra red radiation was removed using a cupric chloride water solution; thus one can reasonably assume that the light used to illuminate the specimens was mainly in the visible. Room temperature electron and hole mobilities were about 1800 and 1200 $cm^2\ V^{-1}s^{-1}$ respectively, and both appeared to vary as $T^{-1.5}$.

Konorova and Shevchenko (1967) found that nine out of ten type Ia diamonds they investigated were n-type under 254, 365 and 380-400 nm illumination; the tenth diamond became p-type in the 380-400 nm region. Denham, Lightowlers and Dean (1967) reported that a type IIa diamond with a strong photoconductivity threshold at 4.05 eV was n-type when this photoconductivity was excited; bearing in mind the photoconductive results reported by Vermeulen and Nabarro (1967), it seems likely that this diamond was either a mixed or intermediate type, or a type Ia.

2.3 Defects in Irradiated Diamond

2.3.1 Introduction

Before the advent of synthetic diamond, the only defects over which the research worker had any measure of control were those produced by exposing the diamonds to irradiation with nuclear particles. Irradiation-induced defects in diamond have been extensively studied by Clark, Ditchburn and Dyer (1956a,b) and subsequent authors, and the properties of irradiated diamond have been reviewed by Mitchell (1965) and Clark and Mitchell (1971).

Clark, Kemmey and Mitchell (1961) estimated the displacement energy of a carbon atom in the diamond lattice to be 80 eV. From their observations it has been inferred that electrons of energy 0.3 - 0.8 MeV produce mainly single defects; however, recent investigations (Lomer and Wild 1971) have indicated that the interstitial carbon atom is mobile below room temperature, and Vandersande (1974) has shown that room temperature irradiation results in the formation of interstitial aggregates. Massarani, Bourgoin and Chrenko (1974) have studied radiation damage in synthetic diamond at low temperature, and have confirmed that the interstitial becomes mobile just below room temperature; they estimate the threshold energy for carbon atom displacement to be as low as 50 eV.

2.3.2 The GR1 band and associated features

Fig. 2.5 shows the two main optical absorption features which are observed in all diamonds after electron irradiation; these are known as the GR1 band and the UV band (Clark, Ditchburn and Dyer 1956a). The GR1 band consists of a zero phonon line at 1.67 eV with associated phonon structure at higher energies. The UV band is an absorption continuum which extends from about 2.8 eV to the fundamental absorption edge at 5.5 eV; on the low energy tail of this continuum are a number of sharp optical absorption lines known as GR2, GR3 ..... GR8, R9 and R10.

Clark and Norris (1971) observed that the luminescence associated with the GR1 centre is unpolarized and suggested that the defect might have tetrahedral symmetry. The GR1 zero phonon line consists of a doublet (Clark and Walker 1971, 1972) with lines at 1.665 and 1.673 eV; investigations of the behaviour of these lines under uniaxial stress (Clark and Walker 1973, Davies and Penchina 1974) have

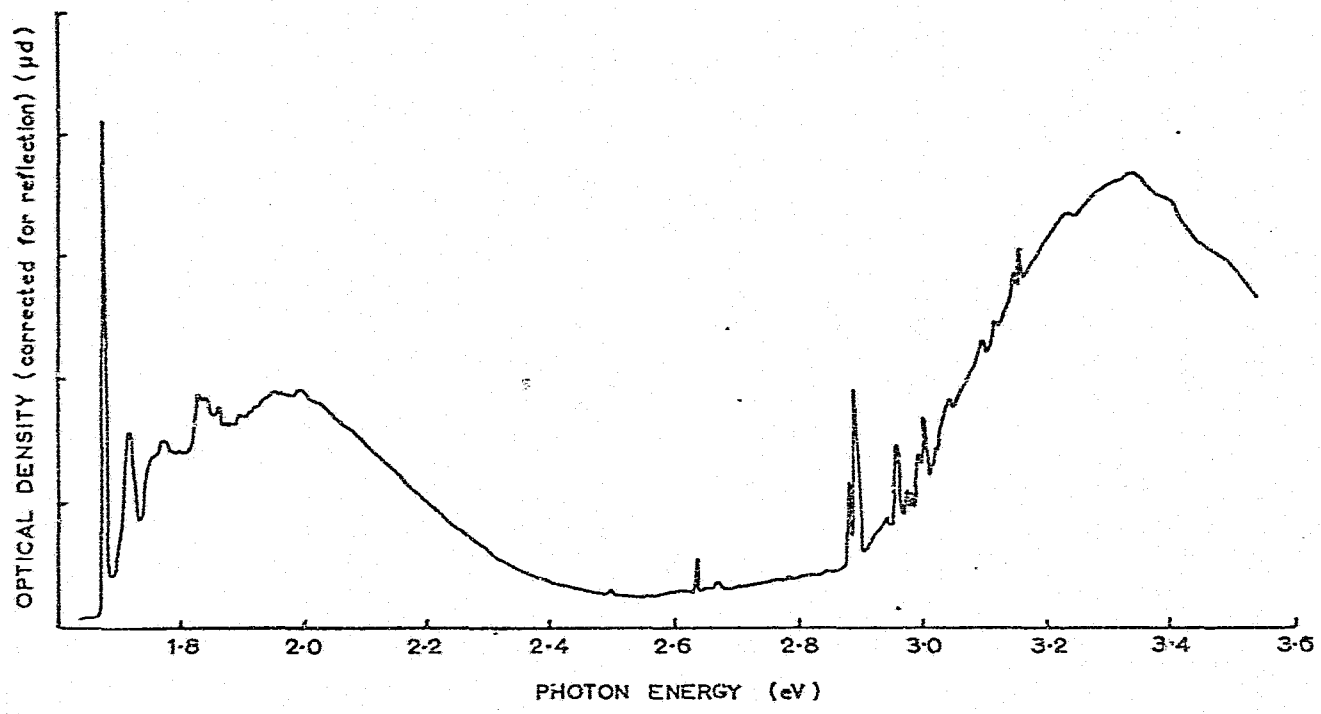


FIG. 2.5 The absorption spectrum recorded at 4.2K of an electron irradiated type II diamond, showing the GR1 band, the UV band and the sharp lines GR2-8, R9 and R10 on the low energy tail of the UV band. Taken from Mitchell (1965).

confirmed that the GR1 centre has tetrahedral symmetry and comparison of the experimental details with theoretical treatments of intrinsic defects in diamonds have led to the identification of the centre as a neutral vacancy, confirming the suggestion which was originally made by Clark, Ditchburn and Dyer (1956b). Dyer and du Preez (1965) suggested that the UV band is due to ionization from the ground state of GR1 centres, and measurements of the temperature dependence and the behaviour under uniaxial stress of the lines GR2 to GR8 have shown that all these transitions occur at the vacancy (Walker, Vermeulen and Clark 1974). Thus it appears that the GR1 band, the UV band and the GR2-8 lines might all be due to excitations at the same centre (the neutral vacancy).

Electrical measurements on semi-conducting diamonds have showed that the free hole concentration is reduced by electron irradiation (Wedepohl 1957b, Mitchell 1959). Dyer and Ferdinando (1966) found that the GR1 and UV bands did not appear in semi-conducting diamonds until the irradiation dose was sufficient to result in compensation of the acceptor centres; they therefore considered the GR1 and UV bands to be associated with irradiation-induced donors. However, Vermeulen, Clark and Walker (1974) have reported the somewhat unexpected finding that the majority carriers produced by broad band excitation with light in the region of both the GR1 and the UV bands are holes; this can be understood if both donors and acceptors are produced by irradiation (Vermeulen and Farrer 1975).

Davies (1974) has made the interesting observation of structure on the GR1 doublet in electron-irradiated type Ia diamonds, which is caused by some GR1 centres having migrated to specific sites close to the nitrogen, where

their symmetry is lowered. He finds that the migration can be completed by annealing, which destroys the centres.

2.3.3 The ND1 band

The ND1 band, shown in Fig. 2.6, consists of a zero phonon line at 3.15 eV followed by characteristic phonon structure at higher energies. Dyer and du Preez (1965) reported that it is created in type Ia diamonds by irradiation accompanied by heating to about 250°C. The localized heating associated with room temperature irradiation is sufficient to produce the band, whereas it is not produced by low temperature irradiation unless this is followed by heat treatment. They suggested that the ND1 centre might be a combination between an interstitial carbon atom and a nitrogen aggregate.

Dyer and du Preez (1967) reported that a further system (the ND2 system), also with a zero-phonon line at 3.15 eV, was produced in type Ib diamonds even when irradiation was carried out at low temperature. They suggested that this might be due to a combination of an interstitial carbon with a substitutional nitrogen atom. It appears, however, that the ND1 and ND2 bands are identical and are both due to the same defect (Davies and Lightowlers 1970).

Observations of the effect of uniaxial stress on the ND1 zero-phonon line have been interpreted by Davies and Lightowlers (1970) in terms of a transition from an A to a T state at a centre with T_d symmetry and they have proposed that the ND1 centre might be an interstitial nitrogen atom. They suggest that interstitial carbon atoms produced by irradiation migrate to nitrogen centres (aggregates in the case of type Ia diamonds) and exchange positions with nitrogen atoms. The higher temperature required to produce the centres in type Ia diamonds is attributed to a higher barrier for exchange at aggregates

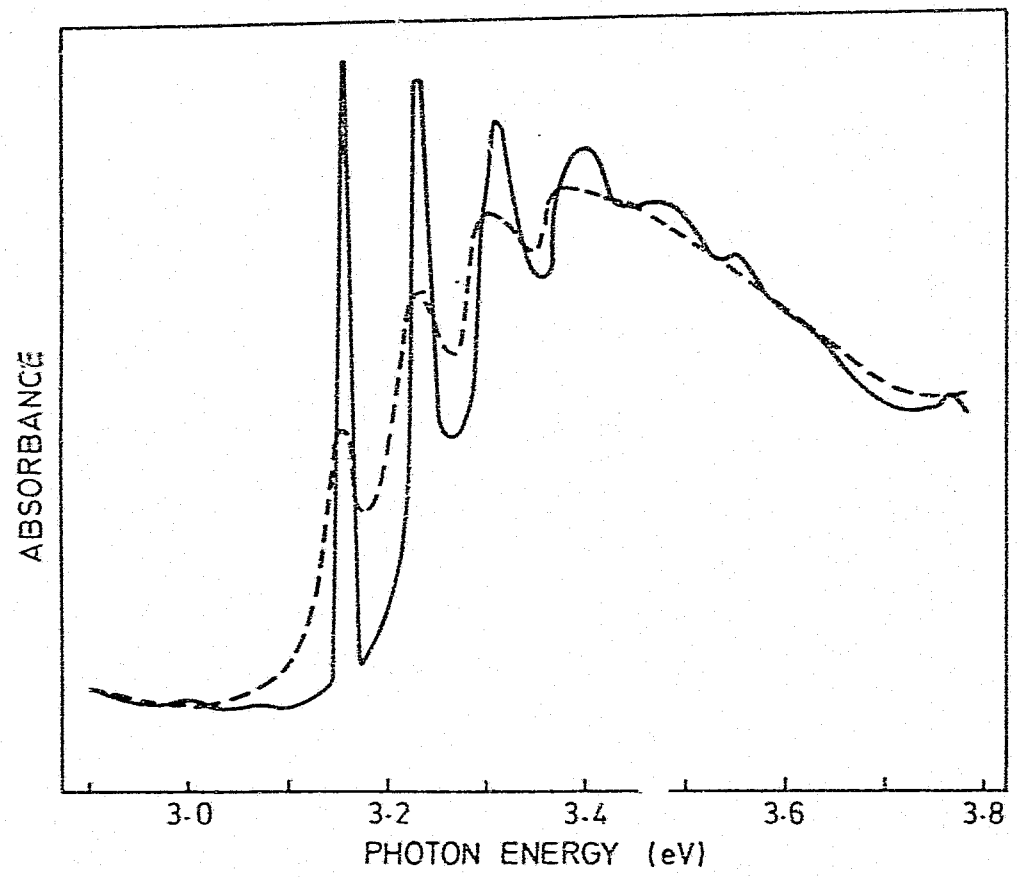


FIG. 2.6 The ND1 optical absorption system measured at room temperature (broken curve) and at 80K (solid curve). Redrawn from Dyer and du Preez (1965).

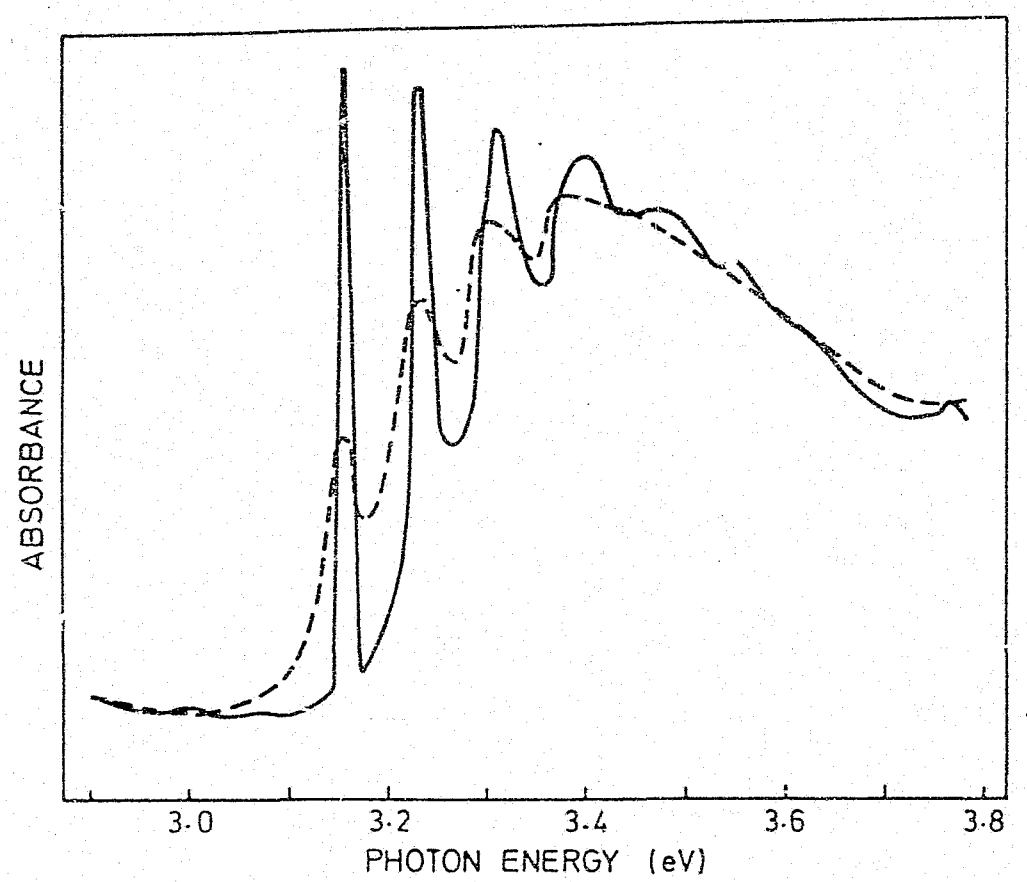


FIG. 2.6 The ND1 optical absorption system measured at room temperature (broken curve) and at 80K (solid curve). Redrawn from Dyer and du Preez (1965).

than at isolated nitrogen atoms. Although preliminary calculations of Messmer and Watkins (1971) indicate that nitrogen is not stable in the interstitial tetrahedral site, the model of Davies and Lightowlers is far more likely to be correct than those of Dyer and du Preez (neither of which is likely to have tetrahedral symmetry).

Dyer and du Preez (1965) observed correlated enhancement and bleaching of the GR1 and ND1 absorption systems in type Ia diamonds. They found that the GR1 and UV bands were enhanced when the ND1 system was bleached (and vice versa) and explained these effects in terms of the transfer of charge carriers between ND1 and GR1 centres via the conduction and valence bands. In their model, the UV band is due to ionization from the ground state of GR1 centres. They proposed that the first excited state of a GR1 centre lies about 1.2 eV below the conduction band, whereas the first excited state of an ND1 centre is fairly close to the conduction band, and photothermal ionization of the ND1 system can take place at room temperature.

Luminescence associated with the GR1 system has been observed and studied by Clark and Norris (1971), confirming that the first excited state of the GR1 centre is a bound state. However, Davies and Lightowlers (1970) have reported that they could detect no luminescence emission associated with the ND1 system, although Dean (1965) had earlier ascribed cathodoluminescence observed by Ralph (1960) to the ND1 system.

Davies (1974) finds that the ND1 zero phonon line possesses long tails in type Ia diamonds which have a high nitrogen content. These are due to ND1 centres which have been perturbed by the nitrogen; on annealing, perturbed centres are captured by the nitrogen and the absorption tails are reduced.

2.3.4 Other optical absorption bands

The H3 and H4 systems (Clark, Ditchburn and Dyer 1956b) are observed in type Ia diamonds which have been irradiated and annealed; the H3 system is also observed in some unirradiated type Ia diamonds, presumably due to natural irradiation and heating at some time in the past. Both systems consist of zero phonon lines (the H3 at 503.2 nm and the H4 at 496.5 nm) and associated vibronic structure at higher energies. Observations of the polarization of luminescence indicate that both defects have monoclinic I symmetry (Clark and Norris 1970, 1971). It has been suggested (Davies 1972b) that the H3 centre is formed when an ND1 centre migrates during thermal annealing and is trapped at an A aggregate of nitrogen, and that the H4 centre is formed in a similar fashion at a B aggregate. An interesting observation reported recently is that the decay time of cathodoluminescence from the H3 centre decreases with increasing nitrogen content; a transfer of energy from the H3 centres to the A form of nitrogen has been proposed to account for this (Crossfield, Davies, Collins and Lightowlers 1974).

An optical absorption system with its zero phonon line at 640 nm was observed by du Preez (1965) in type Ib diamonds which had been irradiated and annealed. He suggested that the defect responsible for this system might be a substitutional nitrogen atom anchored to a GR1 centre (now known to be a vacancy). Measurements of polarized luminescence indicated that the defect has either monoclinic I or trigonal symmetry (Clark and Norris 1971), and recent observations of absorption and luminescence under uniaxial stress confirm that the symmetry is trigonal (Hamer and Davies 1974), which is consistent with the nitrogen-vacacy model.

A centre which gives rise to an optical absorption band

with a zero-phonon line at 503.6 nm (and is clearly different to the H3 centre) is observed in all irradiated diamond (Dugdale 1953, Davies 1974). Walker (1974) has reported that this defect has rhombic I symmetry and has suggested that it might be a negatively charged vacancy or an oxygen-vacancy pair.

The TH5 absorption lines between 540 and 440 nm were observed in irradiated and annealed type IIa diamonds by Clark, Ditchburn and Dyer (1956b), who suggested that they might be due to a pair of GR1 defects (vacancies). Walker (1974) has found that the defect responsible for the TR12 absorption line (Clark, Ditchburn and Dyer 1956a) has monoclinic symmetry and has also suggested the divacancy as a possible model for this centre.

2.3.5 Electron paramagnetic resonance centres

The electron paramagnetic centres observed in diamond after irradiation have been reviewed by Owen (1965), and recent work includes that by Whippey (1972) and Lomer and Wild (1971, 1973). Some of the more interesting centres are briefly discussed here.

Baldwin (1963) observed a spectrum from a centre with spin ½ in what he reported to be a type IIa diamond which had been irradiated. The spectrum could be enhanced by illumination with light of energy greater than 2.8 eV and he suggested that it was due to the ionized vacancy. Although it appears that light of energy greater than 2.8 eV does ionize the vacancy (see section 4.1 of this thesis; Farrer and Vermeulen (1972); Walker, Vermeulen and Clark 1974), some doubt exists about Baldwin's interpretation of the spectrum. Hyperfine structure which he attributed to the presence of ^{13}C nuclei is probably due to some form of nitrogen (Loubser 1974). The diamond in which

Baldwin observed the spectrum was probably either a type Ia or type Ib (or intermediate) since it contained paramagnetic nitrogen. It is therefore probable that the ND1 centre was also present and Loubser (1975) finds that the Baldwin spectrum appears to correlate qualitatively with the ND1 absorption; however, the reported symmetries of the Baldwin centre and the ND1 centre (Davies and Lightowlers 1970) do not correspond, and further work is needed.

Lomer and Wild (1971) observed an electron paramagnetic resonance spectrum in diamonds which were irradiated below 20K. This spectrum annealed out at 140K and they suggested that it is due to the interstitial which becomes mobile at 140K. Other evidence for the mobility of the interstitial below room temperature has been mentioned in 2.3.1.

Faulkner and Lomer (1962) reported two spin 1 centres with axial symmetry and proposed that they arose from a pair of carbon interstitials interacting with a pair of vacancies. Owen (1965) suggested that single interstitials were involved (one of them in distorted surroundings) and his models were supported by Whippey (1972). However, Walker (1973) has pointed out that the results of Whippey (1972) indicate that impurities are probably involved and has suggested that each centre might be a single interstitial-substitutional impurity combination.

Lomer and Wild (1973) have recently observed centres with $\langle 110 \rangle$ symmetry in irradiated and annealed type IIa diamond, which they believe to be linear chains of between 2 and 7 vacancies.

2.4 Discussion of previous work and the aims of this investigation

Investigations into the properties of defects in diamond have yielded a large amount of interesting

information; however, it would appear that only three of the defects which have been identified unambiguously are reasonably well understood. These are the substitutional boron atom in semi-conducting diamond, the isolated vacancy caused by radiation damage and the substitutional nitrogen donor. Perhaps the single most controversial issue which still remains to be resolved concerning these defects is the question of the position in the energy gap of the level formed by the substitutional nitrogen, and in particular, whether the photoconduction threshold at 4 eV in type Ia diamond is the photoionization limit for this level.

It has become accepted in the literature, following the suggestion of Dean (1965), that the nitrogen donor lies 4 eV below the conduction band (eg. Denham et al 1967; Wight et al 1971; Clark and Mitchell 1971; Messmer and Watkins 1973). In their recent theoretical treatment of the substitutional nitrogen centre in diamond, Messmer and Watkins (1973) have commented that 'the reason for its being so deep has been a mystery of considerable concern in the literature.' They point out that nitrogen in diamond is the direct counterpart of phosphorus in silicon, which is a shallow donor (about 0.05 eV below the conduction band). Their calculations place the nitrogen level 2.2 eV above the valence band (i.e. 3.3 eV below the conduction band); however, as Davies (1972a) has pointed out, they predict no energy levels which might explain the absorption tail which commences at about 2 eV and which has been correlated with the substitutional nitrogen.

It has been emphasized by many authors (eg. Davies 1972a) that the classification of natural diamonds into the different types is useful but by no means absolute. 'Intermediate' diamonds, which are homogeneous but show some of the characteristics of more than one of these types, are often encountered. 'Mixed' diamonds, which are inhomogeneous mixtures of more than one type, are also found. In

particular, paramagnetic nitrogen has been observed in small quantities in many type Ia diamonds (du Preez 1965; Lazukin et al 1970; Loubser 1975) and it is possible that the 4 eV threshold, which is believed to be typical of type Ia diamond (Vermeulen and Nabarro 1967) might be a characteristic of the substitutional nitrogen; however, it should also be characteristic of both natural type Ib diamond and synthetic type Ib diamond, which do not contain nitrogen in aggregate form (Dyer et al 1965; Sobolev et al 1969; Chrenko et al 1971). Experimental investigations of the properties of type Ib diamonds (and especially synthetic type Ib diamonds) which might lead to the unambiguous determination of the ionization energy of the substitutional nitrogen donor are therefore of considerable interest. Measurements of photoconductivity, electrical resistance as a function of temperature and identification of the sign of the charge carriers in natural and synthetic type Ib diamond form part of the work reported in this thesis.

The other observations reported in this thesis are measurements of the photoconductivity in the region of the GR1 system, the GR2-8 absorption peaks and the ND1 system in natural type Ia and type IIa diamonds which have been electron-irradiated. Vermeulen (1965) reported that a sharp decrease appeared in the photoconduction spectra of irradiated type IIa diamonds at the position of the GR1 absorption system, and that sharp lines which were observed on the tail of the UV band appeared to coincide with the absorption peaks GR2-8; no investigations of photoconductivity in the neighbourhood of the ND1 system have been reported in the literature except for the work (Farrer and Vermeulen 1972) which is reported in this thesis.

In appearance, the ND1 absorption system is similar to the N3, H3, GR1 and other systems in diamond. The luminescence associated with these defects confirms that the spectra arise from transitions between ground states and

bound excited states of the defects concerned, and the apparent absence of NDl luminescence (Davies and Lightowlers 1970) is of considerable interest. Davies and Lightowlers have considered the possibility that a radiationless de-excitation mechanism might explain the absence of NDl luminescence. They refer to Nelson et al (1966), who have shown that the Auger effect, in which energy difference between the excited state and the ground state of the centre is used to eject an electron, can act as a very efficient mechanism of this kind. Nelson et al (1966) suggest that the probability for such a process can be estimated using an expression adapted from one which is used to calculate the probability of internal conversion in nuclear physics, and Davies and Lightowlers (1970) find that this expression yields a value of 10^{-6} for the ratio of the non-radiative to radiative lifetimes of the NDl centre. While this might be interpreted as evidence for suggesting that an Auger process takes place at the NDl centre, there is some doubt concerning the validity of the calculation in this context. The same value can be obtained for the N3 centre (which is strongly luminescent) since the only variable parameter in the calculation is the wave number of the light quantum from the radiative process.

