

## The effect of high-pressure–high-temperature annealing on paramagnetic defects in diamond

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S2941

(<http://iopscience.iop.org/0953-8984/15/39/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 15:16

Please note that [terms and conditions apply](#).

# The effect of high-pressure–high-temperature annealing on paramagnetic defects in diamond

R N Pereira<sup>1,2,4</sup>, W Gehlhoff<sup>2</sup>, A J Neves<sup>1</sup>, N A Sobolev<sup>1</sup>, L Rino<sup>1</sup> and H Kanda<sup>3</sup>

<sup>1</sup> Department of Physics, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>2</sup> Institute of Solid State Physics, TU-Berlin, D-10623, Germany

<sup>3</sup> National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Japan

Received 30 July 2003

Published 19 September 2003

Online at [stacks.iop.org/JPhysCM/15/S2941](http://stacks.iop.org/JPhysCM/15/S2941)

## Abstract

The formation and annealing out of paramagnetic defects in high-pressure and high-temperature diamond are investigated through a comprehensive heat treatment study of as-grown crystals. Diamond crystals are subjected to a sequence of isochronal anneals in the temperature range between 1550 and 2000 °C and the concentrations of paramagnetic defects are determined by electron paramagnetic resonance measurements after each annealing step. The quantitative data are analysed in the light of recently published results on the behaviour of nickel and/or nitrogen defects upon annealing. Like the P1 and W8 centres, the NIRIM1 nickel-related defects show a strong decrease in their concentration upon annealing at 1900 °C, whereas the NIRIM2 centres seem to be rather stable. The evolution of the nickel-related centre concentration through the annealing sequence shows that not all W8 defects transform into paramagnetic nickel–nitrogen complexes. Indeed, most of the W8 defects are transformed in other non-paramagnetic centres, with the AB1, AB3, and AB6 defects being probably by-products of this process. The relatively low concentration of nickel–nitrogen paramagnetic complexes formed upon annealing shows that their formation does not play any fundamental role in the kinetics of the nitrogen aggregation during heat treatments.

## 1. Introduction

Diamond has attracted science and technology researchers worldwide due to its unique properties. The combination of extreme properties such as high hardness, high thermal conductivity, and optical transparency makes diamond particularly well suited for applications demanding high speed, high power, and high temperature. The interest in diamond increased

<sup>4</sup> Present address: Department of Physics and Astronomy, University of Århus, Århus, Denmark.

in the last decade as a consequence of the developments in its synthesis both by high-pressure–high-temperature (HPHT) methods and by chemical vapour deposition (CVD). The identification and characterization of defects created due to either doping or accidental incorporation during the synthesis turned out to be a major field of research. Diamond, both natural and synthetic, is never free of impurities. Nitrogen is commonly the most abundant impurity in HPHT diamond synthesized without nitrogen getters, such as Ti and/or Zr. In as-grown samples nitrogen is mainly incorporated at isolated substitutional sites both in the neutral  $N_S^0$  (the P1 electron paramagnetic resonance (EPR) centre [1] and the C component in infrared (IR) absorption [2]) and positively charged  $N_S^+$  states [3]. Above 1500 °C nitrogen becomes mobile and heating of nitrogen-rich samples causes the formation of substitutional nearest-neighbour pairs  $N_S-N_S$  (A centres).

Transition elements of the 3d group, namely Ni, Co, or Fe and their alloys, are used as solvents/catalysts for the synthesis of HPHT diamond. A small proportion of these atoms are introduced into the crystal during the growth process and cause the numerous point defects that are detected optically [4] and by means of EPR [5]. At the present time the study of the role of transition metal-related defects in diamond is one of the most active areas of research concerning point defects in diamond [6]. Until now, only the 3d elements nickel [7] and cobalt [8] have been unambiguously identified as constituents of impurity defects. In HPHT diamonds grown from nickel-containing solvents/catalysts, nickel forms the well-known isolated substitutional negatively charged centre  $Ni_S^-$  with electron spin  $S = 3/2$  (W8 EPR signal at  $g = 2.0319$ ) [7, 9]. Some other nickel-related centres give rise to the NE1–NE8 [10], AB1–AB7 [11–13], NIRIM1 and NIRIM2 [14] EPR spectra in as-grown and/or annealed HPHT diamonds.

In the present paper a quantitative investigation of the annealing behaviour of nickel- and/or nitrogen-related paramagnetic defects in HPHT diamond is given for the first time. Preliminary results of a qualitative study are published in [15]. In order to investigate the formation and annealing out of the various centres, sequences of isochronal heat treatments was carried out on crystals grown from nickel-containing solvents/catalysts. The experimental data obtained by EPR and IR absorption spectroscopy are analysed considering the recently published results on the annealing behaviour of nitrogen and nickel defects in diamond. The role of AB nickel-related defects in the aggregation kinetics of nitrogen during high-temperature annealing and their relation with the nickel–nitrogen complexes are discussed.

## 2. Previous annealing studies of Ni-related centres

The nickel-related defects have a complex behaviour upon high-temperature annealing. The transformations of the nickel-related features have been studied by means of optical absorption [16] and photoluminescence (PL) [17]. The annealing of nitrogen- and nickel-containing samples at temperatures in excess of 1600 °C results in the growth of a complex absorption structure in the visible region at the expense of the optical transitions at 1.883 and 2.51 eV, measured for as-grown crystals with high nitrogen content. Most of the new lines exhibit a transitory behaviour upon annealing at increasing temperatures and only a few of them are present after annealing at temperatures higher than 1900 °C [16]. However