An Auger-type process nevertheless remains an interesting possibility as a radiationless de-excitation mechanism for the NDl centre; in this case photoconduction maxima which persist down to very low temperatures should be observed at the positions of the peaks in the NDl absorption system. On the other hand, if the mechanism of photothermal ionization of the NDl system proposed by Dyer and du Preez (1965) is correct, one would expect to observe maxima in the photoconduction spectrum at the NDl peak positions at room temperature which should change to minima at low temperatures.

CHAPTER 3

EXPERIMENTAL METHODS AND APPARATUS

3.1 Measurement of photoconductivity

3.1.1 General description

When a semi-conducting or insulating material is irradiated with light of sufficient energy to excite an electron from the valence band to the conduction band, or to ionize a level within the forbidden energy gap, the free carrier concentration is increased and the electrical conductivity increases; this effect is known as photoconductivity. The measurements of photoconductivity in diamond reported in this thesis were undertaken for two reasons. The study of photoconductivity provides a means of determining whether particular optical absorption features are associated with bound state transitions or with ionization. It also provides a measure of the optical ionization energy of a defect; this is determined by the low energy (or long wavelength) threshold for photoconductivity (Bube 1960).

A block diagram of the experimental arrangement used to measure photoconductivity in the diamonds is shown in Fig. 3.1. Fields of up to 800 V cm^{-1} were applied to the diamonds and photocurrents were measured using either a General Radio type 1230 A or a Keithley type 610 C electrometer. A mercury-indium-thallium amalgam, which is known to make non-rectifying contacts on diamond (Vermeulen 1965) was used as a contacting material.

The diamonds were illuminated with light from a Zeiss prism monochromator (model M4 QII) and continuous photoconduction spectra were obtained by sweeping the monochromator from low to high energy. Two light sources were used with the monochromator - a tungsten source was used in the range

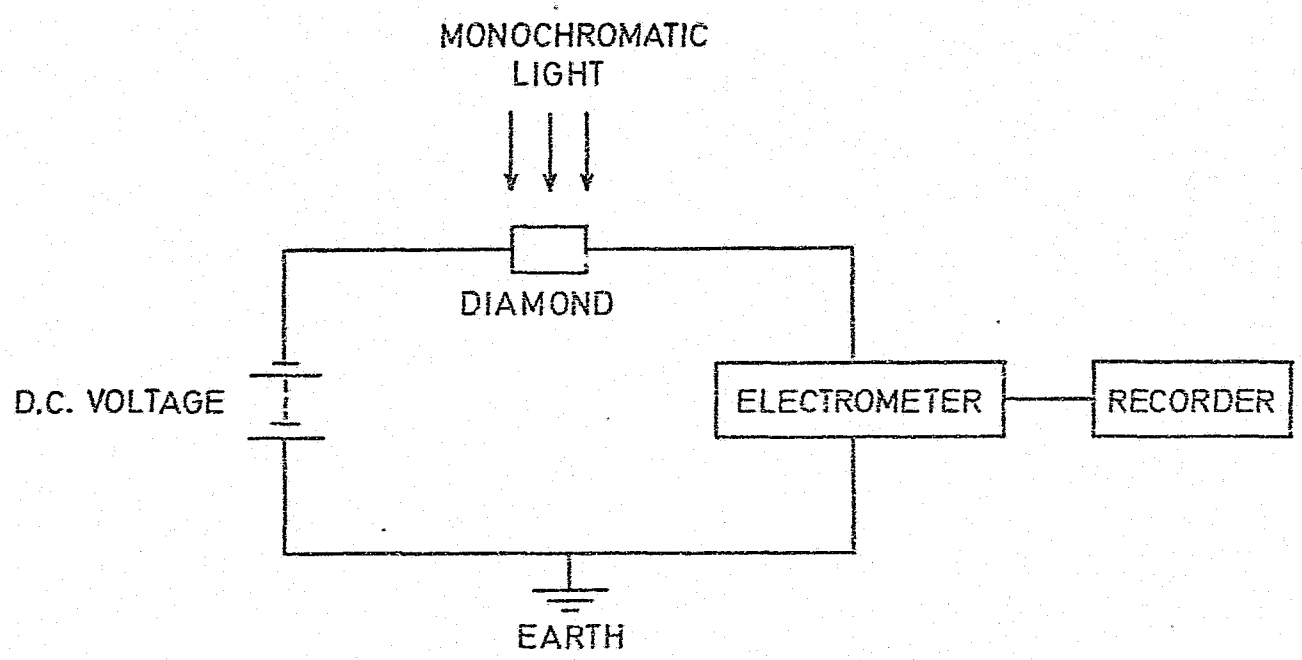


FIG. 3.1 A block diagram of the experimental arrangement used to measure photoconductivity in diamonds.

2.5 μm to 400 nm, and a high pressure deuterium lamp was used from 500 to 200 nm. Both lamps were known to be line free in the ranges over which they were used. The output of the monochromator using these lamps is shown in Figs. 3.2 and 3.3 respectively. These were measured using a type FT16 Hilger Schwartz thermopile which had a Spectrosil window, together with a Keithley type 147 Nanovoltmeter. The monochromator output using the tungsten lamp was subsequently checked using a Hewlett Packard type 8330 A Radiant Flux Meter, which was not sufficiently sensitive to check the output with the deuterium lamp. The dispersion of the monochromator is shown in Fig. 3.4. The data in Figs. 3.2, 3.3 and 3.4 were used when photoconduction spectra were normalised.

3.1.2 The room temperature sample holder

The sample holder which was used for room temperature photoconductive studies is shown in Fig. 3.5. It was made from a modified UHF coaxial socket and could be attached to the electrometer input using a single adaptor.

3.1.3 The liquid helium cryostat

The liquid helium cryostat, which could be used for photoconduction and optical absorption studies, is shown in Fig. 3.6. One of the prime objectives in the design of this cryostat was to avoid the need for electrical insulation directly between the liquid helium and the sample (since almost all electrical insulators are poor conductors of heat), and yet to retain the facility to adjust the sample position and to introduce thermal insulation between the sample holder and the helium can should higher sample

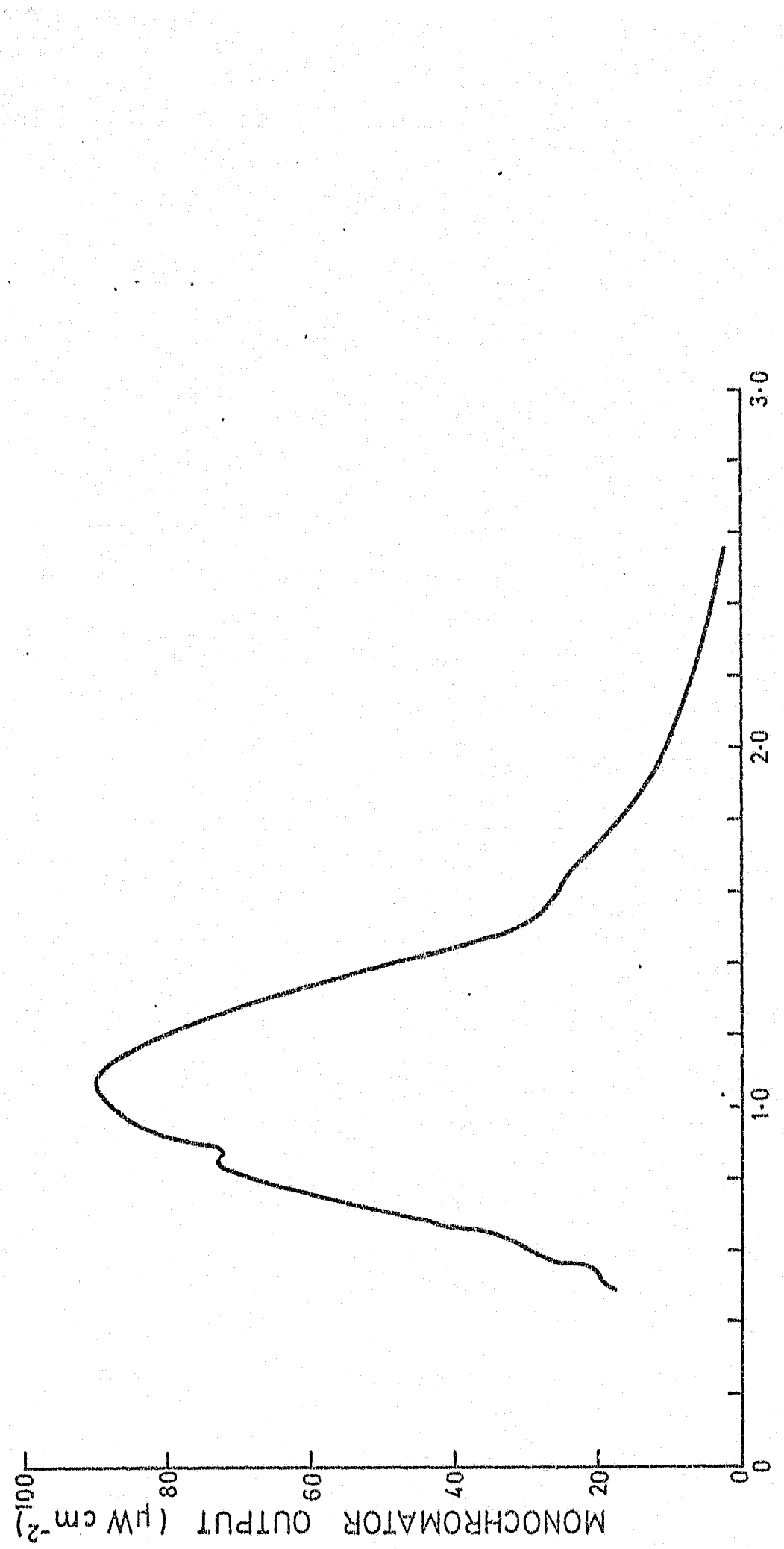


FIG. 3.2 The output of the monochromator using the tungsten lamp (monochromator slitwidth 0.2 mm)

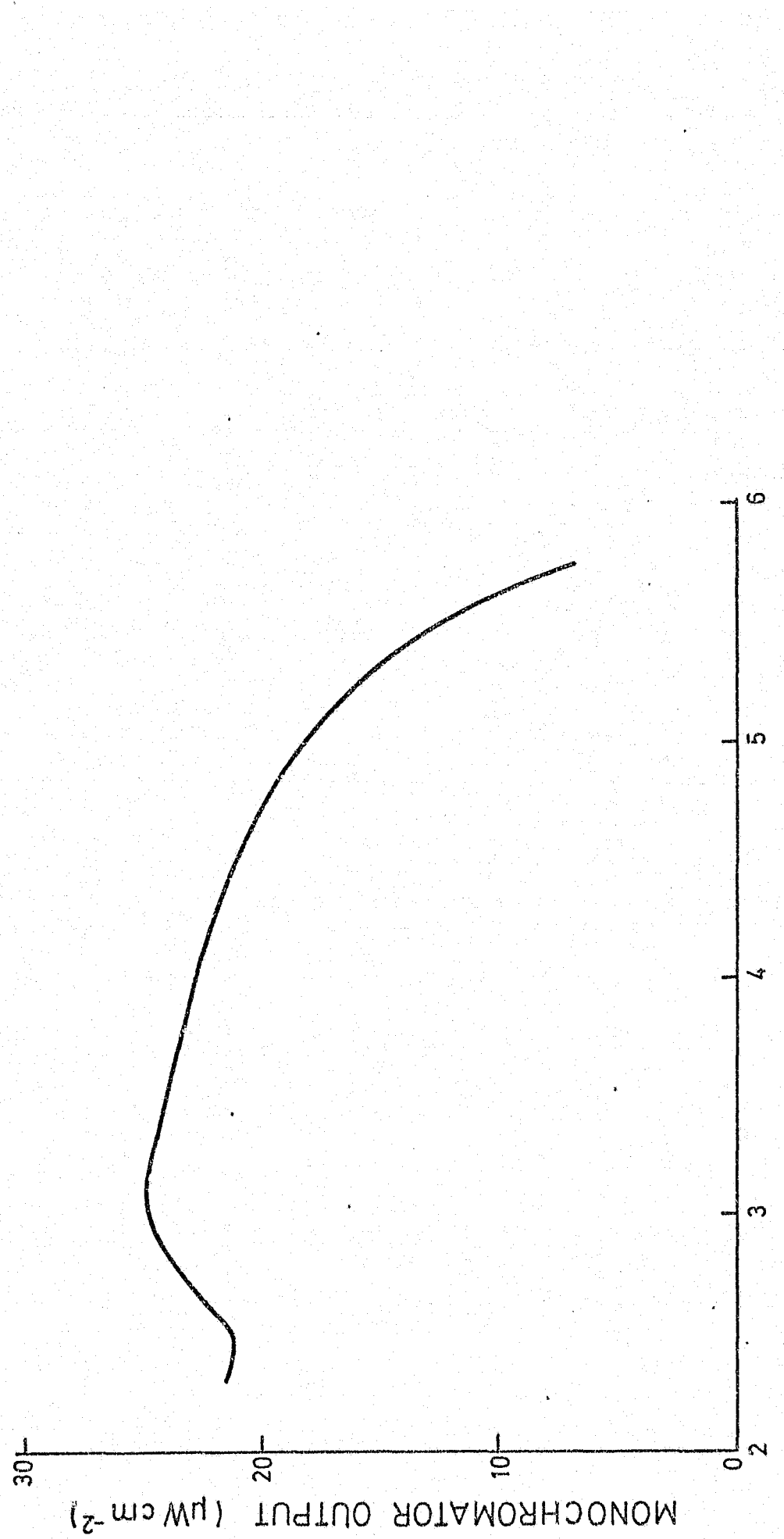


FIG. 3.3 The output of the monochromator using the deuterium lamp. Monochromator slitwidth 2.0 mm.

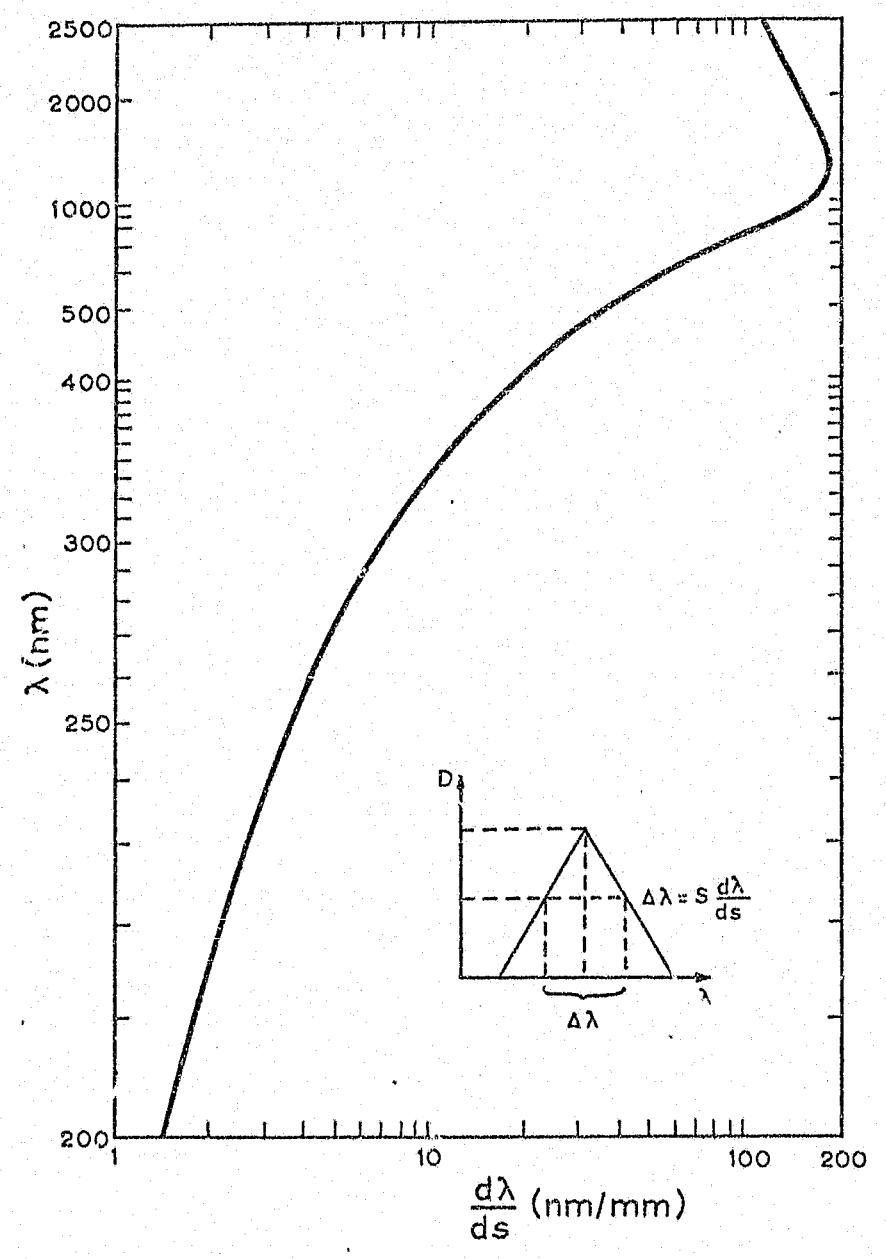


FIG. 3.4 The dispersion of the monochromator. S is the slit-width (in mm).

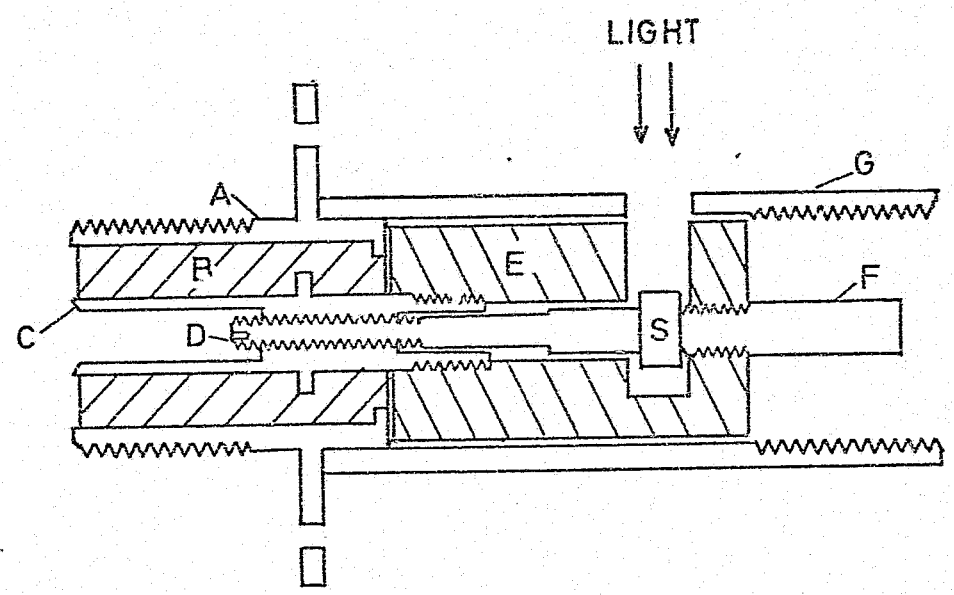


FIG. 3.5 The room temperature sample holder. A - modified chassis-mounting UHF coaxial socket; B - socket insulation; C - socket centre terminal (drilled and tapped); D - adjustable electrode; E - teflon insulation; F - adjustable electrode; G - metal screening cover threaded to receive UHF adaptor; S - diamond sample.

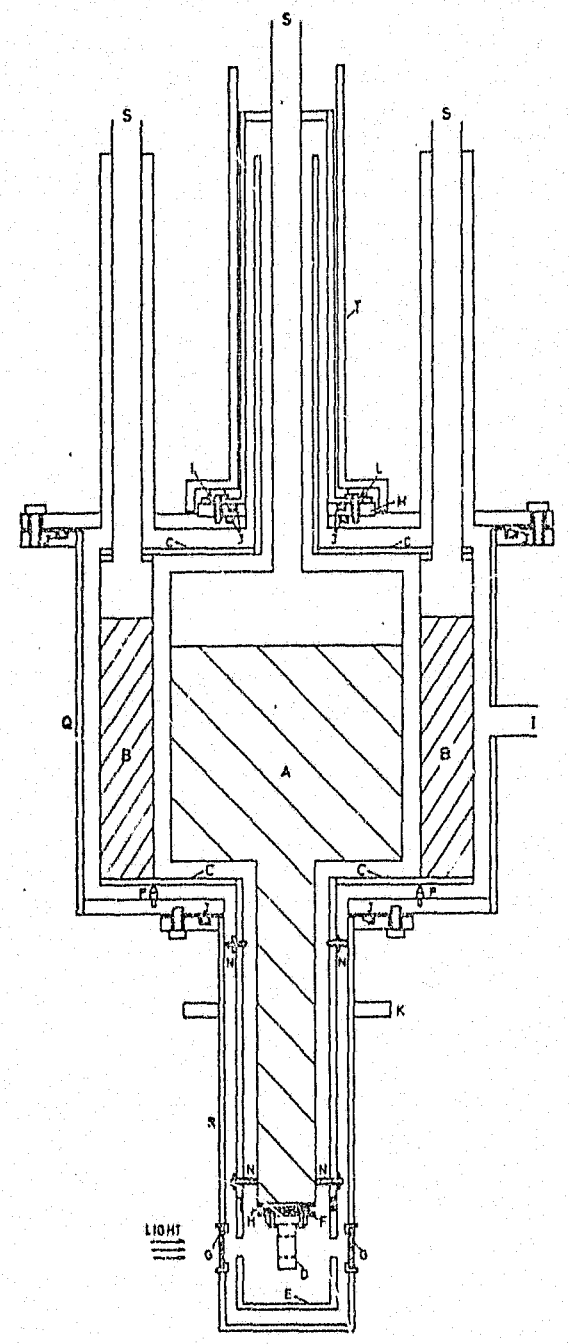


FIG. 3.6 The liquid helium cryostat. A - helium can; B - nitrogen can; C - copper radiation shields; D - sample holder; E - removable radiation shield; F - copper plug; G - silica windows; H - heater; I - vacuum line; J - O rings; K - support for use in spectrophotometer; L - perspex bushes; M - perspex insulating ring; N - nylon bracing screws; P - stainless steel supporting screws; Q - stainless steel outer can; R - brass lower can; S - thin-wall stainless steel tubes; T - insulating cover.

temperatures be required. It is a compact, all-metal cryostat and is fairly conventional in design except for the fact that the sample holder and the whole helium can (including its filling tube assembly) are connected to the DC voltage supply when photoconduction measurements are in progress. Electrical insulation between this can and the rest of the cryostat is maintained by the perspex ring M and bushes L on the top flange of the cryostat and the nylon bracing screws N. All internal surfaces of the cryostat were polished and nickel-plated.

A detailed sketch of the sample holder, which was attached with indium solder to the copper plug at the bottom of the helium can, is shown in Fig. 3.7. The cryostat could be mounted in a Unicam SP800 spectrophotometer for optical absorption measurements in the visible and ultraviolet. When these measurements were made, a mask was fitted onto the sample holder in order to intercept light not passing through the sample.

The temperature of the sample with liquid helium in the inner can was measured using a 47 ohm Allen-Bradley resistor, which was placed in the sample position with the aid of silicon grease to obtain good thermal contact. Clement, Dolocek and Logan (1956) have shown that the variation in resistance with temperature of this type of resistor can be described by a single universal curve, which can be fitted to predict the behaviour of a particular resistor once its resistance has been measured at two known temperatures. The resistor used in these measurements was calibrated at three points - in a mixture of ice and water, in liquid nitrogen and in liquid helium. Fig. 3.8 shows the universal curve fitted to these three points. In the sample position, the resistor measured 219 ohms, indicating a temperature of 8K.

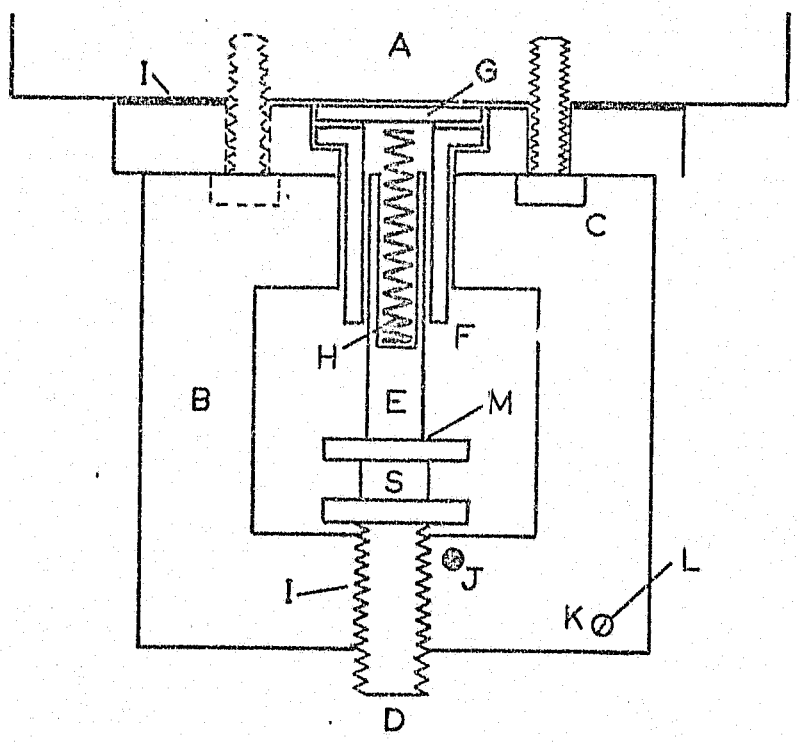


FIG. 3.7 The sample holder in the helium cryostat. A - copper plug in helium can; B - copper sample holder; C - screws; D - adjustable electrode; E - top electrode; F - teflon bush; G - teflon washer; H - spring; I - indium solder; J - hole for carbon resistor for temperature monitoring; K - screw; L - voltage lead; M - signal lead to electrometer; S - sample

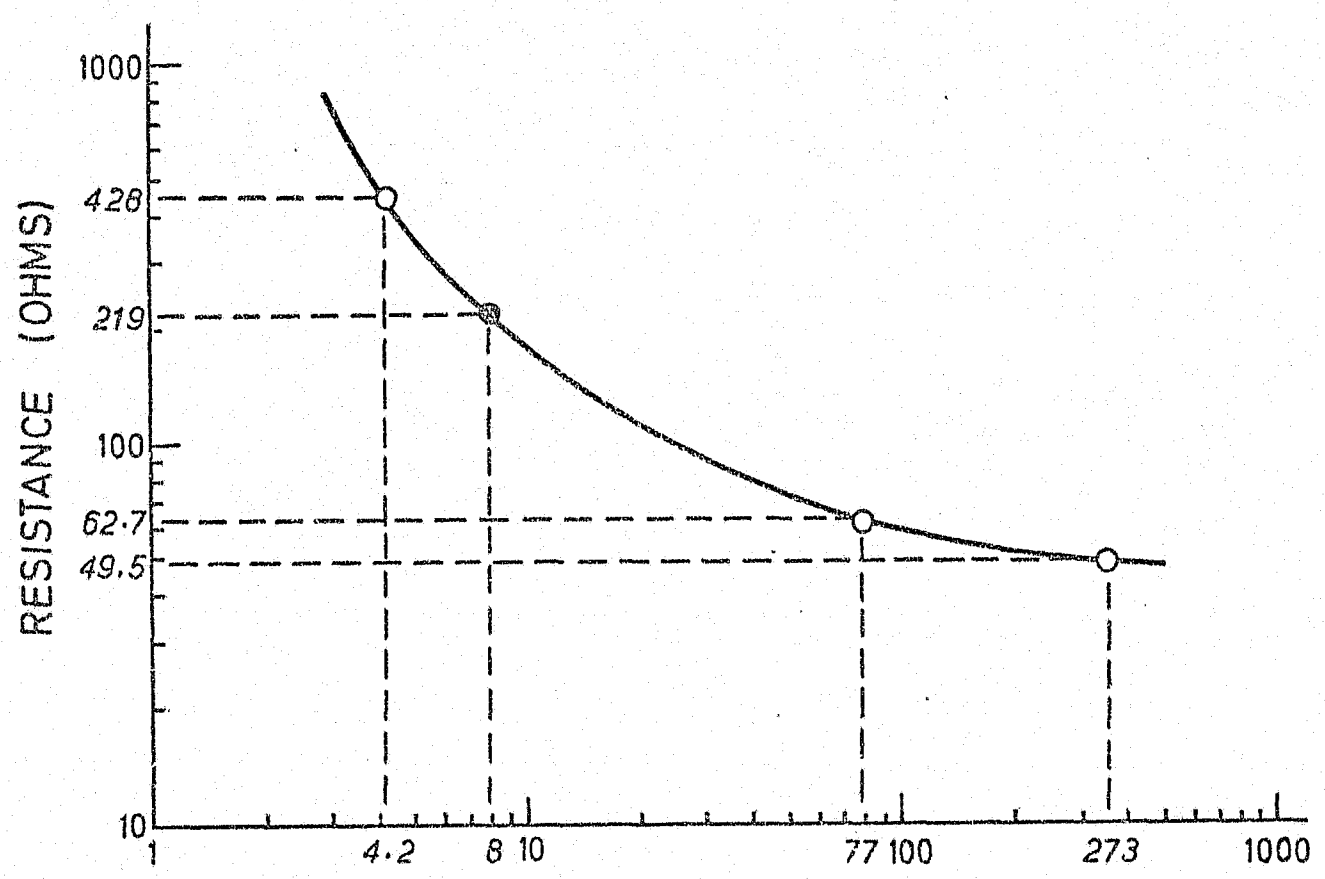


FIG. 3.8 The variation of resistance with temperature of the Allen-Bradley resistor used for temperature measurement in the helium cryostat. The open circles indicate calibration points and the solid line is the universal curve of Clement et al (1956) fitted to these points. Resistance and temperature in the sample position is indicated by the closed circle.

3.2 Measurement of thermal activation energies

3.2.1 The temperature dependence of electrical resistance

Using classical statistics it can be shown (Smith 1959) that the thermally generated free electron concentration n in a compensated semi-conductor or insulator is given by

$$n = \frac{N_D - N_A}{2N_A}\left\{\frac{2\pi m^* kT}{h^2}\right\}^{1.5} \exp(-E/kT) \quad \ldots\ldots \quad (1)$$

where N_D, N_A are the concentrations of donor and acceptor centres respectively, m* is the effective mass of the free electrons, k is Boltzmann's constant, h is Planck's constant, T is the absolute temperature and E is the thermal activation energy for the donor centres. Equation (1) is valid provided that the free electron distribution is non-degenerate and that $n \ll N_A < N_D$. When $N_A > N_D$ a similar expression gives the free hole concentration. n can be measured as a function of T using the Hall effect and E can be obtained from a plot of $k(\log n - 1.5 \log T)$ versus $1/T$. However, measurement of the Hall effect on small insulating samples is extremely difficult and observations of the electrical resistance as a function of temperature is often used instead.

The conductivity σ is given by

$$\sigma = ne\mu \quad \ldots\ldots\ldots \quad (2)$$

where e is the electronic charge and μ is the mobility of the charge carriers. Thus

$$\sigma \propto T^{1.5} . \mu . \exp(-E/kT) \quad \ldots\ldots \quad (3)$$

Measurements have shown that the electron mobility in diamond varies as $T^{-1.5}$ (Redfield 1954) and the hole mobility as $T^{-2.8}$ (Wedepohl 1957). In any event, the right hand side of equation (3) is dominated by the exponential. Thus, to a good approximation,

$$\sigma \propto \exp(-E/kT) \quad \ldots\ldots\ldots \quad (4)$$

If the contacts to the sample are ohmic, then the current i through the sample for a fixed applied voltage is proportional to σ and a plot of log i versus 1/T will be a straight line from which E can be calculated. Activation energies calculated by this method should be accurate to within a few percent (eg. Custers (1955), Brophy (1955) and Leivo and Smoluchowski (1955b) all estimated an activation energy of 0.35 eV from the temperature dependence of resistivity in type IIb diamond).

3.2.2 The general purpose apparatus

A general purpose apparatus which could be used for photoconductive studies at liquid nitrogen temperature and for photoconductive and conductive studies at temperatures up to 400°C is shown in Fig. 3.9. The hollow copper can C suspended at the end of two thin-walled stainless steel tubes S could be filled with liquid nitrogen for low temperature photoconductive studies, or have air blown through it to enable rapid cooling from higher temperatures. The insulation E between the copper disc F (which formed one contact to the sample and was connected to the DC voltage supply) and the can C (which was earthed) had to withstand the full voltage across the diamond sample, and at the same time provide a reasonably low thermal resistance; it was found that a few layers of teflon tape served both these

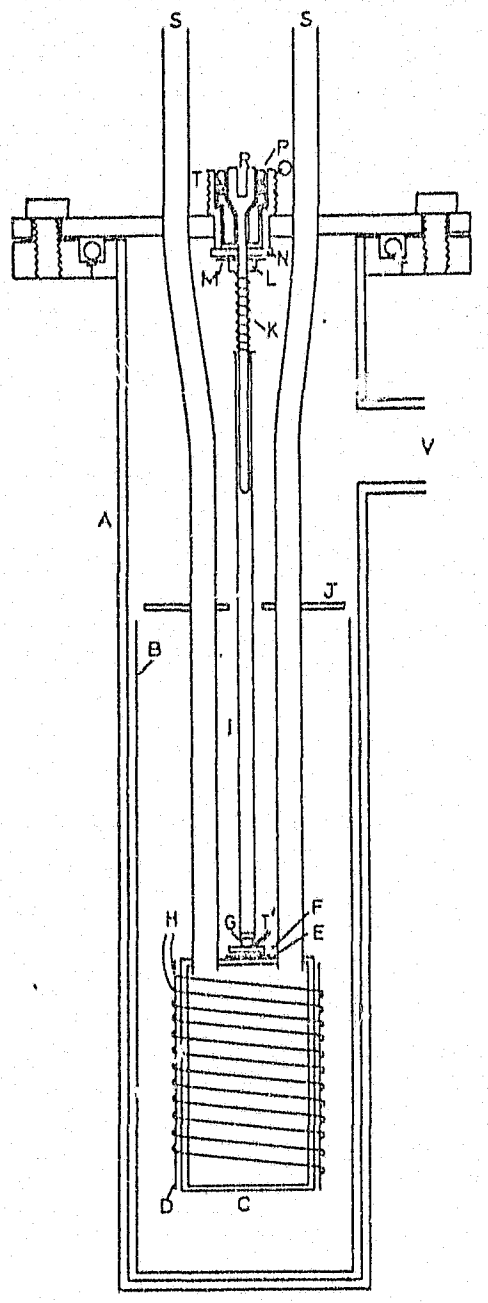


FIG. 3.9 The general purpose apparatus. A - brass outer can; B - radiation shield; C - copper can; D - mica; E - teflon tape insulation; F - copper disc; G - sample; H - heater; I - thin-walled stainless steel tube; J - radiation shield; K - spring; L - nut; M - washer; N - teflon washer; O - modified UHF socket; P - teflon insulation; R - central electrode; S - stainless steel tubes; T - O rings; V - vacuum line, Silica windows in outer can not shown; T' - thermocouple.

purposes very well, since the teflon softened and adhered to the metal surfaces during the first heating cycle, and retained its electrical resistance provided it was not heated to too high a temperature. The sample temperature was measured with a copper-constantan thermocouple junction between the sample G and disc F. The sample could be illuminated through quartz windows in the outer can A.

Observations of the temperature dependence of the electrical resistance of the diamonds were made in a point by point fashion and both the temperature and the current through the diamond were allowed to stabilize before a set of readings was taken.

Fig. 3.10 shows a plot of current versus voltage for a synthetic diamond at 290°C. A straight line through the origin is an extremely good fit to the experimental points, showing that the contacts to the diamond were ohmic.

3.3 Determination of the sign of the charge carriers

3.3.1 The thermoelectric effect

The sign of the charge carriers in a semi-conducting sample is usually obtained from Hall effect measurements. In the investigations reported in this thesis, the Hall effect was not used because:

(i) under narrow band illumination the resistance of insulating diamonds is still so high that the Hall effect is extremely difficult (if not impossible) to observe

(ii) the three or four contacts necessary for the Hall effect observations could not be applied to the synthetic diamonds, which were very small.

It can readily be shown (eg. Smith 1968) that the thermo-

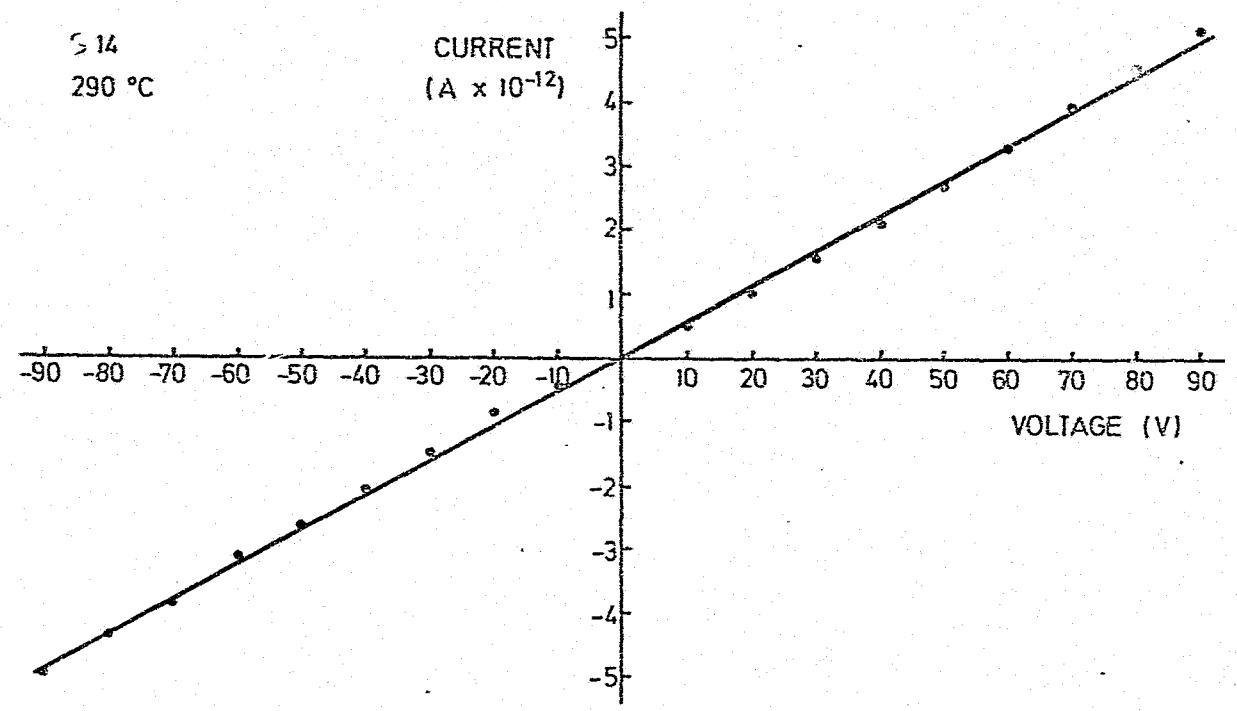


FIG. 3.10 The current-voltage characteristic of a synthetic diamond at 290°C. The behaviour is ohmic.

electric power of a non-degenerate n-type semi-conductor is negative and that of a p-type semi-conductor is positive. The sign of the thermoelectric power is therefore a simple alternative to the Hall effect as a method for the determination of carrier sign, and is reliable provided the contacts to the sample are ohmic (Gould 1962). This method has been used as a check on the conductivity type of synthetic diamond by Wentorf and Bovenkerk (1962) and Bourgoin et al (1972) and the temperature dependence of the thermoelectric power of a type IIb diamond was studied by Goldsmid, Jenns and Wright (1959); all these authors found that the sign of the thermoelectric effect indicated the type of conductivity correctly.

3.3.2 The thermoelectric effect apparatus

The general purpose apparatus was modified for the observation of the thermoelectric effect in type Ib diamond. A sketch of the lower portion of the apparatus is shown in Fig. 3.11. When the electrical supply to the heater H was switched on, the heat generated was conducted through the sample to the copper block E, which acted as a heat sink; consequently, while the heater was operating and the average temperature of the sample was increasing, a temperature gradient was set up such that the lower face of the sample was hotter than the upper face. The direction of this thermal gradient could be changed by switching off the supply to the heater and blowing cold air down into the upper can C through one of the tubes S; during this process the average temperature of the sample decreased. Fig. 3.12 (a) shows how the temperature difference varied during one such heating and cooling cycle, as measured by a differential thermocouple with junctions clamped between each side of a fairly large natural type IIb diamond.

Fig. 3.12(b) shows the the moelectric voltage generated

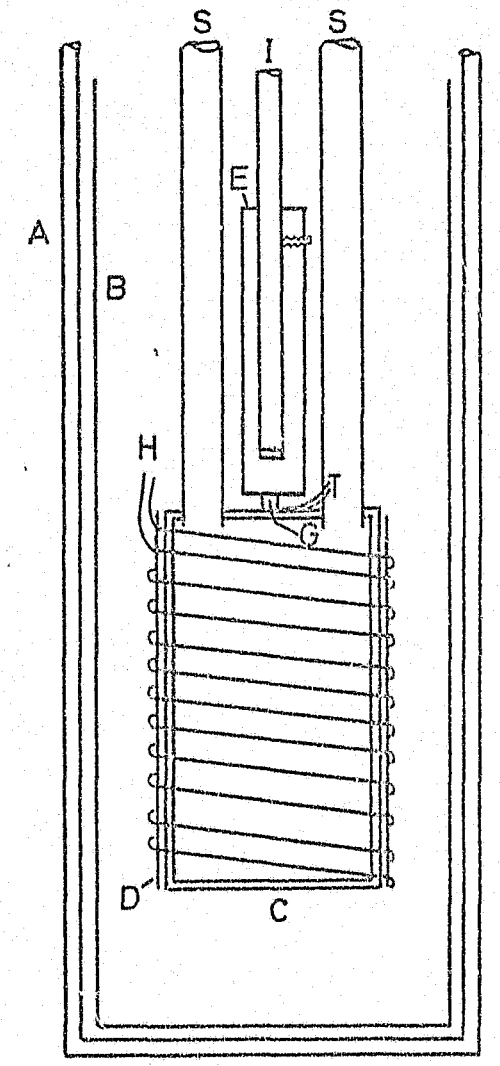
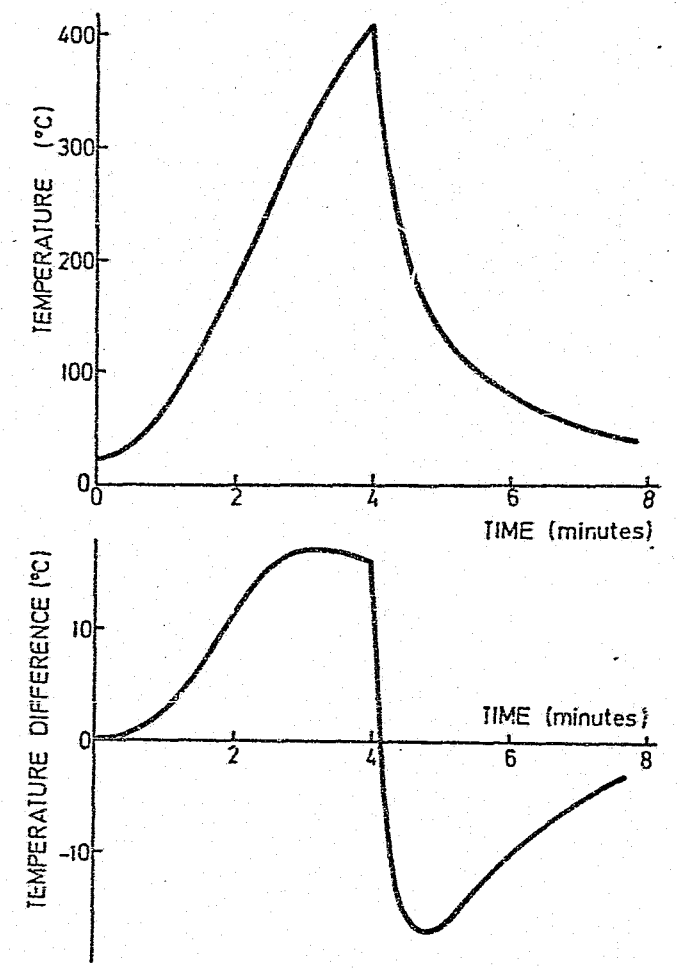


FIG. 3.11 The general purpose apparatus, as modified for observation of the thermoelectric effect. A - outer can; B - radiation shield; C - copper can; D - mica insulation; E - copper heat sink; G - sample; H - heater; I - thin-walled stainless steel tube; T - thermocouple.



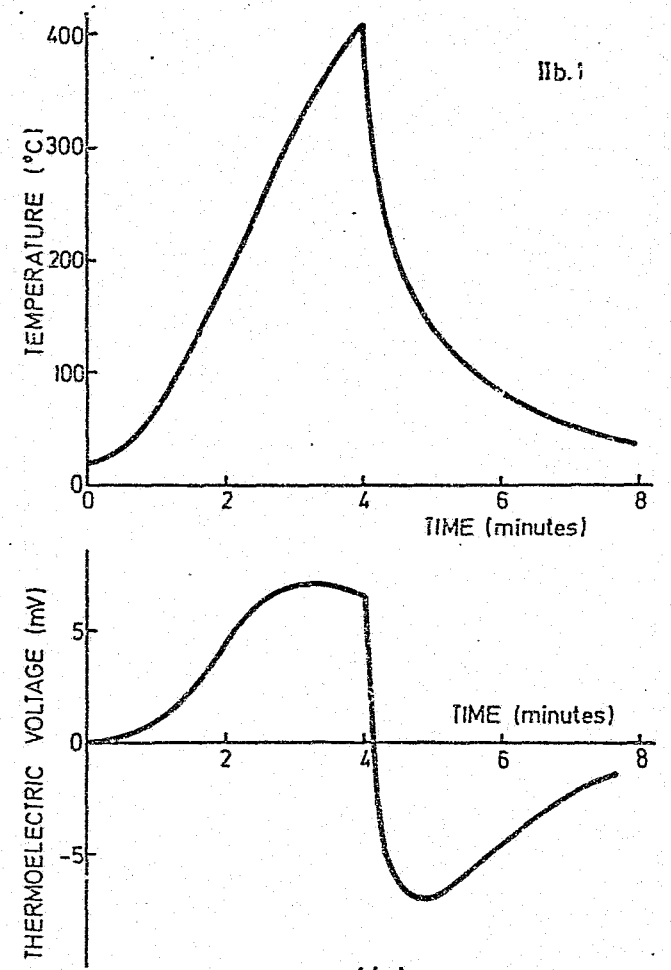


FIG. 3.12 (a) The temperature of, and the temperature difference across, a type IIb diamond during observation of the thermoelectric effect. The lower face of the sample was hotter than the upper face during heating, and cooler during cooling. (b) The thermoelectric voltage observed in the type IIb diamond. The upper face was positive with respect to the lower face during heating, and negative during cooling. The sign of the thermoelectric voltage is consistent with the fact that the sample is p-type.

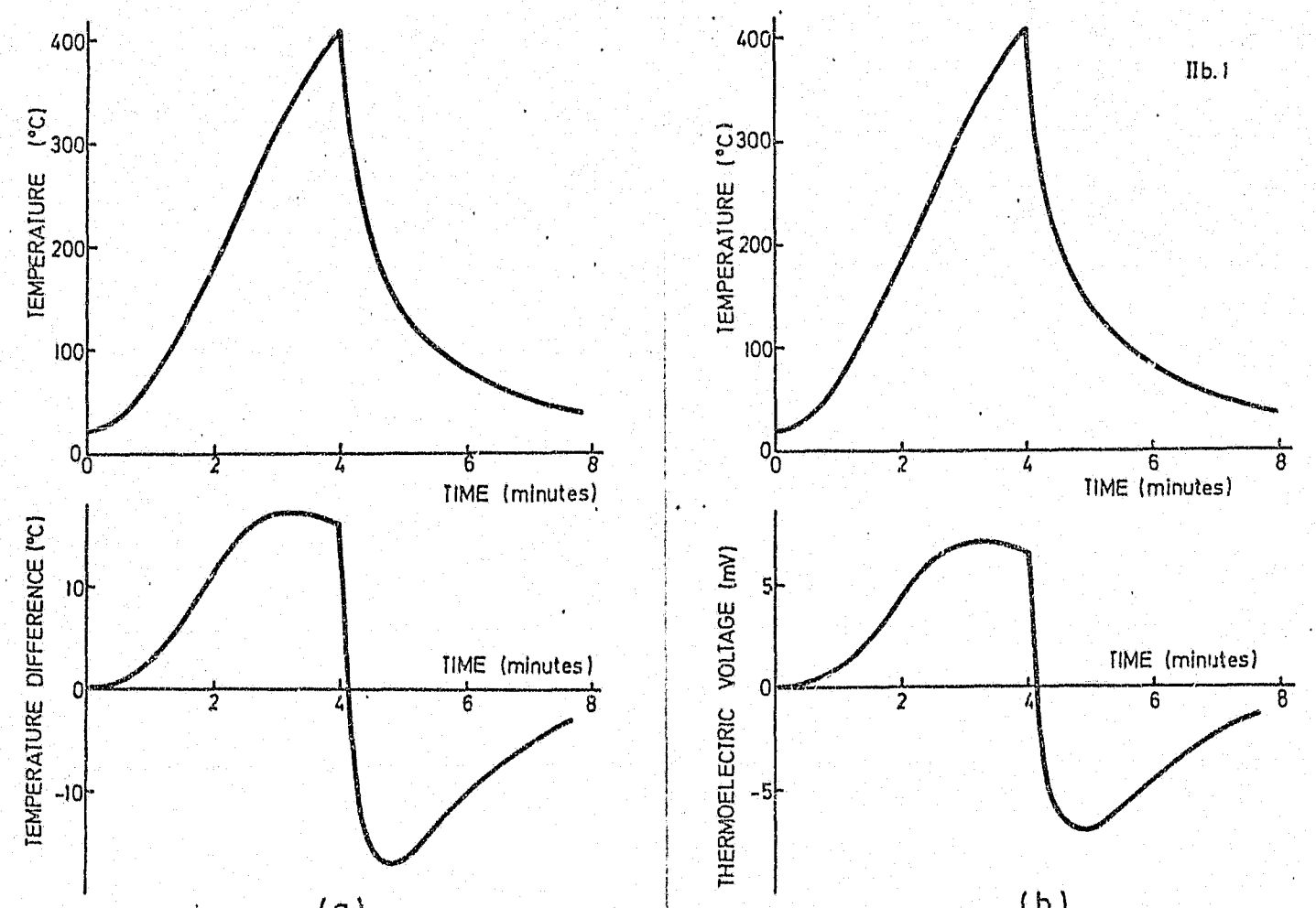


FIG. 3.12 (a) The temperature of, and the temperature difference across, a type IIb diamond during observation of the thermoelectric effect. The lower face of the sample was hotter than the upper face during heating, and cooler during cooling. (b) The thermoelectric voltage observed in the type IIb diamond. The upper face was positive with respect to the lower face during heating, and negative during cooling. The sign of the thermoelectric voltage is consistent with the fact that the sample is p-type.

in this diamond during a similar cycle. The colder face of a p-type sample would be expected to be positive with respect to the hotter face (Gould 1962); thus, during the heating half of the cycle, a positive signal should be recorded by the electrometer, and a negative signal would be expected during the cooling. Fig. 3.12(b) confirms that this was observed.

CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Electron-irradiated type Ia and type IIa diamonds

4.1.1 Introduction

Two type Ia and two type IIa diamonds, which had been irradiated with approximately 10^{18} electrons cm^{-2} of energy 0.78 MeV, were available for investigation. All four specimens were polished blocks and optical absorption spectra were measured with the Unicam SP800 spectrophotometer. The photoconduction spectra reported in this chapter have not been normalized, but their interpretation in terms of the associated optical absorption features is unambiguous.

4.1.2 Photoconduction

Fig. 4.1 compares the optical absorption and photoconduction in the neighbourhood of the GR1 band in an electron-irradiated type IIa diamond at 80K. There is clearly an inverse correlation between the two spectra; on a background of photoconduction, competitive absorption by the GR1 band produces minima in the photoconduction spectrum at the positions of maxima in the absorption.

The optical absorption and photoconduction at 80K in the region GR2 to GR8, R9 and R10 in the same type IIa diamond are shown in Fig. 4.2. Direct correspondence between the optical absorption and photoconduction peaks is observed here, indicating that absorption by the peaks GR2 etc. creates free charge carriers.

The photoconduction spectrum in Fig. 4.3 was observed at 80K in an electron-irradiated type Ia diamond. In addition to the peaks GR2 etc., a further sequence of photoconduction peaks starting at 3.15 eV is observed.

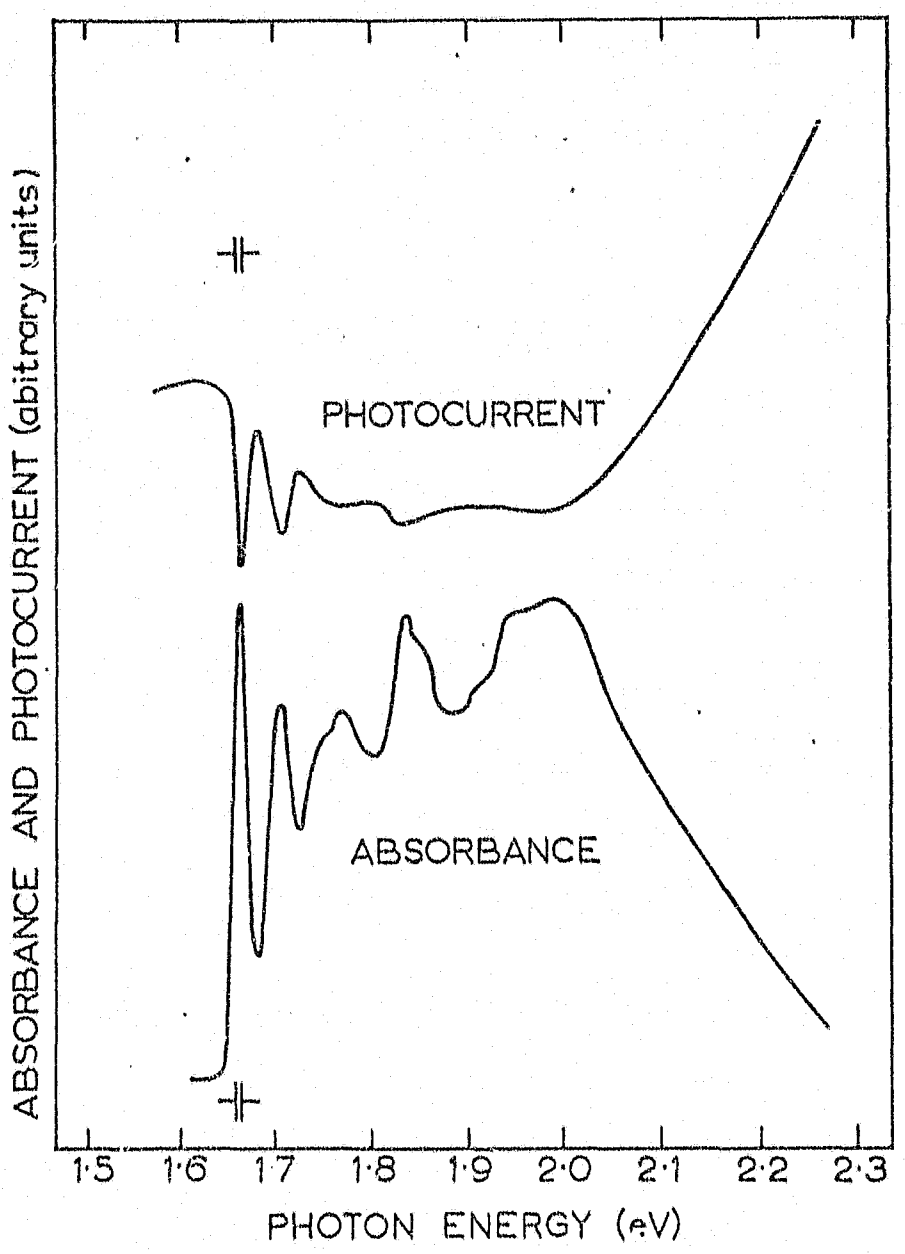


FIG. 4.1 Photoconduction and optical absorption at 80K in the neighbourhood of the GR1 band in an electron-irradiated type IIa diamond. The tungsten lamp was used with the monochromator.

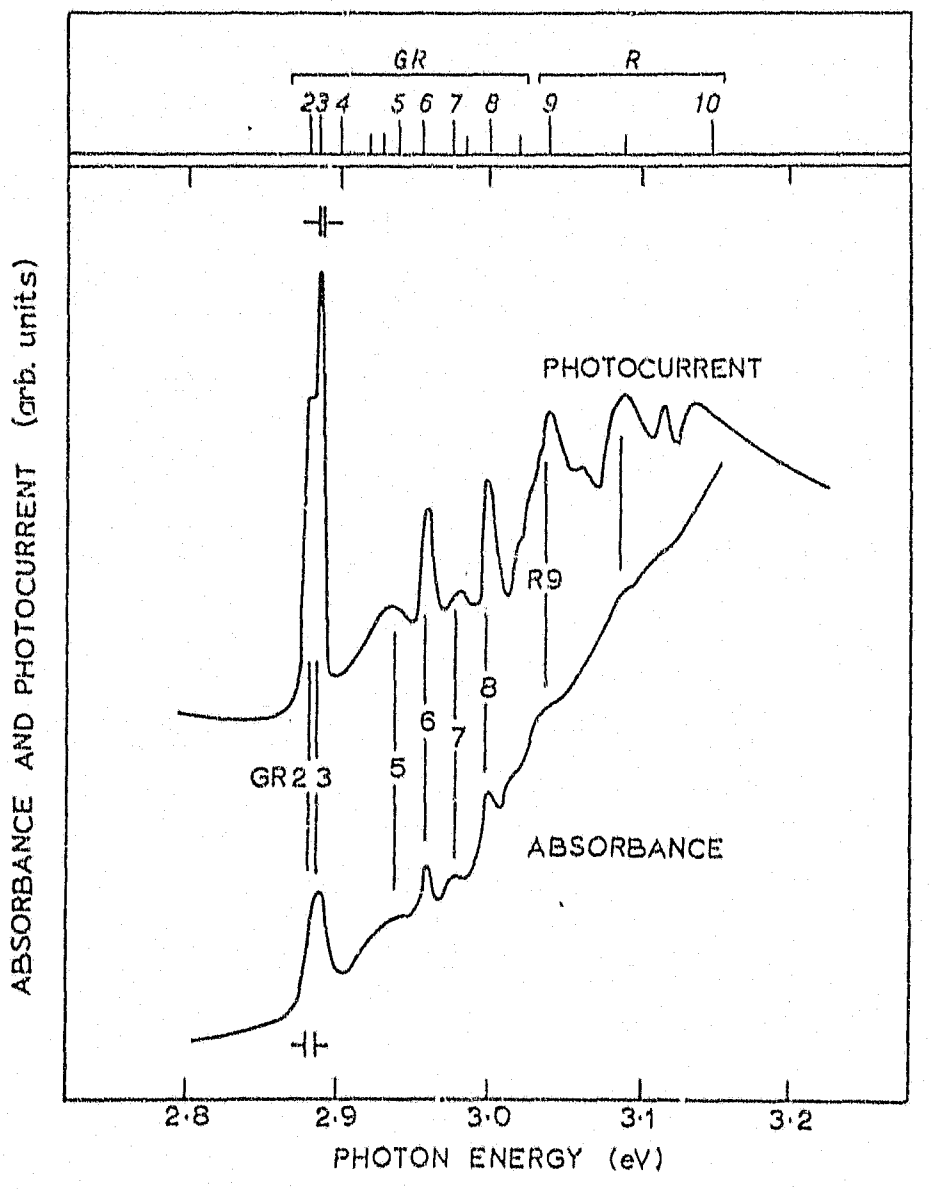


FIG. 4.2 Photoconduction and optical absorption spectra in the neighbourhood of the GR2 to GR8, R9 and R10 lines in an electron-irradiated type IIa diamond, using the tungsten lamp with the monochromator. Both measurements were made at 80K. The positions of the GR2 to GR8, R9 and R10 absorption lines, as given by Clark, Ditchburn and Dyer (1956), are shown at the top of the figure.

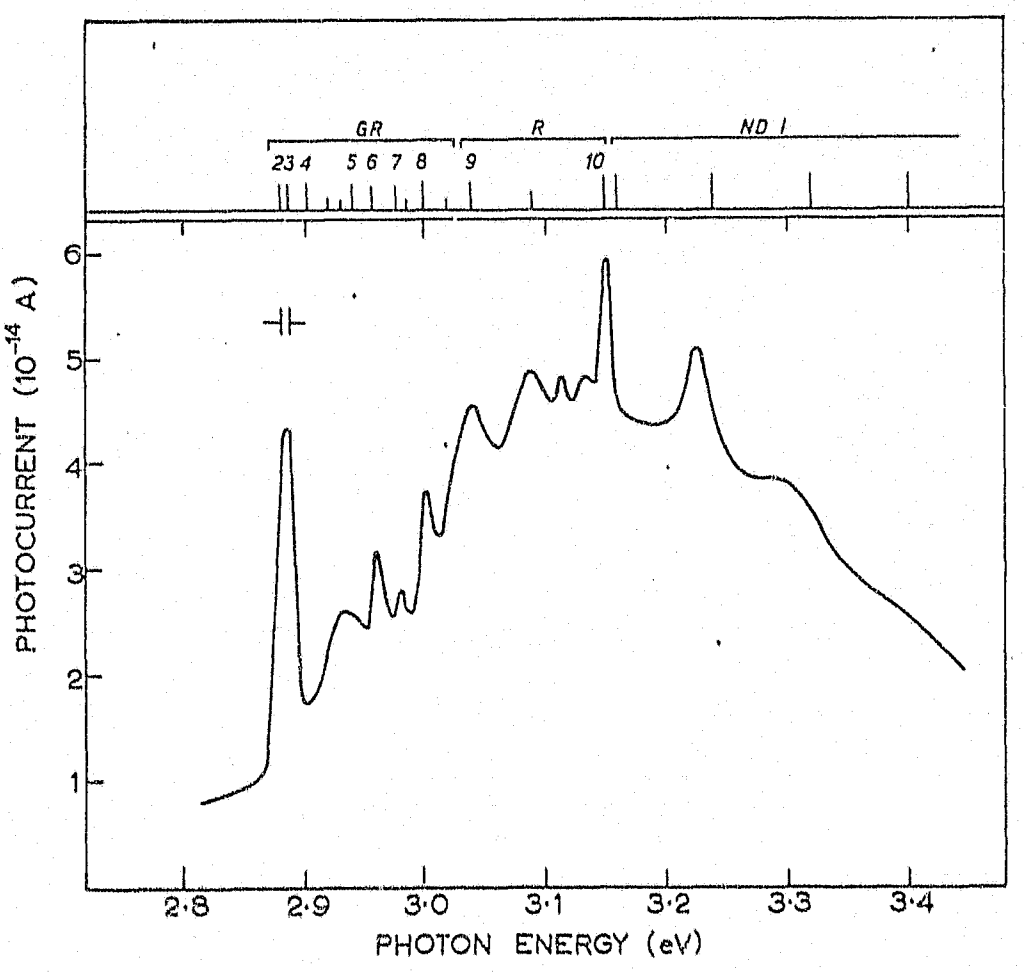


FIG. 4.3 The photoconduction spectrum at 80K of an electron-irradiated type Ia diamond in the neighbourhood of the GR2 to GR8, R9 and R10 lines, and the ND1 absorption system. At the top of the figure are shown the positions of the GR2 to GR8, R9 and R10 lines, as given by Clark, Ditchburn and Dyer (1956), and the absorption lines of the ND1 system (Dyer and du Preez, 1965). The tungsten lamp of the monochromator was used.

These peaks coincide with the positions of the optical absorption maxima in the ND1 system.

The spectra in Figs. 4.4 and 4.5 illustrate that the correspondence between the photoconduction and optical absorption peaks of the ND1 system is preserved at temperatures down to 8K. In Fig. 4.4 the photocurrent was excited with monochromatic light from the deuterium lamp and the monochromator slitwidth had to be opened considerably in order to measure the spectrum; however, the output is maintained at higher energies, and five (and possibly six) maxima can easily be seen in the photoconduction spectrum. Fig. 4.5 compares directly the recorder traces of photoconduction at 80K and 8K in an irradiated type Ia diamond under identical conditions of monochromator sweep, slitwidth, applied voltage and electrometer sensitivity; in this case the tungsten lamp was used with the monochromator. No reduction is observed in the photoconductive response on reducing the temperature from 80K to 8K; at 8K the peaks are slightly narrower and possibly slightly larger.

Fig. 4.6 shows the photoconduction spectrum at 80K of an irradiated type Ia diamond in which both the N3 and ND1 systems are present. The first two lines of the N3 system appear as minima on the background of photoconduction, in contrast to the maxima at the positions of the ND1 peaks. This clearly illustrates the opposite behaviour of these two systems in photoconduction, although they appear very similar in optical absorption (both in structure and position in the absorption spectrum of diamond).

4.1.3 Summary of results

Minima are observed in the photoconduction spectrum of irradiated diamonds at the positions of maxima in the GR1 absorption system. Photoconduction maxima are observed at the positions of the GR2-8, R9 and R10 lines and at the

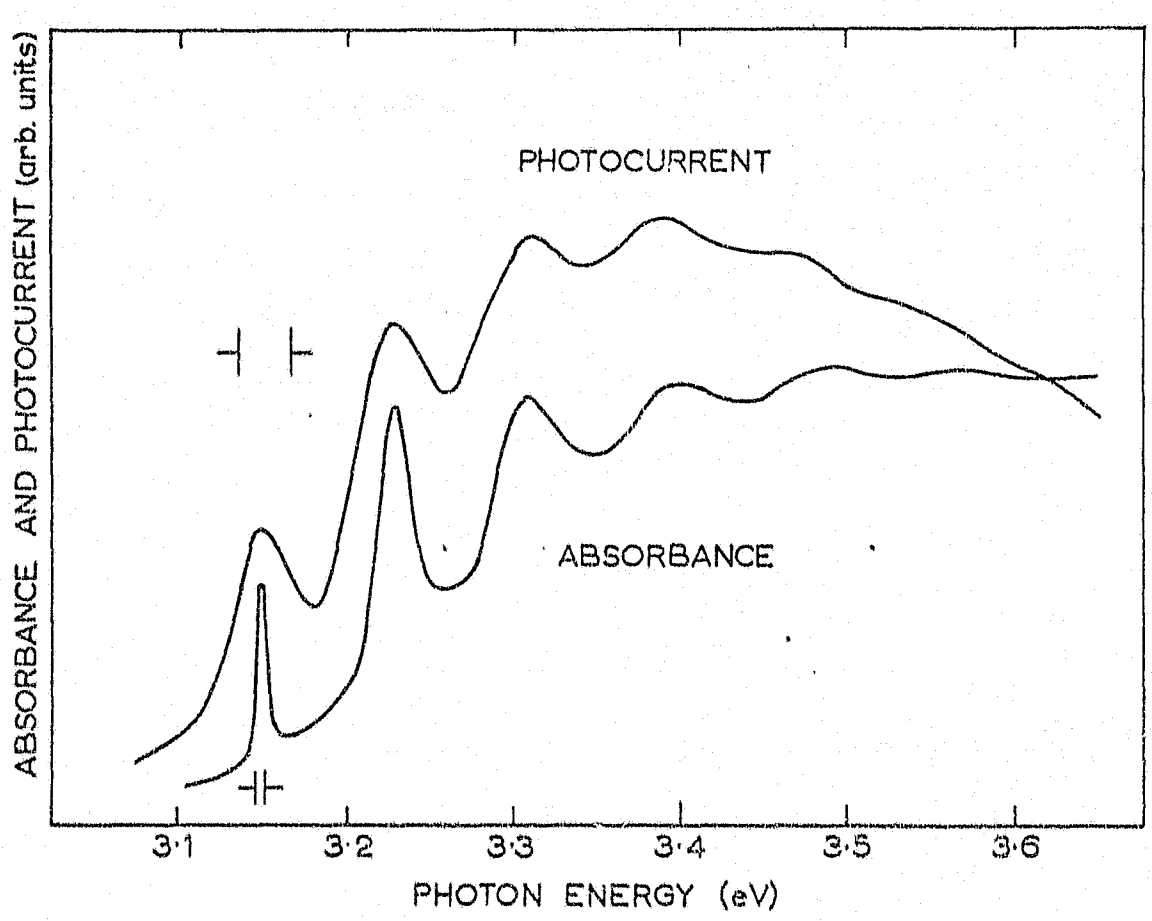


FIG. 4.4 Photoconduction and optical absorption spectra at 8K in the neighbourhood of the ND1 system in an electron-irradiated type Ia diamond. The deuterium lamp was used with the monochromator.

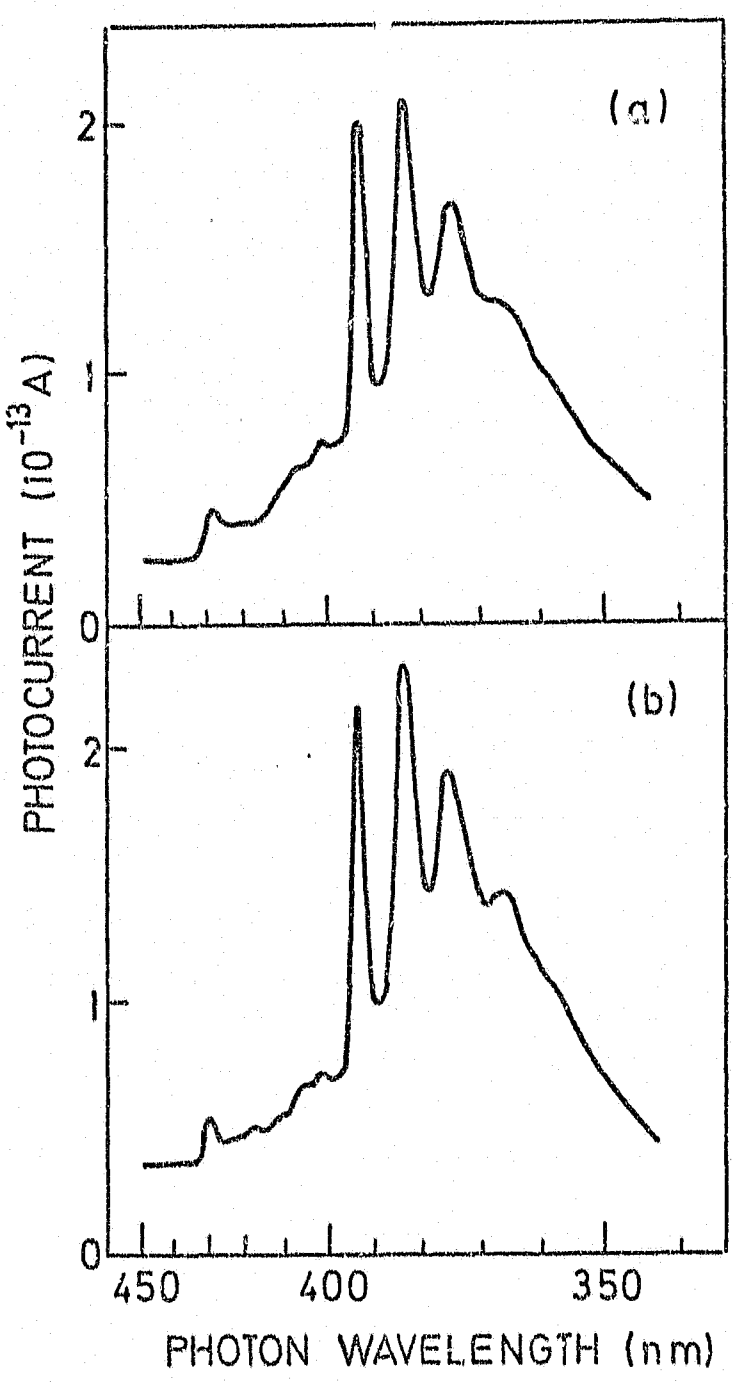


FIG. 4.5 Photoconductivity in an electron-irradiated type Ia diamond under identical experimental conditions, except that (a) was measured at 80 K and (b) at 8 K. The GR2-8 lines between 430 and 400 nm are followed by the ND1 system (with its zero phonon line at 394 nm). The tungsten lamp was used with the monochromator.

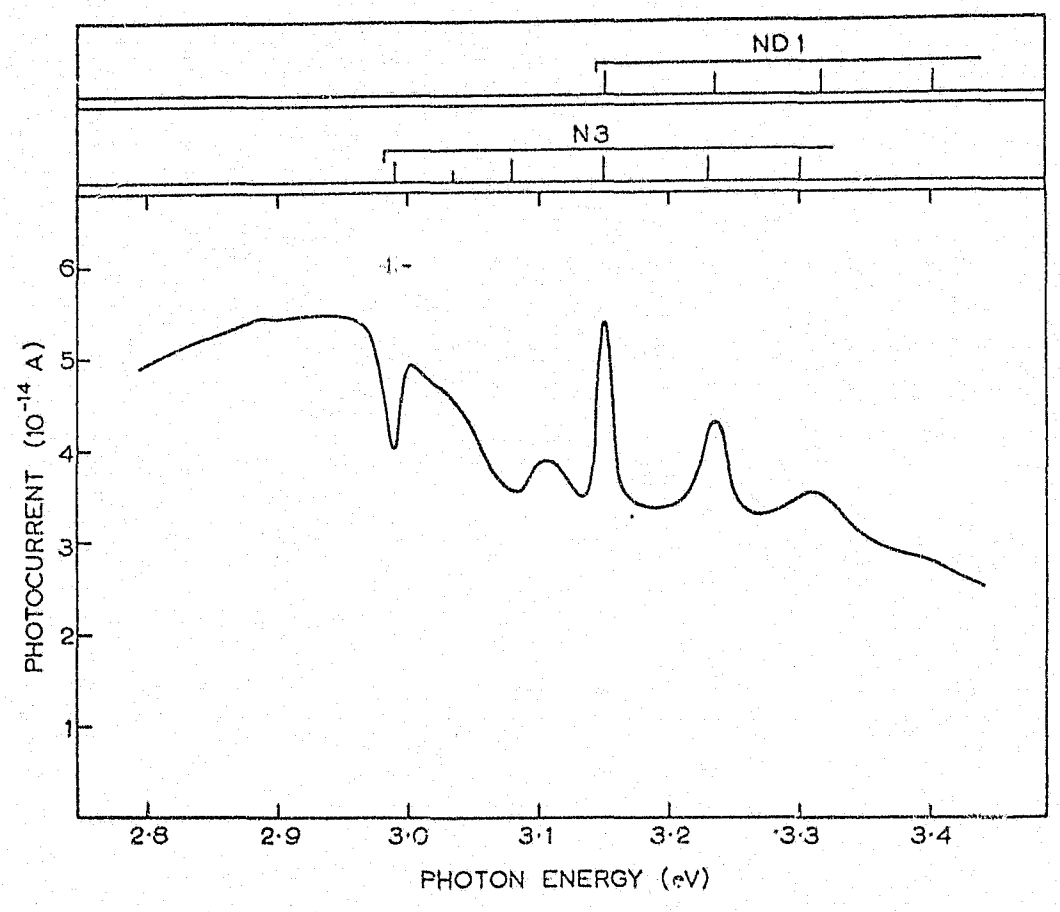


FIG. 4.6 The photoconductivity spectrum at 80K in an irradiated type Ia diamond which contains both the N3 and ND1 systems. The first two lines of the N3 system appear as minima followed by maxima at the positions of the ND1 maxima. The tungsten lamp was used with the monochromator.

positions of the maxima in the ND1 absorption system. These photoconduction maxima appear to be undiminished at temperatures down to 8K.

4.2 Natural type Ib diamonds

4.2.1 Introduction

Five natural type Ib diamonds were made available for this investigation. Two of them had been cut into rectangular blocks and polished, and optical absorption measurements could be made on these samples. Electron spin resonance observations showed that all five diamonds contained approximately 10^{18} single substitutional nitrogen atoms per cm^3.

4.2.2 Room temperature photoconduction and optical absorption

Four of the five diamonds investigated had similar photoconduction spectra, and showed no increase in photoconduction beyond 4 eV. A typical spectrum of one of these specimens is given by the continuous curve in Fig. 4.7(a). The remaining diamond showed strong photoconduction between 4.0 and 5.5 eV, the low-energy threshold for this peak being at 4.05 eV; the spectrum of this diamond is shown in Fig. 4.7(b).

In all specimens, photoconduction at energies less than about 1.7 eV was due to trapping levels, and could be removed by optical bleaching. The broken curves in Fig. 4.7 were measured after bleaching with light of energy up to 2.5 eV. The low-energy thresholds of these spectra all lay between 1.70 and 1.75 eV ($\pm$ 0.05 eV).

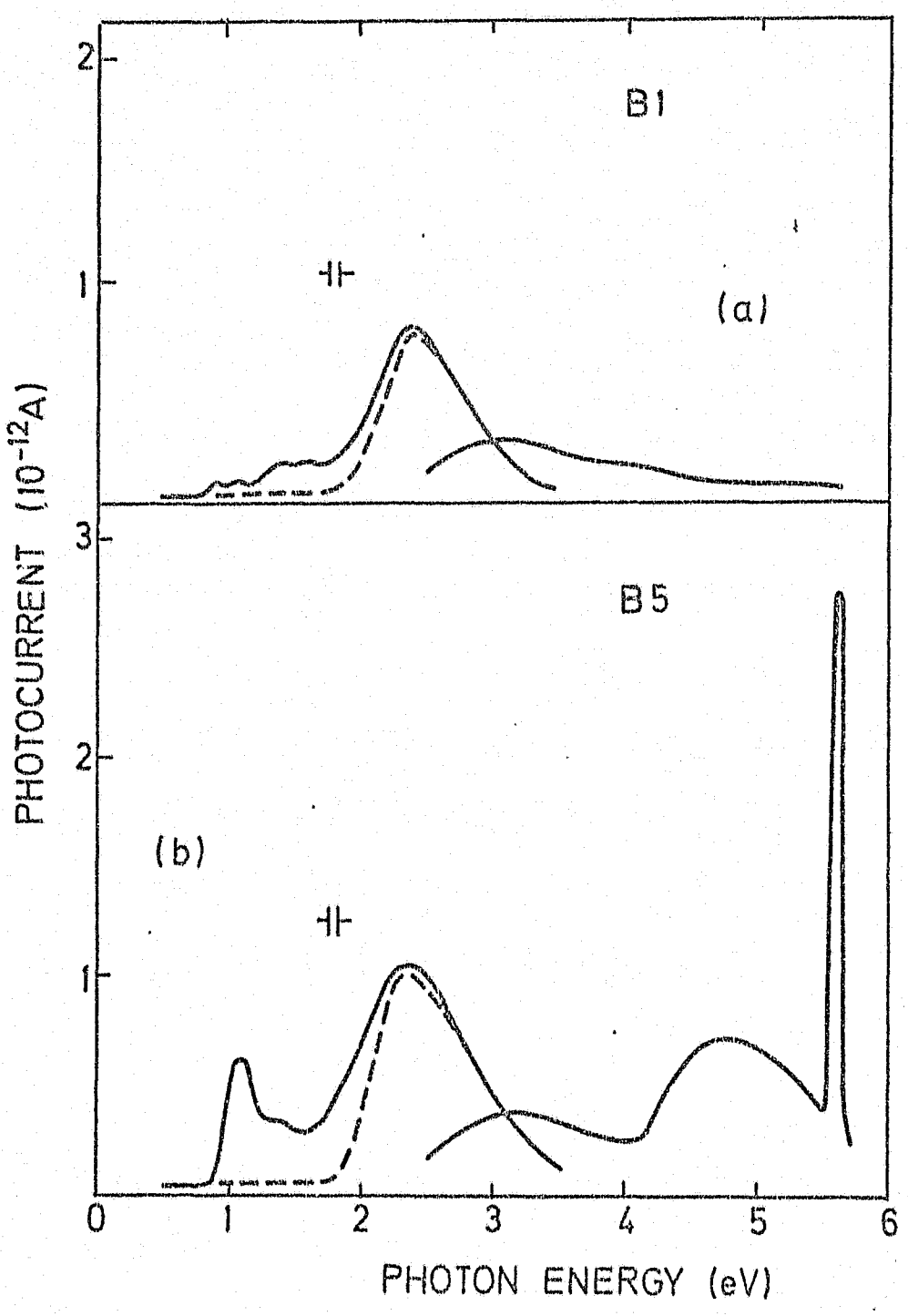


FIG. 4.7 Room temperature photoconduction spectra of two natural type Ib diamonds. Four of the five diamonds investigated showed spectra similar to (a); the spectrum of the remaining diamond is shown in (b). The broken curves were obtained after optical bleaching of the low energy trapping levels.

Fig. 4.8 shows a comparison for diamond B1 of the optical absorbance between 1.7 and 2.9 eV and the normalized photoconduction in the same range. In order to minimise possible changes in the effective field in the diamond (due to preferential trapping of charge carriers near the electrodes), these photoconduction measurements were repeated until successive spectra were identical. Corrections have been made for variations in the intensity and bandwidth of the light from the monochromator to give the relative photocurrent per photon at each point. All absorbance readings have been multiplied by a constant factor which was chosen to make the absorbance and photocurrent curves coincide at 2.0 eV. This comparison was also made for specimen B2 and results similar to those shown in Fig. 4.8 were obtained.

4.2.3 Electrical resistance and thermoelectric effect

Fig. 4.9 is a plot of log i versus 1/T for diamond B3, where i is the current measured through the diamond for a fixed applied voltage and T is the absolute temperature. Similar measurements on the other diamonds also gave straight lines, and the thermal activation energies calculated from these graphs lay between 1.69 and 1.75 eV.

Fig. 4.10 shows a comparison of the themoelectric effect in a p-type semi-conducting diamond and a natural type Ib diamond, which is clearly n-type. Observations were made in the manner described in section 3.3. The other natural type Ib diamonds showed similar behaviour.

4.2.4 Photoconduction and optical absorption after heating

When photoconduction measurements were made immediately

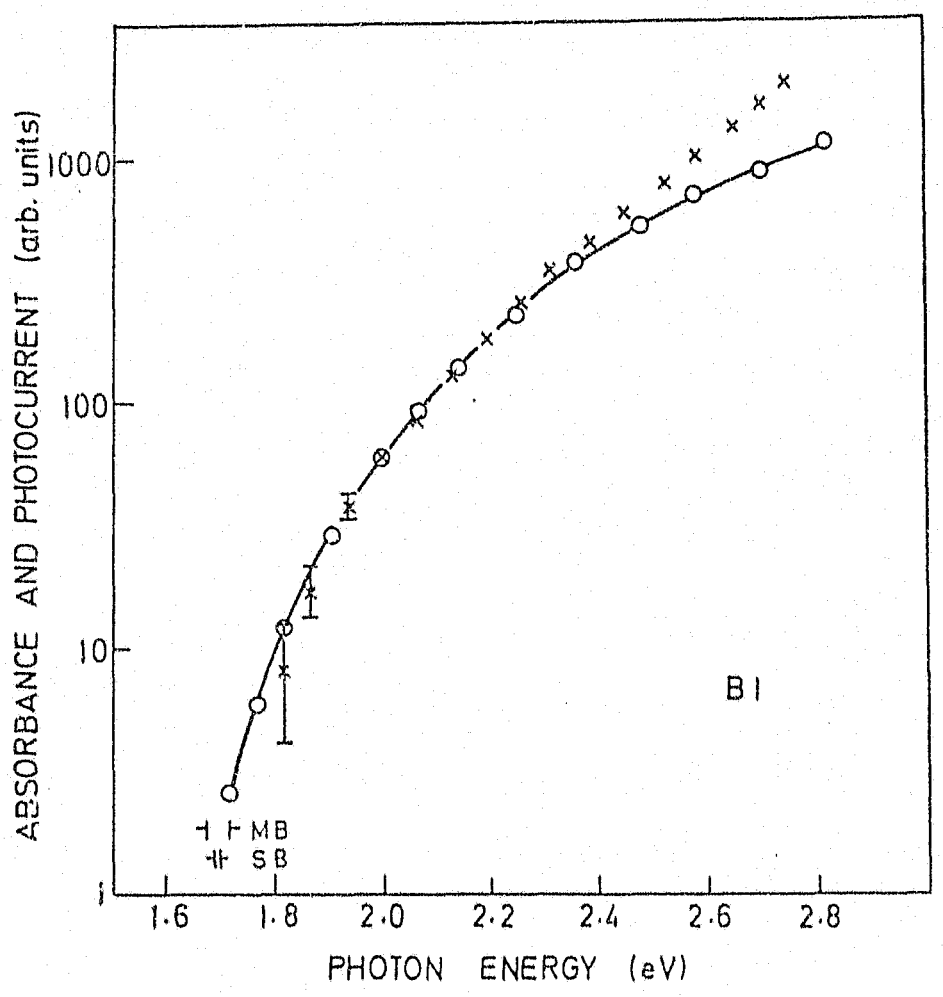


FIG. 4.8 A comparison of photoconduction and optical absorption in diamond B1 at room temperature.
O - Normalized photocurrent (arbitrary units)
X - Absorbance (arbitrary units)
MB - Monochromator bandwidth at 1.7 eV
SB - Spectrophotometer bandwidth at 1.7 eV

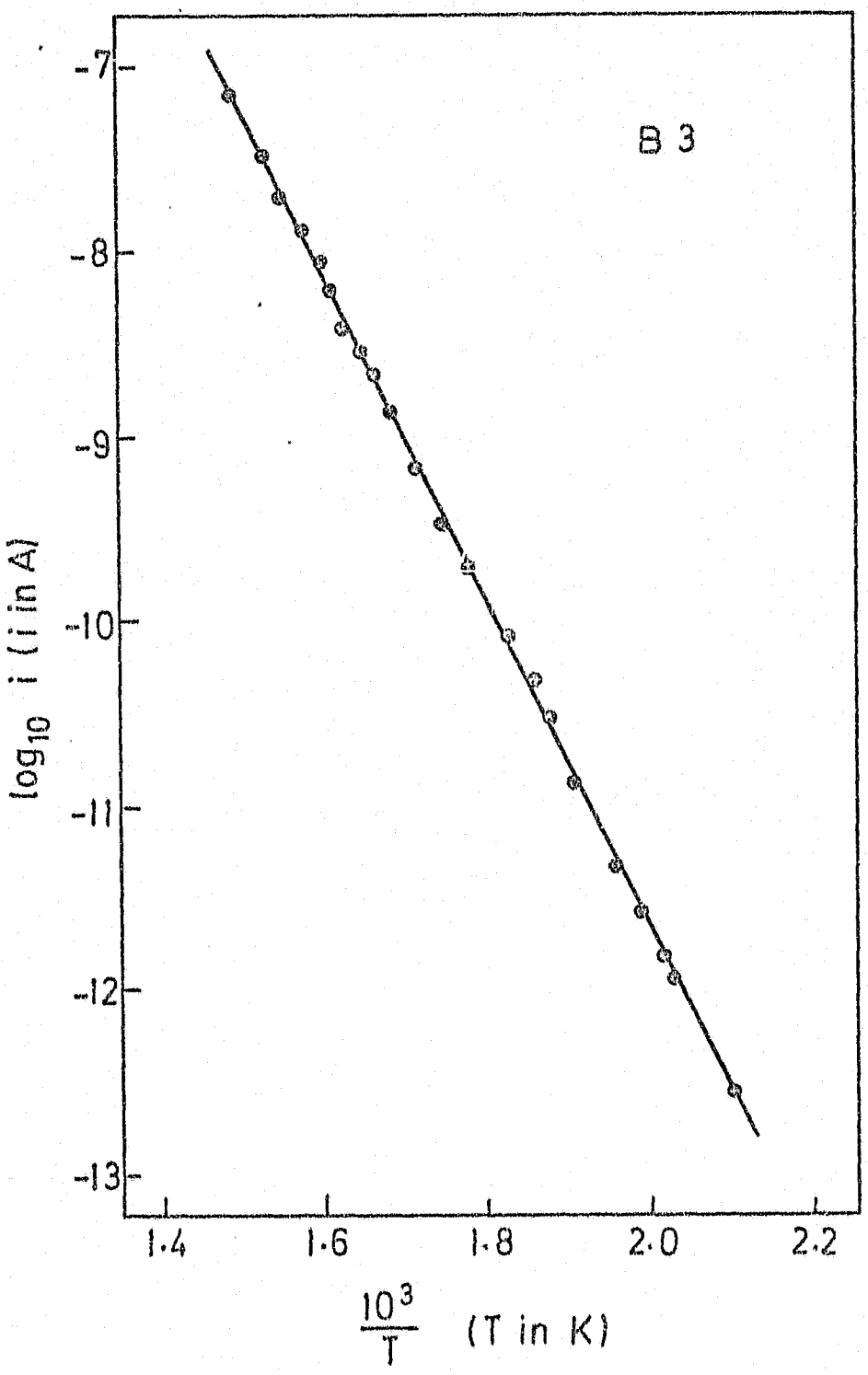


FIG. 4.5 The current i through diamond B3 as a function of temperature T, with a fixed applied voltage of 180V.

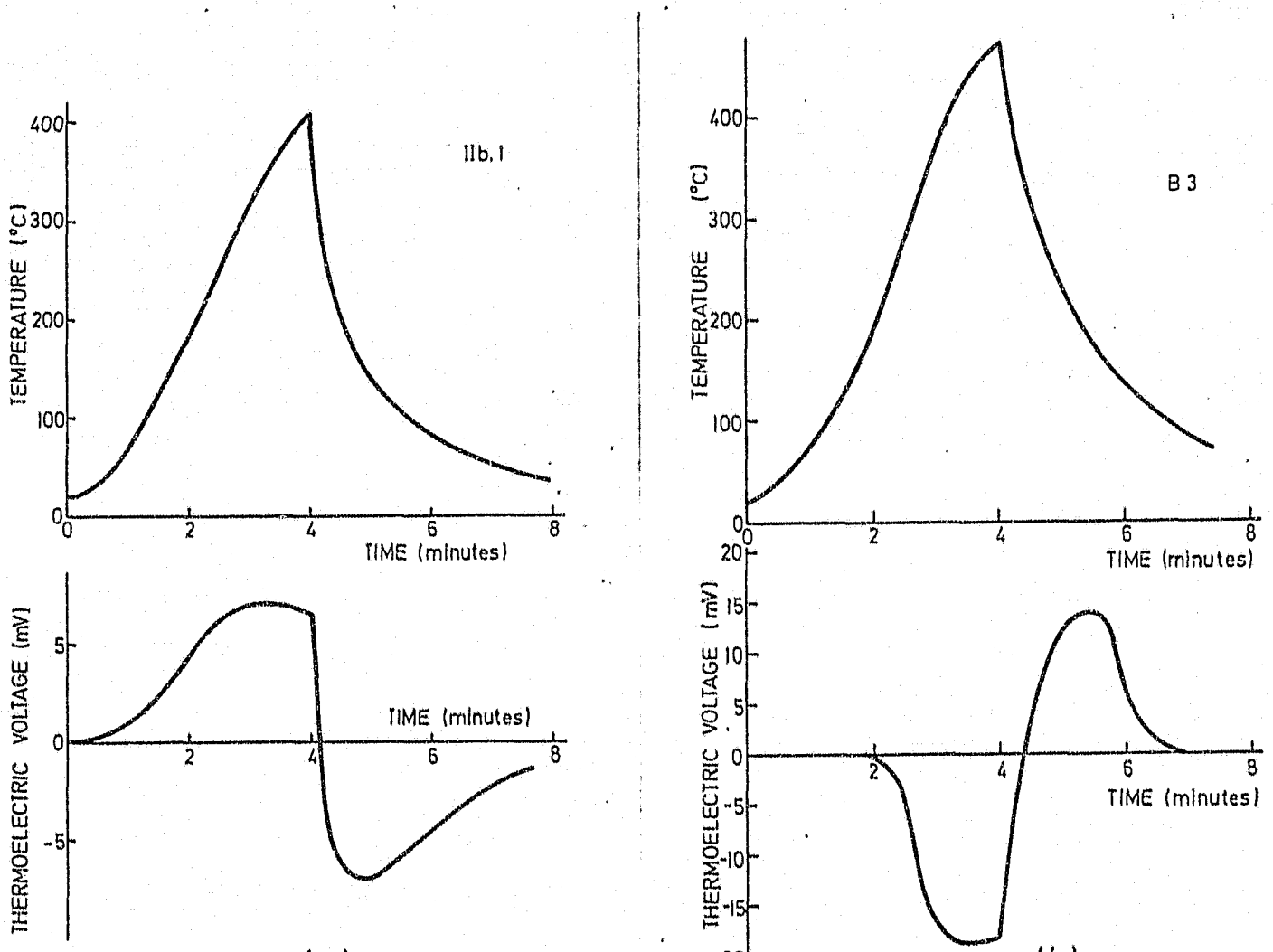


FIG. 4.10 The thermoelectric effect observed under identical experimental conditions in (a) a p-type semiconducting diamond (see Fig. 3.12) and (b) in diamond B3, which is clearly n-type.

after measurements of the electrical resistance as a function of temperature (which involved heating the diamonds to 400°C), increased photoconductivity at energies above 1.7 eV was observed. The optical absorption after heating showed a similar increase compared with that measured after bleaching with light of energy up to 2.5 eV. This effect as observed in diamond B2 is shown in Figs. 4.11 and 4.12.

Fig. 4.11 shows (a) the optical absorption immediately after cooling from 400°C and (b) the absorption after bleaching with light of energy 2.5 eV; both measurements were made at room temperature. Fig. 4.12(a) and (b) show the unnormalized room temperature photoconduction spectrum of the same diamond after the same treatment. The spectrum at 80K after heating to 400°C was similar to curve (a), and (c) is the 80K spectrum after bleaching with 2.5 eV light.

Two effects can clearly be seen. Firstly, there is a photoconduction and associated optical absorption feature with its low energy threshold at 1.7 eV at both room temperature and 80K; this feature is activated by heating to 400°C. Secondly, the low energy threshold of the background photoconduction, which is about 1.7 eV at 293K, moves to higher energies at 80K.

4.2.5 Summary of results

The 4.05 eV photoconduction threshold has been observed in only one out of five natural type Ib diamonds and it cannot be considered to be characteristic of this type of diamond. Reasonable agreement has been obtained between the shape of the absorption tail and the normalised photoconduction spectra in the visible, both of which start at about 1.7 eV. This suggests that the absorption tail is due to transitions between a defect level or levels and the conduction or valence bands. Thermal activation energies

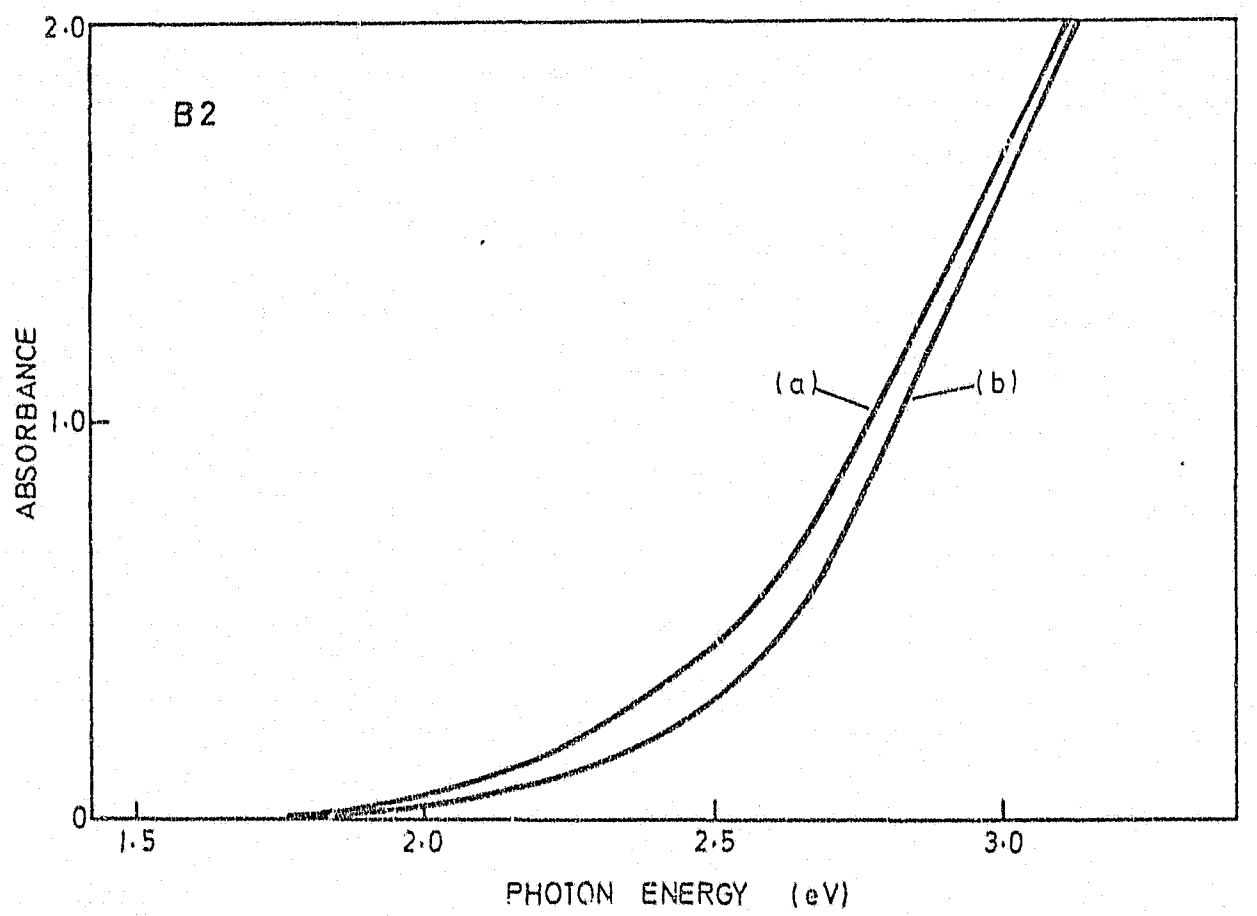


FIG. 4.11 The room temperature optical absorption spectrum of a natural type Ib diamond (B2) (a) after cooling from 400°C and (b) after bleaching with 2.5 eV light.

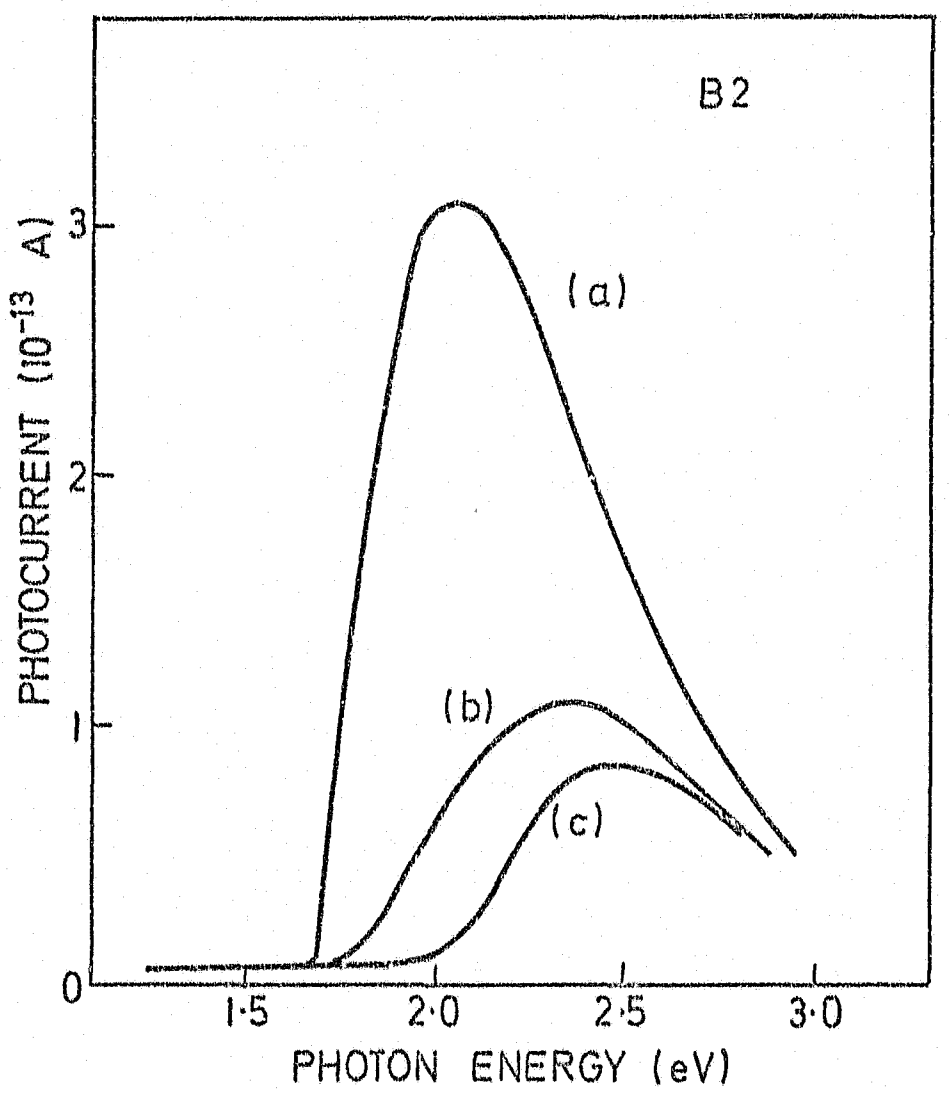


FIG. 4.12 The unnormalized photoconduction spectrum of diamond B2 using the tungsten lamp
(a) at room temperature after heating to 400°C
(b) at room temperature after bleaching with 2.5 eV light
(c) at 80K after bleaching with 2.5 eV light
The 80K spectrum after heating to 400°C is similar to (a).

of about 1.7 eV have been measured, and the thermally generated carriers are electrons.

A broad photoconduction peak, with a sharp threshold at 1.7 eV at both room temperature and 80K, is enhanced by heating the natural Ib diamonds to 400°C. An increase is also observed in the optical absorption. The existence of this additional photoconduction feature makes unambiguous interpretation of the photoconduction spectra difficult. However, it appears to have an origin different from that of the background photoconduction tail, since the low-energy threshold of the latter is clearly temperature dependent.

4.3 Synthetic type Ib diamond

4.3.1 Introduction

A number of yellowish synthetic diamonds with diameters up to about 2 mm were made available by the Diamond Research Laboratories, Johannesburg. The smaller stones tended to be purer and to have fewer visible defects and inclusions. Ten of these (with diameters up to 1 mm) were selected for the investigations to be reported in this section. One diamond was large enough for reliable optical absorption measurements; its infrared spectrum between 1000 and 1400 cm^{-1} is shown in Fig. 4.13 and its visible-ultraviolet spectrum is shown in Fig. 4.14. Both of these spectra are typical type Ib spectra as reported in the literature (Dyer et al 1965; Chrenko et al 1971).

4.3.2 Photoconduction

Typical room temperature photoconduction spectra observed in these samples are shown in Figs. 4.15 and 4.16.

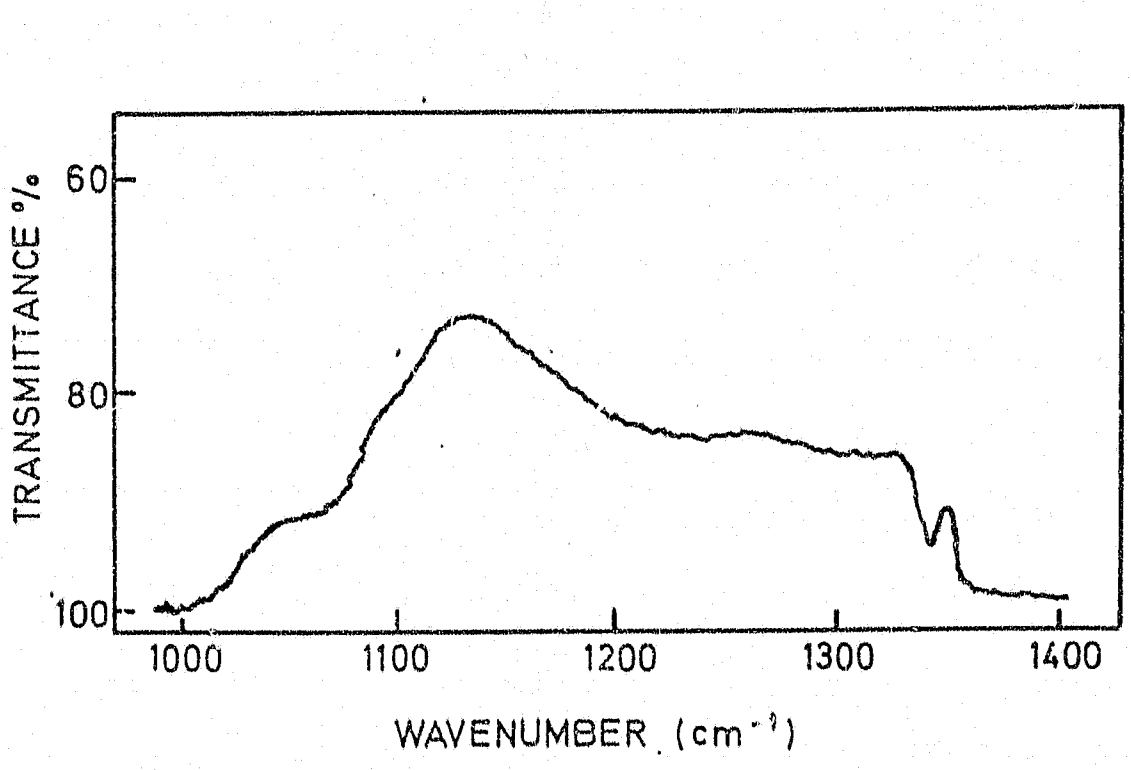


FIG. 4.13 The one-phonon infrared spectrum (corrected for reflection) of synthetic diamond S10.

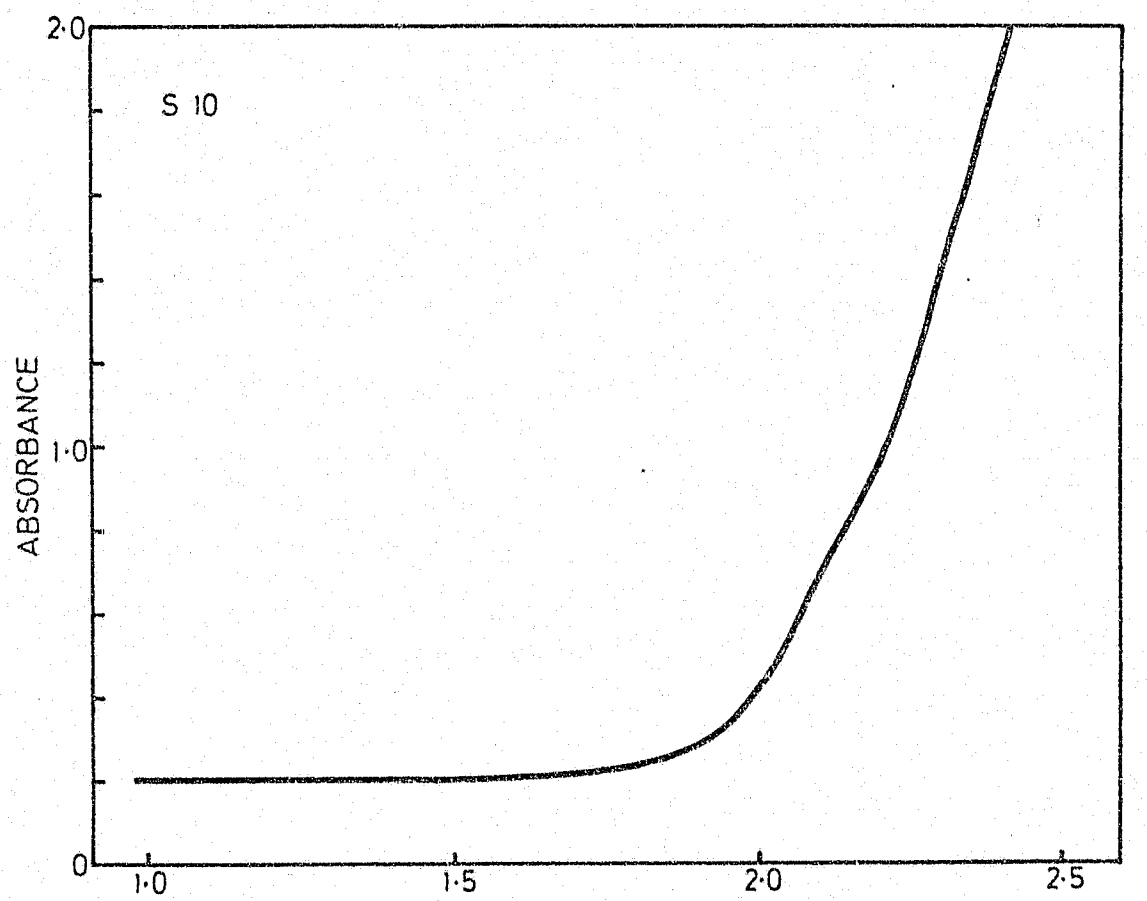


FIG. 4.14 The visible-ultraviolet spectrum of synthetic diamond S10.

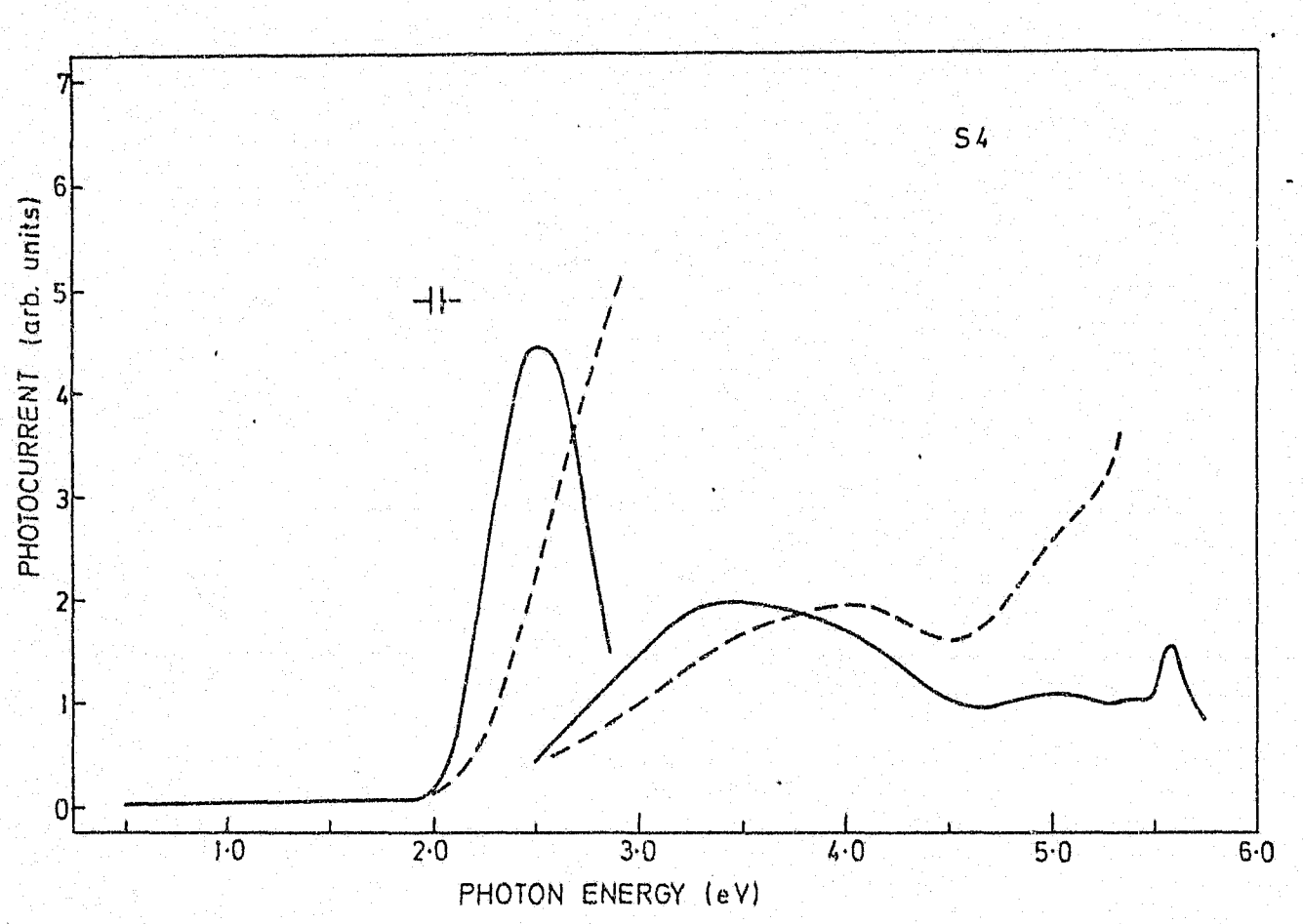


FIG. 4.15 The room temperature photoconduction spectrum of synthetic sample S4. The solid line is the unnormalized spectrum; the broken line is the normalized spectrum.

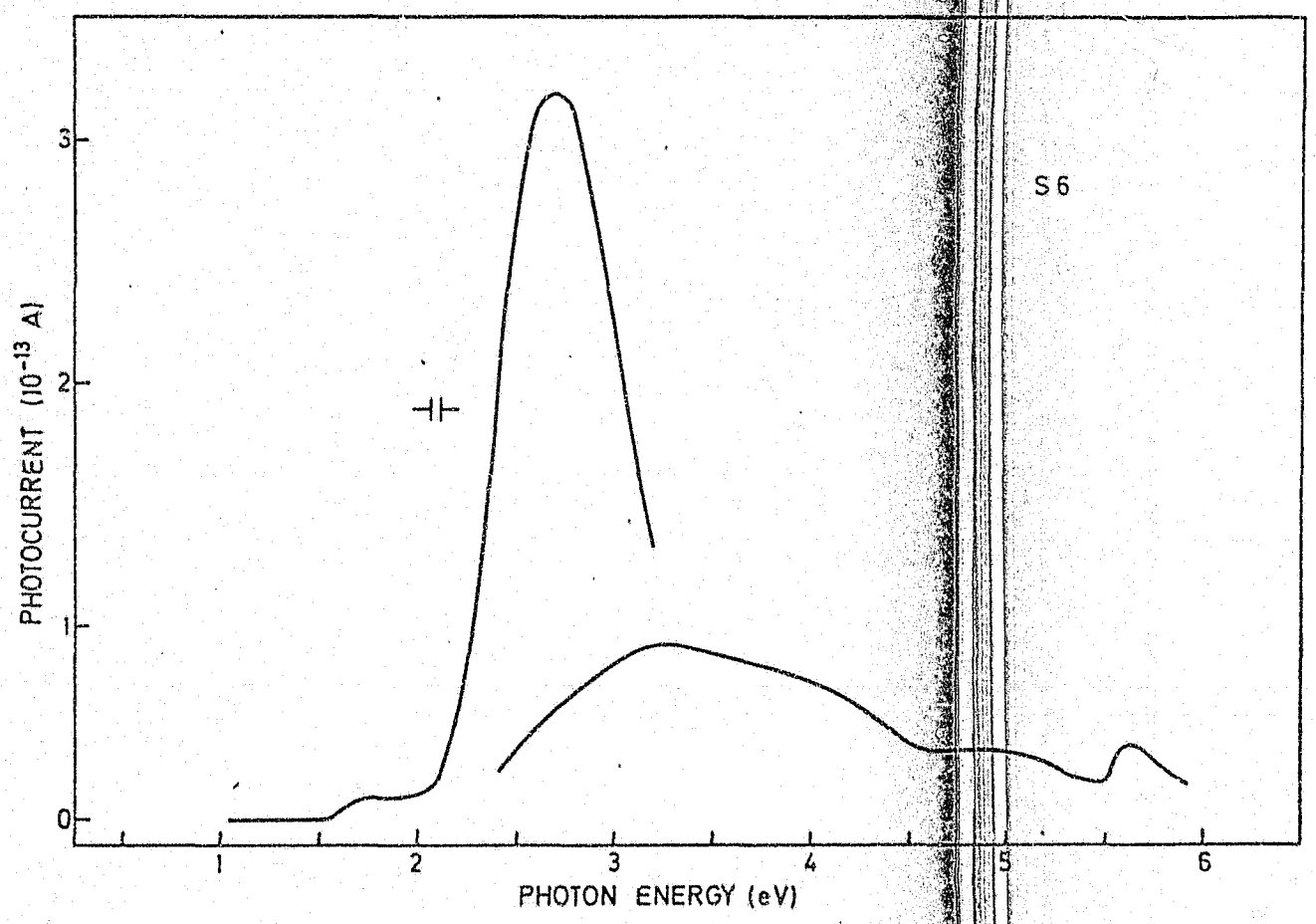


FIG. 4.16 The room temperature (unnormalized) photoconduction spectrum of synthetic diamond S6.

The spectra of nine of the samples were similar in overall appearance, with slight quantitative variations from sample to sample; the other sample (S12) is discussed in section 4.3.4. Characteristic features of the spectra are the threshold at about 2 eV and the dip at about 4.6 eV; no threshold at 4 eV was observed.

Fig. 4.17 depicts the behaviour of the 2 eV photoconduction threshold as the temperature is varied between 80K and 460K (above which the dark current became too large for photoconduction measurements to be made). As the temperature is raised, the position of the threshold moves to lower energies. This effect was observed in four samples; at 80K the threshold was at 2.15 $\pm$ 0.05 eV in all four, and at about 450K it had decreased to 1.65 $\pm$ 0.05 eV.

No increased photoconductivity was observed in these samples after heating to 400^{o}C.

4.3.3 Electrical resistance and thermoelectric effect

Fig. 4.18 is a plot of log i versus 1/T for synthetic sample S8. Similar measurements on the other samples also gave straight lines and the thermal activation energies for nine of them all lay between 1.61 and 1.69 eV, with the exception once again of sample S12 (see section 4.3.4).

Fig. 4.19 depicts the observation of the thermoelectric effect in sample S8, which is clearly n-type. The thermoelectric effect of the natural type IIb diamond is again shown for comparison. All nine synthetic samples described above were found to be n-type.

4.3.4 Sample S12

Sample S12 showed unusual properties compared with

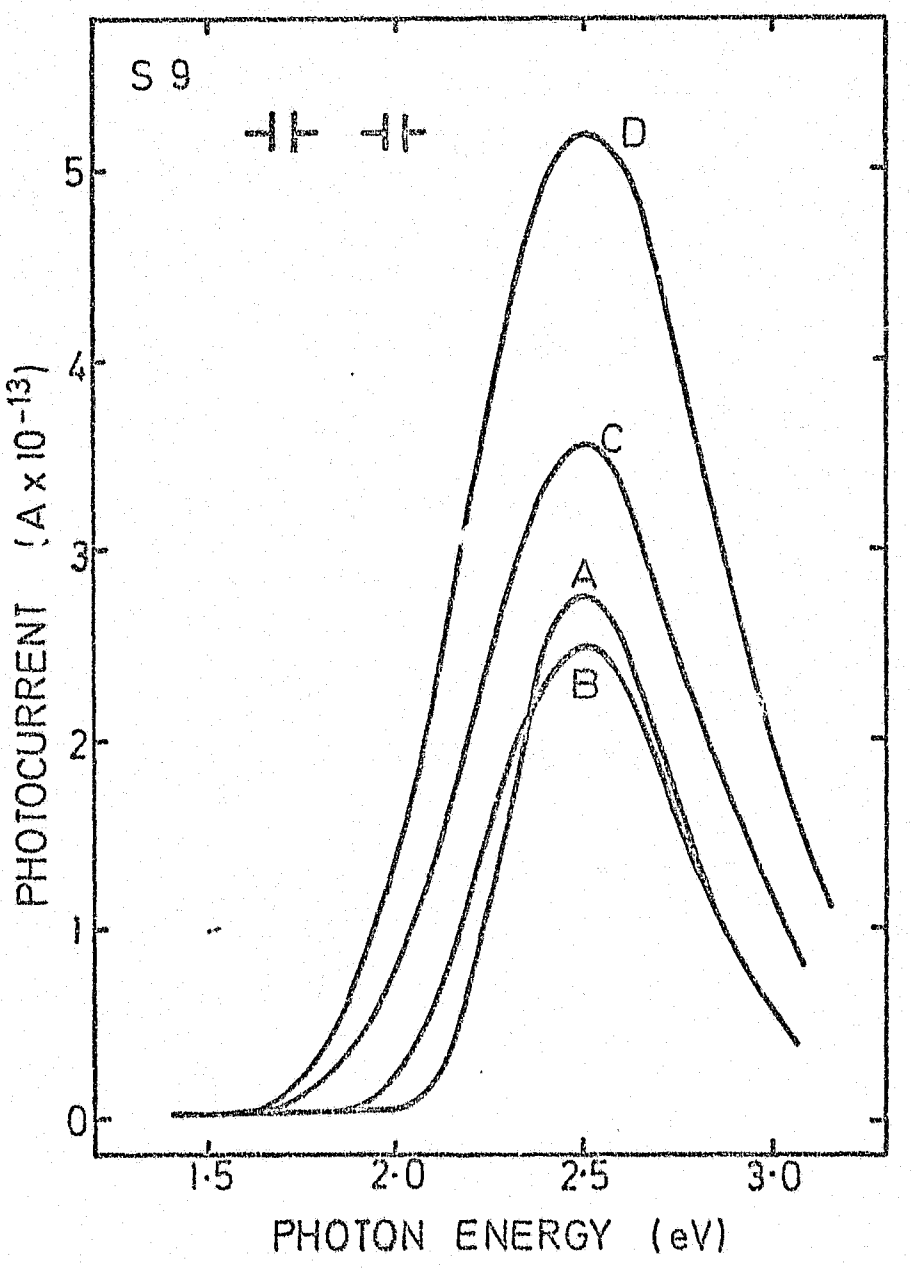


FIG. 4.17 The temperature dependence of the 2 eV threshold in synthetic diamond.
A - 80K B - 293K C - 400K D - 460K

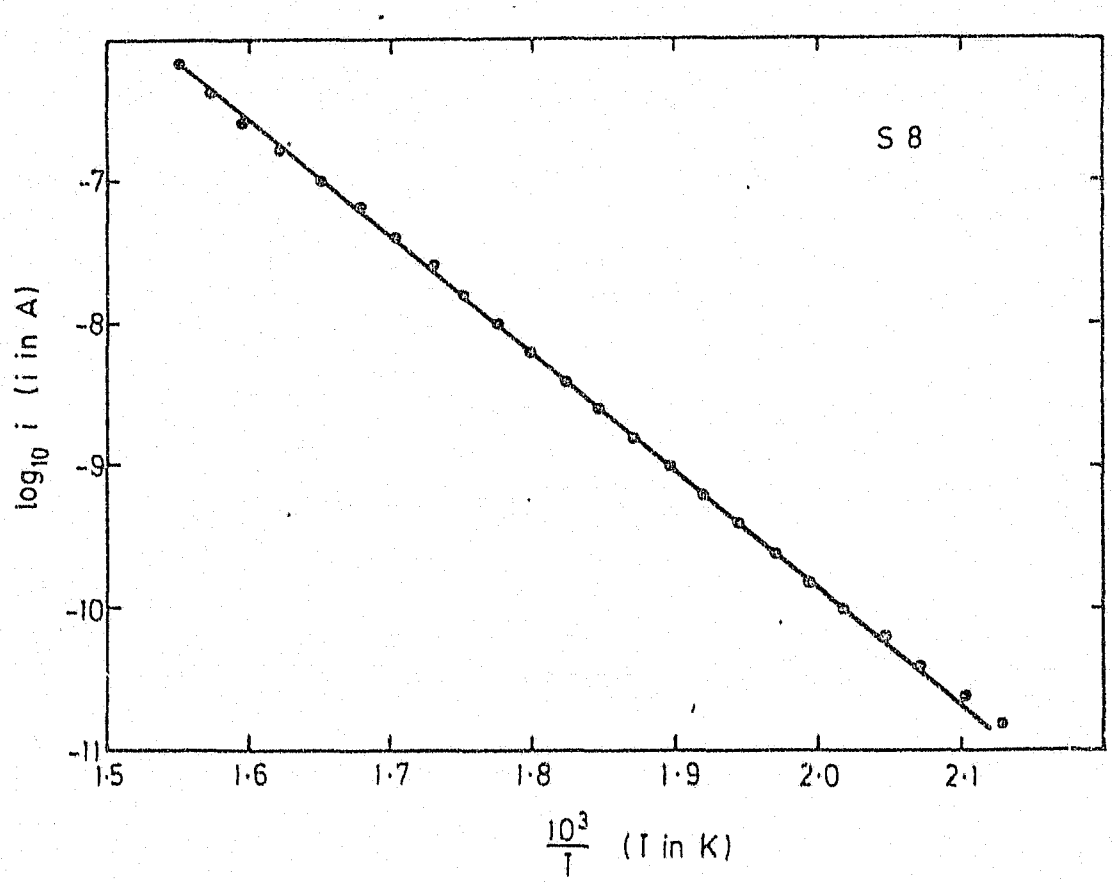


FIG. 4.18 The current i through synthetic diamond S8 as a function of temperature T, with a fixed applied voltage of 90V.

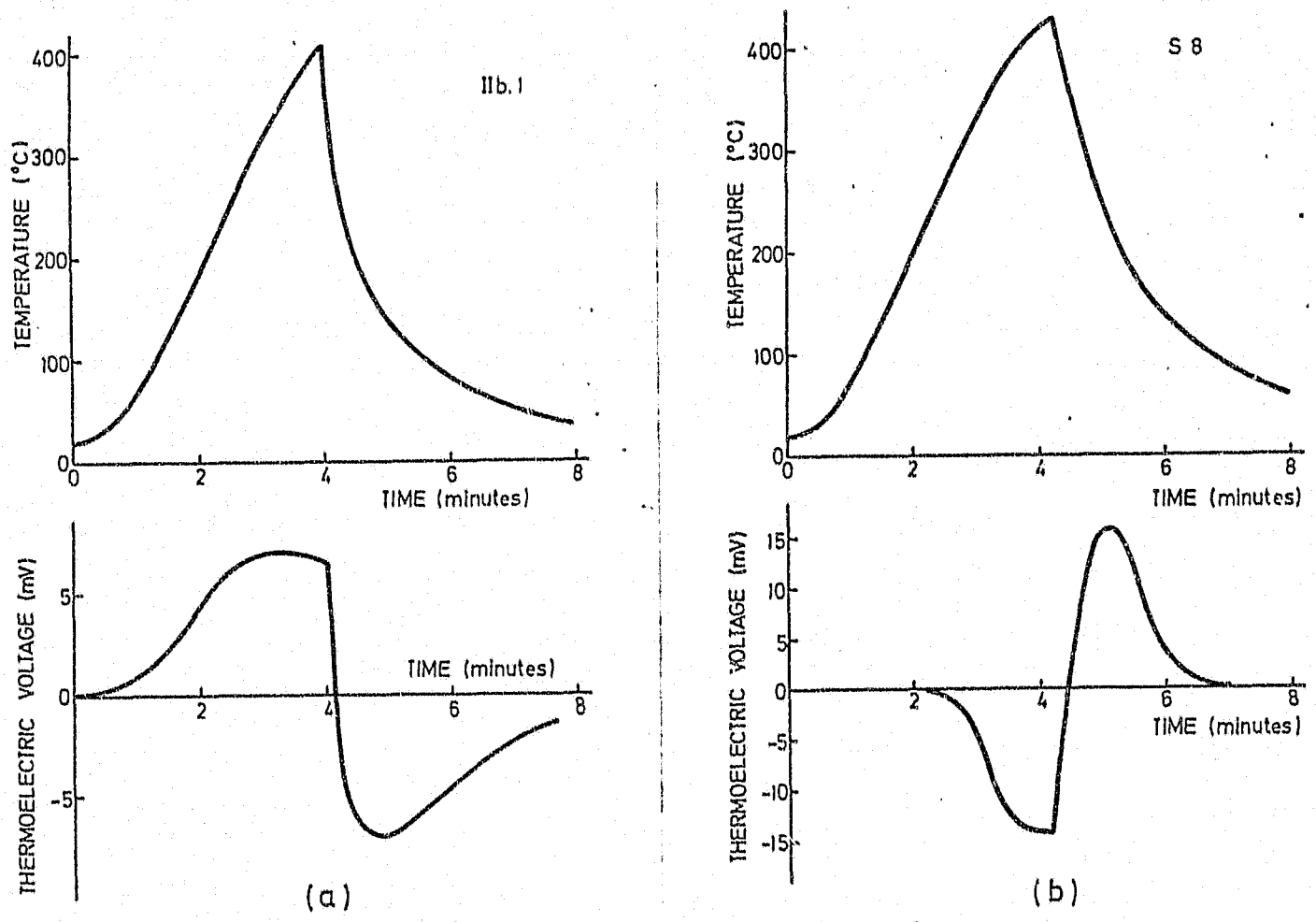


FIG. 4.19 The thermoelectric effect observed under identical experimental conditions in (a) a p-type semiconducting diamond (see Fig. 3.12), and (b) in diamond S8, which is clearly n-type.

the other nine diamonds investigated. Its room temperature resistance was too low for photoconduction measurements to be made at that temperature. At 80K it showed considerable photoconduction between 0.5 and 1.5 eV, together with the photoconduction typical of the other specimens - a threshold at about 2.2 eV followed by a broad photoconduction spectrum extending to the fundamental absorption edge. This is shown in Figs. 4.20 and 4.21. The spectrum between 0.5 and 1.5 eV is clearly a typical type IIb spectrum, as has been observed by many authors (eg. Hardy et al 1962; Collins et al 1969).

The electrical resistance of S12 as a function of temperature yielded an activation energy of 0.35 eV (see Fig. 4.22) and the thermoelectric effect showed that the conductivity was p-type. However, the characteristic electron spin resonance lines of the single substitutional nitrogen atoms could be detected at 80K (Loubser 1974).

4.3.5 Summary of results

The experimental investigations reported in this section have shown that the photoconduction spectra of synthetic Ib diamonds show no threshold at 4.05 eV. A typical spectrum consists basically of a single broad feature. The low energy threshold of this feature is temperature dependent - it increases from about 1.65 eV at 450K to about 2.1 to 2.2 eV at 80K.

The thermal activation energies measured in these diamonds at temperatures up to 400°C lie between 1.6 and 1.7 eV, in agreement with the high temperature optical ionization threshold. The thermally generated free charge carriers are electrons.

One sample (S12) showed properties characteristic of p-type semi-conducting diamond in addition to the photo-

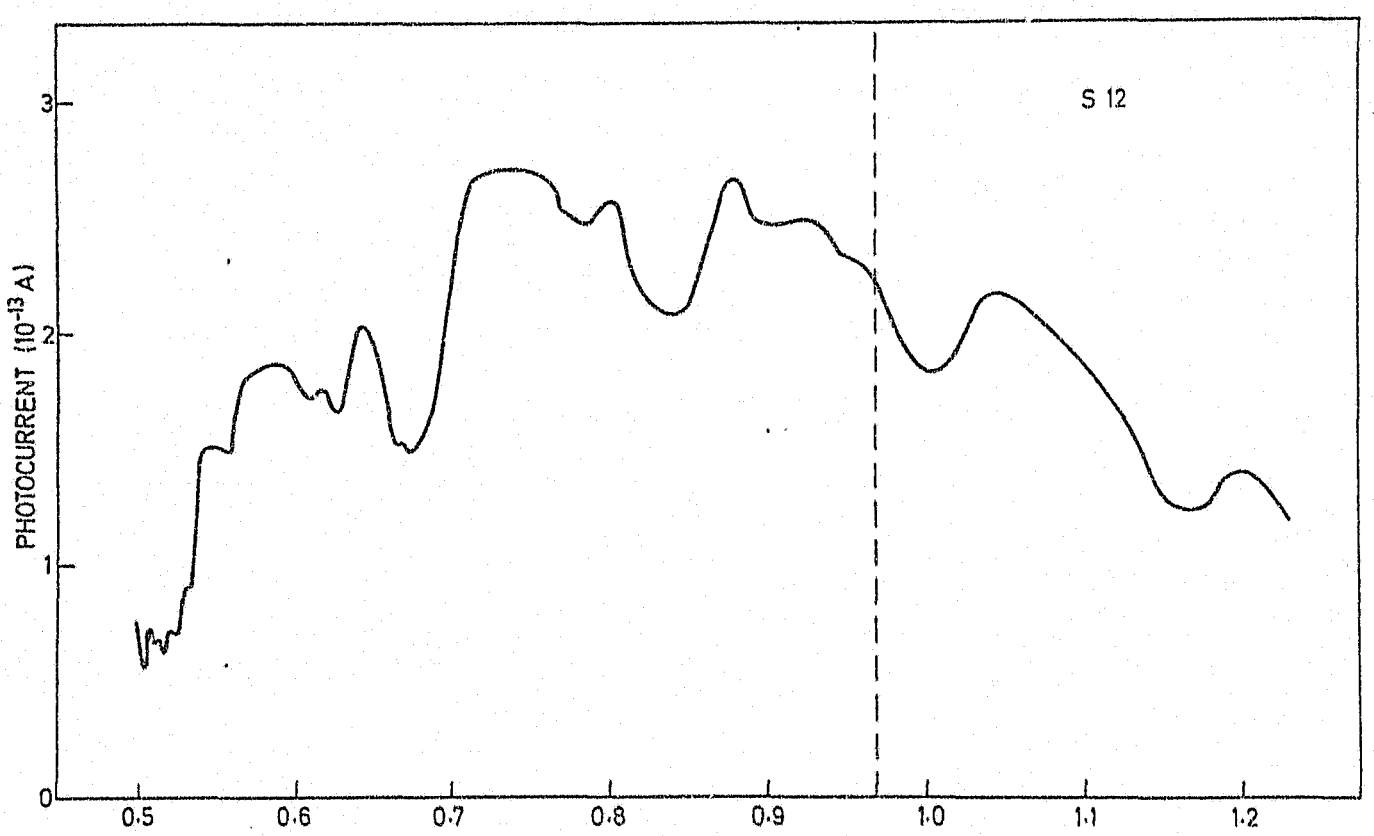


FIG. 4.20 The infrared photoconductivity spectrum of sample S12 at 80K. See Fig. 4.21 for the spectrum to the right of the broken line.

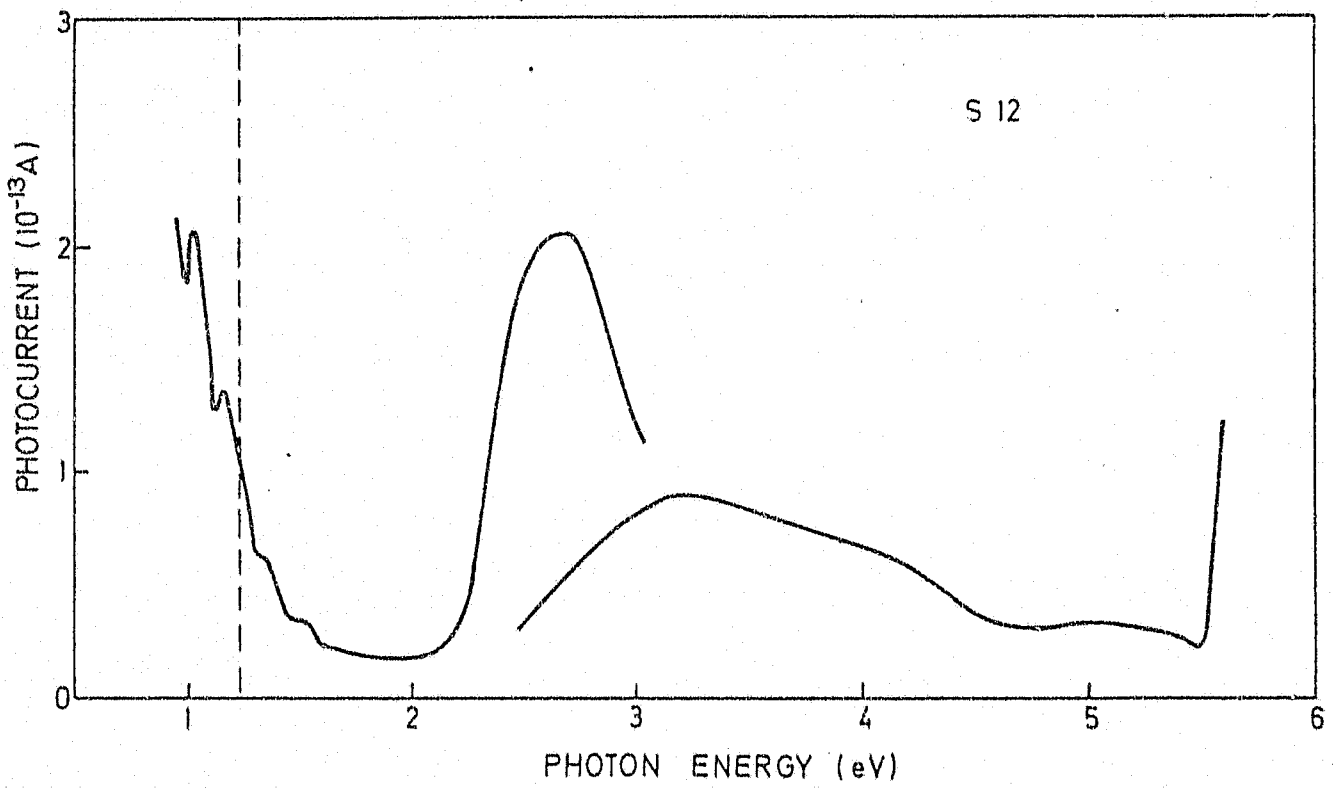


FIG. 4.21 The photoconduction spectrum of sample S12 at 80K. See Fig. 4.20 for the spectrum to the left of the broken line.

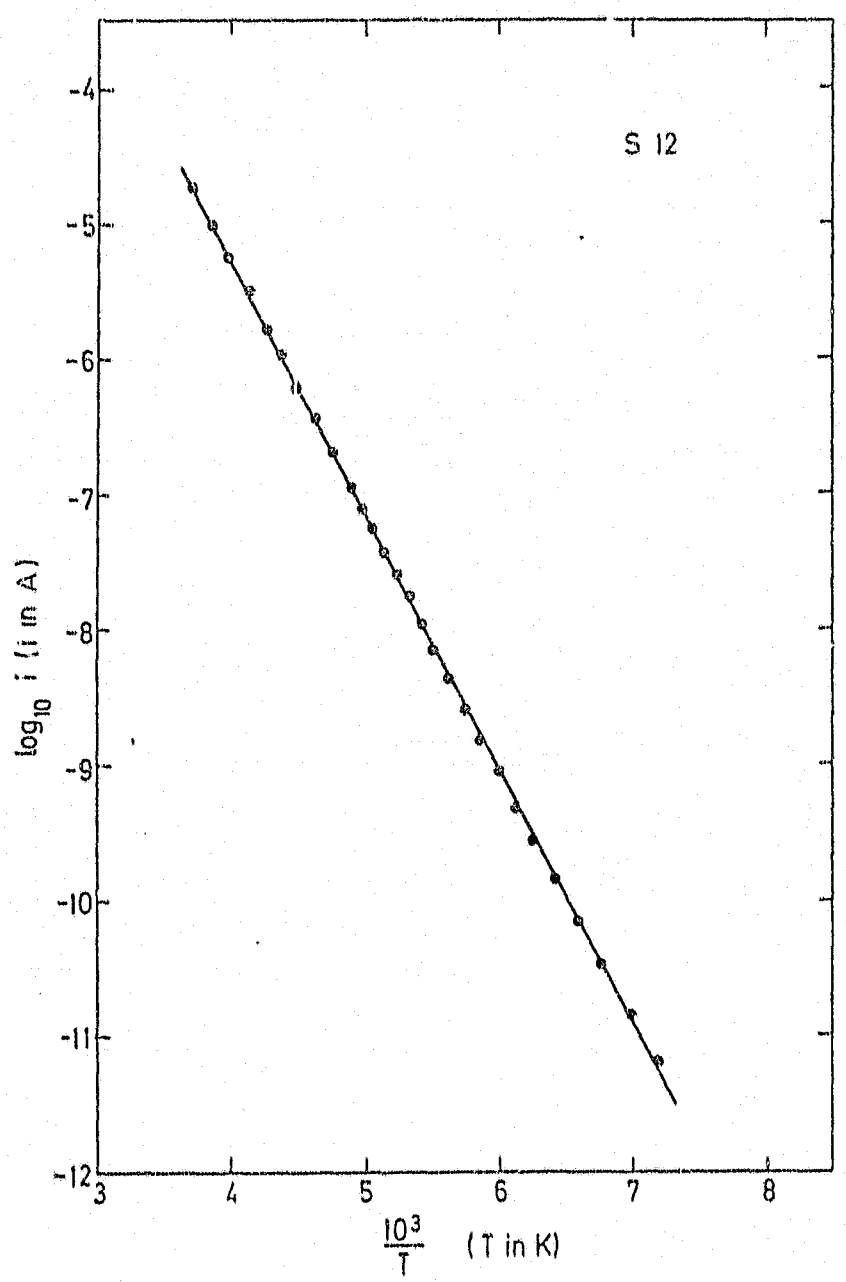


FIG. 4.22 The current i through synthetic diamond S12 as a function of temperature T with a fixed applied voltage of 1.5V.

conduction which is characteristic of synthetic type Ib diamond and is presumed to contain separate regions which are typically type IIb and type Ib respectively.

CHAPTER 5

DISCUSSION, CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1 Irradiated diamonds

The photoconductivity minima observed at the positions of maxima in the GR1 absorption system show that absorption by this system gives rise to few (if any) free charge carriers, which is consistent with the observation that it is a luminescent system (Clark and Norris 1971) and with a model in which the first excited state of a GR1 centre lies well away from the band edge. In contrast, absorption by the ND1 system and the peaks GR2-8 clearly results in photoconduction. The reported absence of luminescence associated with the ND1 system can be understood since the excitation of ND1 carriers from the ground to the excited state creates free charge carriers even at temperatures as low as 8K. The appearance of the UV band and the lines GR3 and GR6 in the excitation spectrum of GR1 luminescence (Clark and Norris 1971) could be due to the trapping at ionized GR1 centres of free charge carriers created by UV band and GR2-8 absorption. In addition, the GR2-8 transitions (which take place at the GR1 centre) may not always result in the freeing of carriers and GR1 luminescence would be observed from those electrons which remained bound.

The occurrence of sharp peaks in the photoconduction spectra of solids is unusual. Sharp peaks in optical absorption are normally associated with transitions between bound states, whereas transitions involving the conduction or valence bands are characterised by broad absorption features. The ionization of a level within the forbidden energy gap usually gives rise to a shoulder or broad peak in the photoconduction spectrum - in diamond the width of

these peaks is usually of the order of an electron volt or more (eg. Vermeulen and Nabarro 1967). The mechanism whereby photoconductivity arises from irradiation into the ND1 and GR2-8 absorption lines therefore merits some discussion.

A number of authors have attributed observations of temperature dependent photoconduction peaks and fine structure to the mechanism of photothermal ionization, in which optical excitation to an excited state is followed by thermal ionization to the conduction or valence bands (eg. Collins and Lightowlers 1968; Sah et al 1971; Kirkman and Stradling 1973). The identifying characteristic of this mechanism is the decrease in the size of the peaks as the temperature is lowered, and their eventual disappearance when the temperature is low enough for the thermal process to be quenched. The observation reported in this thesis that there is no apparent decrease in the ND1 and GR2-8 peaks at 8K as compared with 80K indicates that a thermally assisted process is highly unlikely. This belief does not substantially alter the model of Dyer and du Preez (1965) for the reciprocal bleaching and enhancement of the ND1 and GR1 bands, which only requires that the centres exchange charge carriers via the bands. Vermeulen, Clark and Walker (1974) have reported from subsequent investigations that photoconductivity due to the GR2-8 lines increases as the temperature is decreased from 100 to 40K, and it is suggested that a detailed study of the temperature dependence of the ND1 and GR2-8 photoconduction peaks should be made in a cryostat in which the temperature can be controlled and which is capable of achieving sample temperature lower than 8K.

Various mechanisms have been proposed whereby excitons might give rise to free charge carriers, in order to account for sharp photoconduction peaks at energies close to the intrinsic absorption edge in the spectra of a number of substances, eg. Cu_2O (Coret and Nikitine 1969), CdS and

CdSe (Park and Reynolds 1963, Gross and Novikov 1959) and diamond (Nahum and Halperin 1962, Denham et al 1967), and also to account for anomalously low efficiencies of luminescence lines close to the absorption edge (Nelson et al 1966). At sufficiently high temperatures an exciton can thermally dissociate into a free electron and hole. An Auger process, in which an exciton ionizes a defect centre, could take place even at low temperatures (Nelson et al 1966). Coret et al (1971) have also suggested that excitons might dissociate in regions of high local fields. However, it is unlikely that any process involving band-gap excitons is responsible for the ND1 and GR2-8 photoconduction peaks since these occur at about 3 eV, and the band gap of diamond is 5.5 eV.

Davies and Lightowlers (1970) suggested that an Auger-type process, in which the energy difference between the excited state and ground state is used to eject an electron, could explain the apparent absence of luminescence associated with the ND1 centre. This process would give rise to photoconduction peaks such as those reported in this thesis; however, there is as yet no evidence (either from optical absorption or from photoconduction measurements) of an electron which is weakly bound to the ND1 or GR1 centres and which might be ejected in such a process, and the ND1 and GR1 transitions are generally believed to be transitions to the first excited states.

While considering criteria for the occurrence of luminescence, Dexter, Klick and Russell (1955) suggested that the autoionization of excited states of simple centres in solids might give rise to photoconductivity upon irradiating into discrete absorption lines even at very low temperatures. Recently Boyn, Dziesiaty and Wruck (1970) have observed peaks in the photoconduction spectrum of Ti-doped CdS, and suggested that the excited states of the Ti^{2+} centres responsible for these peaks might lie above the minimum of the conduction band, thus leading to auto-

ionization. They refer to the work of Kaplan (1963) and Bassani, Iadonisi and Preziosi (1969), who investigated the dependence of impurity states on band structure, and found that when subsidiary extrema occur in the conduction or valence bands, it might be possible to obtain excited states of a centre which are in resonance with that band. The theoretical and experimental evidence for the existence of such resonant states has been extensively reviewed by Bassani, Iadonisi and Preziosi (1974). Resonant states of boron acceptors in silicon due to spin-orbit splitting of the top of the valence band have been observed by Zwerdling, Button, Lax and Roth (1960), Colbow (1963) and Onton, Fisher and Ramdas (1967). Donor resonant states associated with secondary minima in the conduction band have been observed in GaP by Onton (1971) and in InP by Onton, Yacobi and Chicotka (1972). Saddle points in the band should also give rise to resonant impurity states.

It is not possible, from the measurements reported in this thesis, to establish the precise mechanism which gives rise to the photoconduction in the ND1 and GR2-8 lines. It is suggested, however, that these might well be due to autoionization from discrete excited states within the conduction or valence bands. There is evidence from theoretical work (Pryce 1965; Painter, Ellis and Lubinsky 1971) and from reflectance measurements (Roberts and Walker 1967) that the conduction band of diamond might have subsidiary energy minima, and the valence band would be split due to spin-orbit coupling (eg. Phillips 1973). Preliminary measurements have indicated that the free carriers generated by GR2-8 illumination might be electrons (Vermeulen 1975); an identification of the sign of the ND1 carriers would be of considerable interest. Unfortunately, no theoretical calculations concerning the ND1 centre or the excited states of the vacancy higher than the first have been made; it is hoped that the unusual observations reported in this thesis will stimulate interest in such calculations.

5.2 Type Ib diamonds

The observations reported in this thesis show conclusively that the photoconduction threshold at 4.05 eV is not characteristic of type Ib diamond. The view of Dean (1965) and Denham, Lightowlers and Dean (1967) that this threshold is the photoionization limit for the isolated substitutional nitrogen donor is therefore believed to be incorrect. The photoconduction spectrum which is typical of type Ib diamond consists essentially of a single broad feature which extends from about 2.2 eV at 80K to the intrinsic absorption edge. This photoconduction continuum is similar in appearance and position to the type Ib optical absorption tail which has been correlated with the isolated substitutional nitrogen (Dyer, Raal, du Preez and Loubser 1965; Sobolev et al 1969b; Chrenko, Strong and Tuft 1971). It is therefore suggested that the photoionization threshold for the substitutional nitrogen donor is 2.2 eV at 80K.

Experimental observations of photoconductivity in type Ia diamonds are consistent with this suggestion. Most type Ia diamonds contain detectable amounts of isolated substitutional nitrogen and it is likely that small concentrations of this defect are present in all type Ia diamonds. A pnotoconductive threshold at 2.2 eV (at 80K) is observed in all type Ia diamonds (Vermeulen and Nabarro 1967). Photo-Hall effect observations have shown that type Ia diamonds are n-type under illumination with visible light (Vermeulen 1975; Klick and Maurer 1951; Redfield 1954) and the observation by the author (quoted by Vermeulen and Nabarro (1967)) that type Ia diamonds are p-type during illumination with light of energy 2.2 eV is probably incorrect.

The activation energy for thermally generated free carriers in type Ib diamond, as estimated from measurements of electrical resistance as a function of temperature up to 400^{o}C, is about 1.65 eV; observations of the thermo-

electric effect have shown that these carriers are electrons. The low-energy threshold for the single photoconduction feature typical of type Ib diamond (about 2.2 eV at 80K) decreases with increasing temperature and reaches the thermal activation energy value of 1.65 eV when the temperature is about 450K. It is concluded from these observations that the thermally generated carriers and the carriers giving rise to the photoconduction originate from the same donor level - the isolated substitutional nitrogen donor. Although there is some doubt about the quantitative validity of the calculations of Messmer and Watkins (1973), it is interesting to note that the measured thermal activation energy of 1.65 eV agrees well with their value of 1.5 eV for the distance below the conduction band of the nitrogen donor level before distortion.

The observation that there is a marked difference between the thermal and low temperature optical ionization energies deserves discussion. The Jahn-Teller distortion experienced by the nitrogen centre is generally believed to be large; estimates of the distortion energy range from about 2.8 eV (from the prediction by Öpik and Pryce (1957) that this reduction should be about four times the height of the barrier to reorientation when the distortion arises from the electrons coupling to a single T vibrational mode) to about 5 eV (calculated by Messmer and Watkins (1973)). The ionized donor is electronically non-degenerate and will not suffer an asymmetric distortion. The Franck-Condon principle dictates that optical transitions take place with no change in the lattice configuration; optical ionization of the nitrogen centre therefore takes place from the distorted configuration. In thermal transitions, the lattice configuration can change and transitions occur at the lowest accessible energy, which is the energy difference between the equilibrium lattice configurations for the bound and ionized states. A marked difference between the optical and thermal ionization energies of the

nitrogen donor is therefore to be expected. Stoneham (1974) has pointed out that this difference should be at least as much as the height of the barrier to reorientation, since the centre could reorient through the symmetrical position. The barrier height is about 0.7 eV and the difference between the optical and thermal activation energies reported in this thesis is about 0.55 eV. There is clearly a need for further work to investigate this discrepancy. It is possible that measurements of photoconductivity at liquid helium temperatures might reveal a further increase in the 2.2 eV photoconduction threshold.

A study of the photoconductivity of synthetic type Ib diamonds as a function of the concentration of dispersed nitrogen might also yield interesting results. The absorption spectra reported by Chrenko, Strong and Tuft (1971) (see Fig. 2.3) show a low energy threshold at about 600 nm (about 2 eV) for a yellow diamond containing a relatively large amount of dispersed nitrogen; this value is in good aggrement with the 2 eV room temperature photoconduction threshold reported in this thesis. However, the absorption threshold shown by Chrenko et al appears to have moved to about 470 nm (2.65 eV) for a colourless diamond containing far less nitrogen, which suggests the possibility that the photoionization threshold might decrease with increasing nitrogen concentration. The observations of Loubser, van Ryneveld and du Preez (1965) indicate that nitrogen centres become close enough for exchange interaction to be observed at concentrations of about 10^{18} to 10^{19} nitrogen atoms per cm^3, and the possibility that such an interaction might cause a decrease in the photoionization threshold should be investigated. The thermal ionization energy would have to remain unaltered(or decrease by a smaller amount) if the discrepancy discussed above is to be explained. However, Sturge (1967) reports an enhancement of the strain due to the Jahn-Teller effect at acceptors in silicon when their

concentrations are high - which would cause an increase in optical ionization energy.

The peak at 4.6 eV in the absorption spectrum of type Ib diamond still remains unexplained. It is tempting to attribute it to transitions from the nitrogen donor to the conduction band minimum at the centre of the Brillouin zone, which Roberts and Walker (1967) suggest to be about 7.3 eV above the valence band edge. This gives an energy difference of about 1.8 eV between the conduction band minima. If the nitrogen donor is 2.2 eV below the conduction band, transitions to the central band edge minimum would occur from about 4 eV onwards, which is the position of the threshold of the ultraviolet absorption peak. The decrease in photoconductivity in this region could be attributed to the lower lifetime of free carriers at the surface than in the volume. As the optical absorption increases, a greater proportion of the carriers is excited at the surface, where recombination is more rapid than in the volume. For this reason it is common for photoconduction spectra to show a decrease at energies greater than the intrinsic absorption edge (Bube 1960 p230) and similar behaviour would be expected for strong absorption systems other than the absorption edge. The observation of fine structure on this peak at 80K by Dyer et al (1965) should be verified in synthetic diamond - it was observed in the spectra of natural Ib diamonds, which does not clearly establish it as a characteristic of dispersed nitrogen, since natural diamonds can be intermediate in type. Structure is observed at the same positions on the 4 eV photoconduction threshold (Denham, Lightowlers and Dean 1967) which is characteristic of type Ia diamond (Vermeulen and Nabarro 1967).

The additional photoconduction which is observed in natural type Ib diamonds after heating, and which can be optically bleached, is probably associated with the Leivo electron paramagnetic resonance centre, which is known to

be present in at least two of the diamonds which were studied (including sample B2 - see Figs. 4.11 and 4.12). A similar enhancement of the optical absorption in natural type Ib diamonds, accompanied by decreases in the e.p.r. associated with both the single nitrogen and the Leivo centre, have been interpreted by Loubser (1973) in terms of electron transfer between the single nitrogen and the Leivo centre. A thermal activation energy of 1.7 eV for ionization of the single nitrogen was estimated by Loubser (1973), in good agreement with the results reported in this thesis. The photoconduction measurements reported here indicate that the low energy limit for optical ionization of the Leivo centre is 1.7 eV. A systematic investigation of optical absorption, photoconduction and electron paramagnetic resonance in these diamonds would be rewarding.

5.3 Additional suggestions for further work

Much of the recent experimental work which has been undertaken to investigate the properties of defects in diamond has centred on optical techniques - especially optical absorption and emission. The electrical properties of diamond have been somewhat neglected - probably because it is difficult (and sometimes impossible) to make electrical measurements on highly insulating samples. However, with measuring equipment and electrical insulation materials which are now available, electrical measurements such as the Hall effect, resistivity and thermoelectric effect are experimentally feasible, especially at elevated temperatures. For instance, it should be possible to measure the Hall effect by conventional means in natural insulating diamond from about 600K upwards. Redfield (1954) and Konorova and Shevchenko (1967) have both reported that electron and hole mobilities vary as $T^{-1.5}$ in insulating diamond. Wedepohl

(1957) found that hole mobilities vary as $T^{-2.8}$; it would be interesting to check on the temperature dependence of the electron mobility.

The thermoelectric effect has been shown to be a useful means of identifying the sign of the charge carriers in insulating diamond at elevated temperatures. Interesting extensions of this type of measurement are the photothermoelectric effect and thermally stimulated thermoelectric effect, which can be used for carrier identification and, in some cases, to obtain quantitative information such as electron density and mobility (Lawrence and Bube 1968; Harper, Matthews and Bube 1970; Kwok and Bube 1973). These techniques could probably be used to great advantage in insulating diamond.

An interesting observation which has recently been made is the existence of the ND1 band, as observed in photoconduction, in several small type Ia gem sand diamonds (see Fig. 5.1). These diamonds were among those selected for an investigation of the counting properties of diamond (Vermeulen 1965). Initial tests showed them to be poor counters and they were not investigated any further. It is estimated that they were subjected to a maximum irradiation dose of 10^6 electrons per cm^2 of energy 0.61 and 2.2 MeV. It is interesting to speculate whether this system is present in some natural type Ia diamond, or whether it was produced by the small radiation dose to which these diamonds were subjected; normally, radiation doses of the order of 10^{17} electrons per cm^2 are needed to induce measurable radiation damage in diamond. Further investigations of photoconductivity in this type of diamond are required.

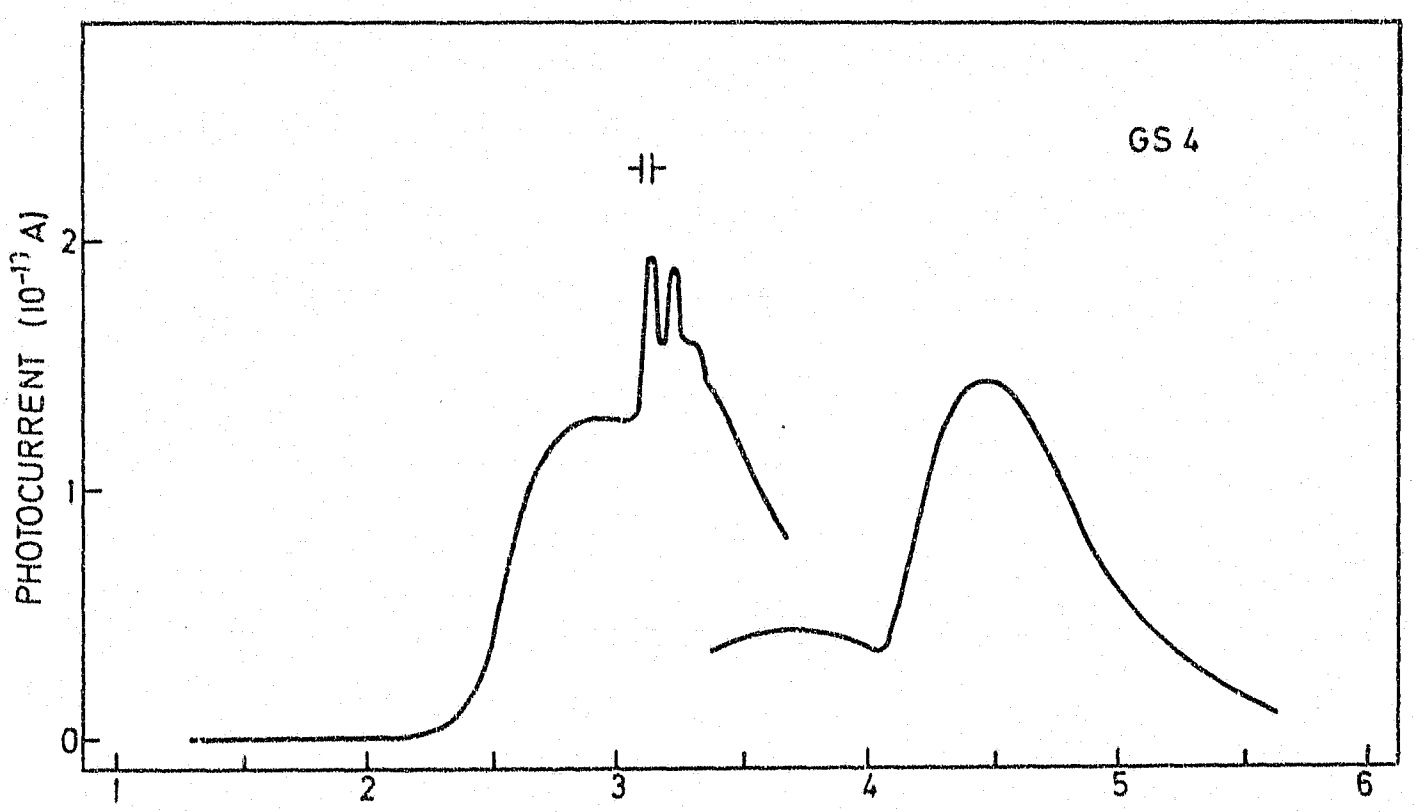


FIG. 5.1 The photoconduction spectrum at 80K of a type Ia gem sand diamond. The ND1 system, centred at 3.3 eV, is extremely prominent

REFERENCES

Austin IG and Wolfe R 1956 Proc. Phys. Soc. B69 329

Baldwin JA 1963 Phys. Rev. Lett. 10 220

Bassani F, Iadonisi G and Preziosi B 1969 Phys. Rev. 186 735

Bassani F, Iadonisi G and Preziosi B 1974 Rep. Prog. Phys. 37 1099

Bastin JA, Mitchell EWJ and Whitehouse J 1959 Brit. J. Appl. Phys. 10 412

Bell MD and Leivo WJ 1967 J. Appl. Phys. 38 337

Bourgoin JC, Brosious PR, Kim YM, Corbett JW and Chrenko RM 1972 Phil. Mag. 26 1167

Boyn R, Dziesiaty J and Wruck D [illegible] ys. Status Solidi 42 K197

Brophy JJ 1955 Phys. Rev. 99 1336

Bropny JJ 1956 Physica 22 156

Bube RH 1960 Photoconductivity of Solids (John Wiley & Sons, New York) p135

Charette JJ 1961 J. Chem. Phys. 35 1906

Chrenko RM 1973 Phys. Rev. B 7 4560

Chrenko RM, Strong HM and Tuft RE 1971 Phil. Mag. 23 313

Colbow K 1963 Can. J. Phys. 41 1801

Collins AT, Dean PJ, Lightowlers EC and Sherman WF 1965 Phys. Rev. 140 A1272

Collins AT and Lightowlers EC 1968 Phys. Rev. 171 843

Collins AT, Lightowlers EC and Dean PJ 1969 Phys. Rev. 183 725

Collins AT and Williams AWS 1971 J. Phy . C: Solid State Phys. 4 1789

Coret A and Nikitine S 1969 Solid State Comm. 7 87

Coret A, Nikitine S, Zielinger JP and Zouaghi M 1971 Proc. Third Int. Conf. Photoconductivity ed Erik M Pell (Pergamon, Oxford) p81

Coulson CA 1972 Proc. Int. Conf. Radiation Damage and Defects in Semi-conductors, Reading ed JE Whitehouse (Institute of Physics, London) p249

Crossfield MD, Davies G, Collins AT and Lightowlers EC 1974 J. Phys. C: Solid State Phys. 7 1909

Crowther PA and Dean PJ 1967 J. Phys. Chem. Solids 28 1115

Crowther PA, Dean PJ and Sherman WF 1967 Phys. Rev. 154 772

Custers JFH 1952 Physica 18 489

Custers JFH 1955 Nature, Lond. 176 173

Davies G 1971 Proc. Int. Conf. on Phonons, Rennes, France ed MA Nusimovici (Flammarion, Paris) p382

Davies G 1972a Diamond Research 1972 (Industrial Diamond Information Bureau, London) p21

Davies G 1972b J. Phys. C: Solid State Phys. 5 2534

Davies G 1974 Proc. R. Soc. Lond. A336 507

Davies G and Lightowlers EC 1970 J. Phys. C: Solid State Phys. 3 638

Davies G and Penchina CM 1974 Proc. R. Soc. Lond. A338 359

Davies G and Summersgill I 1973 Diamond Research 1973 (Industrial Diamond Information Bureau, London) p6

Dean PJ 1965 Phys. Rev. 139 A588

Dean PJ, Lightowlers EC and Wight DR 1965 Phys. Rev. 140 A352

Denham P, Lightowlers EC and Dean PJ 1967 Phys. Rev. 161 762

Dexter DL, Klick CC and Russell GA 1955 Phys. Rev. 100 603

Dugdale RA 1953 Brit. J. Appl. Phys. 4 334

du Preez L 1965 Ph D Thesis, University of the Witwaters-rand

Dyer HB and du Preez L 1965 J. Chem. Phys. 42 1898

Dyer HB and du Preez L 1967 Science and Technology of Industrial Diamonds 1 ed J Burls (Industrial Diamond Information Bureau, London) p23

Dyer HB and Ferdinando P 1966 Brit. J. Appl. Phys. 17 419

Dyer HB and Matthews IG 1957 Proc. R. Soc. Lond. A243 320

Dyer HB, Raal FA, du Preez L and Loubser JHN 1965 Phil. Mag. 11 763

Elliott RJ 1960 Proc. Phys. Soc. 76 787

Elliott RJ, Matthews IG and Mitchell EWJ 1958 Phil. Mag. 11 763

Evans T 1972 Diamond Conference, Bristol (unpublished)

Evans T 1973 Diamond Research 1973 (Industrial Diamond Information Bureau, London) p2

Evans T and Phaal C 1962 Proc. R. Soc. Lond. A270 538

Every AG 1963 M Sc Thesis, University of the Witwatersrand

Every AG 1970 Ph D Thesis, University of Reading

Farrer RG and Vermeulen LA 1972 J. Phys. C: Solid State Phys. 5 2762

Farrer RG 1969 Solid State Comm. 7 685

Faulkner EA and Lomer JN 1962 Phil. Mag. 7 1995

Ferdinando P 1967 Ph D Thesis, University of Reading

Frank FC 1956 Proc. R. Soc. Lond. A237 168

Goldsmid HJ, Jenns CC and Wright DA 1959 Proc. Phys. Soc. 73 393

Gould HJ 1962 Rev. Sci. Instr. 33 1471

Gross EF and Novikov BV 1959 Sov. Phys. - Solid State 1 321

Gudden B and Pohl RW 1920 Zeit. Phys. 3 123

Halperin A and Nahum J 1962 Luminescence of Organic and Inorganic Materials ed HP Kallman and GM Spruch (John Wiley, New York) p252

Hamer MF and Davies G 1974 Diamond Conference, Oxford (unpublished)

Hardy JR 1962 Proc. Phys. Soc. 79 1154

Harper JG, Matthews HE and Bube RH 1970 J. Appl. Phys. 41 765

Hoerni JA and Wooster WA 1955 Acta. Cryst. 8 187

Huggins CM and Cannon P 1962 Nature, Lond. 194 829

Kaiser W and Bond WL 1959 Phys. Rev. 115 857

Kaplan H 1963 J. Phys. Chem. Solids 24 1593

Kemmey PJ and Wedepohl PT 1965 Physical Properties of Diamond ed R Berman (Clarendon Press, Oxford) p325

Kirkman RF and Stradling RA 1973 J. Phys. C: Solid State Phys. 6 L324

Klick CC and Maurer RJ 1951 Phys. Rev. 81 124

Klingsporn PE, Bell MD and Leivo WJ 1970 J. Appl. Phys. 41 2977

Konorova EA and Shevchenko SA 1967 Sov. Phys. - Semiconductors 1 299

Konorova EA, Sorokina LA and Shevchenko SA 1965 Sov. Phys. - Solid State 7 876

Kwok HB and Bube RH 1973 J. Appl. Phys. 44 138

Lannoo M and Stoneham AM 1968 J. Phys. Chem. Solids 29 1987

Larkins FP 1971a J. Phys. C: Solid State Phys. 4 3065

Larkins FP 1971b J. Phys. C: Solid State Phys. 4 3077

Larkins FP 1973 J. Phys. C: Solid State Phys. 6 L345

Lawrence R and Bube RH 1968 J. Appl. Phys. 39 1807

Lax M and Burstein E 1955 Phys. Rev. 97 39

Lazukin VN and Terenk'erstu AN 1970a Sov. Phys. - Doklady 14 793 1970b Sov. Phys. - Doklady 14 989

Leivo WJ and Smoluchowski R 1955 Phys. Rev. 98 1532

Leivo WJ and Smoluchowski R 1955b Bull. Amer. Phys. Soc. 30 9

Lenz H 1927 Ann. Phys. 83 941

Lidiard AB 1972 Proc. Int. Conf. Radiation Damage and Defects in Semi-conductors, Reading ed JE Whitehouse (Institute of Physics, London) 202

Lomer JM and Wild AMA 1971 Phil. Mag. 24 273

Lomer JN and Wild AMA 1973 Radiation Effects 17 37

Loubser JHN 1973 Diamond Conference, Reading (unpublished)

Loubser JHN 1974 Private communication

Loubser JHN 1975 Private communication

Loubser JHN and du Preez L 1965 Brit. J. Appl. Phys. 16 457

Loubser JHN and van Ryneveld WP 1967 Brit. J. Appl. Phys. 18 1029

Loubser JHN, van Ryneveld WP and du Preez L 1965 Solid State Communications 3 307

Loubser JHN and Wright ACJ 1973 Diamond Research 1973 (Industrial Diamond Information Bureau, London) p16

Mani A 1944 Proc. Ind. Acad. Sci. A19 231

Massarani B, Bourgoin JC and Chrenko RM 1974 Proc. Int. Conf. Lattice Defects in Semi-conductors, Freiburg (to be published).

Messmer RP and Watkins GD 1970 Phys. Rev. Lett. 25 656

Messmer RP and Watkins GD 1971 Radiation Effects 9 9

Messmer RP and Watkins GD 1973 Phys. Rev. B 7 2568

Mitchell EWJ 1959 J. Phys. Chem. Solids 8 444

Mitchell EWJ 1964 Diamond Research 1964 (Industrial Diamond Information Bureau, London) p13

Mitchell EWJ 1965 Physical Properties of Diamond ed R Berman (Clarendon Press, Oxford) p394

Mitchell EWJ 1967 Science and Technology of Industrial Diamonds ed J Burls 1 (Industrial Diamond Information Bureau, London) p17

Moore EB and Carlson CM 1971 Phys. Rev. B4 2063

Nahum J and Halperin A 1962 J. Phys. Chem. Solids 23 345

Nayar PGN 1941 Proc. Ind. Acad. Sci. A14 1

Nelson DF, Cuthbert JD, Dean PJ and Thomas DG 1966 Phys. Rev. Lett. 17 1262

Onton A 1971 Phys. Rev. B4 4449

Onton A, Fisher P and Ramdas AK 1967 Phys. Rev. 163 686

Onton A, Yacobi Y and Chicotka RJ 1972 Phys. Rev. Lett. 28 966

Öpik U and Pryce MHL 1957 Proc. R. Soc. Lond. A238 425

Owen J 1965 Physical Properties of Diamond ed R Berman (Clarendon Press, Oxford) p274

Painter GS, Ellis DE and Lubinsky AR 1971 Phys. Rev. B4 3610

Park YS and Reynolds DC 1963 Phys. Rev. 132 2450

Phillips JC 1973 Bonds and Bands in Semiconductors (Academic Press, New York) p111

Pryce MHL 1965 Physical Properties of Diamonds ed R Berman (Oxford University Press, London) p256

Ralph JE 1960 Proc. Phys. Soc. 76 688

Raman CV and Nilakantan P 1940 Proc. Ind. Acad. Sci. A11 389

Redfield AG 1954 Phys. Rev. 94 526

Roberts RA and Walker WC 1967 Phys. Rev. 161 730

Robertson R, Fox JJ and Martin AE 1934 Phil. Trans. R. Soc. Lond. A232 463

Runciman WA 1965 Proc. Phys. Soc. 86 629

Sah CT, Ning TH, Rosier LL and Forbes L 1971 Solid State Communications 9 917

Shcherbakova M Ya, Sobolev EV and Nadolinnyi VA 1972 Sov. Phys. - Doklady 17 513

Shcherbakova M Ya, Sobolev EV, Samsonenko ND and Akserov VK 1969 Sov. Phys. - Solid State 11 1104

Shul'man LA, Zaritskii IM and Podzyarei GA 1967 Sov. Phys. - Solid State 8 1842

Smith RA 1959 Semiconductors (Cambridge University Press) p90

Smith RA 1968 Semiconductors (Cambridge University Press) 1968 p172

Smith WV, Gelles JR and Sorokin PP 1959 Phys. Rev. Lett. 2 39

Smith WV, Sorokin PP, Gelles IL and Lasher GJ 1959 Phys. Rev. 115 1546

Sobolev EV, Il'in VE, Gil'bert. EI and Lenskaya S'. 1969a Sov. Phys. - Solid State 11 200

Sobolev EV and Lisoyvan VI 1972 Akademia Nauk SSSR 204 88

Sobolev EV, Lisoivan VI and Lenskaya SV 1968 Soviet Physics - Crystallography 12 665

Sobolev EV, Litvin Yu A, Samsonenko ND, Il'in VE, Lenskaya SV and Butuzov VP 1969b Sov. Phys. - Solid State 10 1789

Stoneham AM 1974 Diamond Conference, Oxford (unpublished)

Sturge MD 1967 Solid State Physics 20 (Academic Press, New York) p151

Sutherland GBBM, Blackwell DE and Simeral WG 1954 Nature, Lond. 174 901

Taylor KW Ph D Thesis, University of London.

Urlau RR, Logie JH and Nabarro FRN 1961 Proc. Phys. Soc. 78 256

Vandersande J 1974 Proc. Int. Conf. Lattice Defects in Semiconductors, Freiburg (to be published)

Vermeulen LA 1975 Private communication

Vermeulen LA, Clark CD and Walker J 1974 Proc. Int. Conf. Lattice Defects in Semiconductors, Freiburg (to be published)

Vermeulen LA and Farrer RG 1975 Diamond Research 1975 (Industrial Diamond Information Bureau, London) (to be published)

Vermeulen LA and Nabarro FRN 1967 Phil. Trans. R. Soc. Lond. A262 251

Walker J 1973 Ph D Thesis, University of Reading

Walker J 1974 Proc. Int. Conf. Lattice Defects in Semiconductors, Freiburg (to be published)

Walker J, Vermeulen LA and Clark CD 1974 Proc. R. Soc. Lond. A341 253

Wedlake RJ 1972 Diamond Conference, Bristol (unpublished)

Wentorf RH and Bovenkerk HP 1962 J. Chem. Phys. 36 1987

Taylor KW Ph D Thesis, University of London.

Urlau RR, Logie JH and Nabarro FRN 1961 Proc. Phys. Soc. 78 256

Vandersande J 1974 Proc. Int. Conf. Lattice Defects in Semiconductors, Freiburg (to be published)

Vermeulen LA 1975 Private communication

Vermeulen LA, Clark CD and Walker J 1974 Proc. Int. Conf. Lattice Defects in Semiconductors, Freiburg (to be published)

Vermeulen LA and Farrer RG 1975 Diamond Research 1975 (Industrial Diamond Information Bureau, London) (to be published)

Vermeulen LA and Nabarro FRN 1967 Phil. Trans. R. Soc. Lond. A262 251

Walker J 1973 Ph D Thesis, University of Reading

Walker J 1974 Proc. Int. Conf. Lattice Defects in Semiconductors, Freiburg (to be published)

Walker J, Vermeulen LA and Clark CD 1974 Proc. R. Soc. Lond. A341 253

Wedlake RJ 1972 Diamond Conference, Bristol (unpublished)

Wentorf RH and Bovenkerk HP 1962 J. Chem. Phys. 36 1987

Wedepohl PT 1957 Proc. Phys. Soc. B70 177

Wedepohl PT 1957b Ph D Thesis, University of Reading

Whippey PW 1972 Can. J. Phys. 50 803

Wight DR and Dean PJ 1967 Phys. Rev. 154 689

Wight DR, Dean PJ, Lightowlers EC and Mobsby CD 1971 J. Lum. 4 169

Zwerdling S, Button KJ, Lax B and Roth LM 1960 Phys. Rev. Lett. 4 173

Clark CD 1965a Physical Properties of Diamond ed R Berman (Clarendon Press, Oxford) p297

Clark CD 1965b Physical Properties of Diamond ed R Berman (Clarendon Press, Oxford) p303

Clark CD, Ditchburn RW and Dyer HB 1956a Proc. R. Soc. Lond. A234 363

Clark CD, Ditchburn RW and Dyer HB 1956b Proc. R. Soc. Lond. A237 75

Clark CD, Kemmey P and Mitchell EWJ 1961 Disc. Faraday Soc. 31 96

Clark CD and Mitchell EWJ 1971 Radiation Effects 9 219

Clark CD and Norris CA 1970 J. Phys. C: Solid State Phys. 3 651

Clark CD and Norris CA 1971 J. Phys. C: Solid State Phys. 4 2223

Clark CD and Walker J 1971 Diamond Conference, Cambridge (unpublished)

Clark CD and Walker J 1972 Diamond Research 1972 (Industrial Diamond Information Bureau, London) p2

Clark CD and Walker J 1973 Proc. R. Soc. Lond. A334 241

Clement JR, Dolocek RL and Logan JK 1956 Advances in Cyrogenic Engineering 2 (Plenum, New York) quoted by Rose-Innes AC Low Temperature Techniques (English Universities Press, London) p110

Author Farrer R G
Name of thesis Electronic conduction phenomena in various kinds of diamond 1975

PUBLISHER:
University of the Witwatersrand, Johannesburg
©2013

LEGAL NOTICES:

Copyright Notice: All materials on the University of the Witwatersrand, Johannesburg Library website are protected by South African copyright law and may not be distributed, transmitted, displayed, or otherwise published in any format, without the prior written permission of the copyright owner.

Disclaimer and Terms of Use: Provided that you maintain all copyright and other notices contained therein, you may download material (one machine readable copy and one print copy per page) for your personal and/or educational non-commercial use only.

The University of the Witwatersrand, Johannesburg, is not responsible for any errors or omissions and excludes any and all liability for any errors in or omissions from the information on the Library website.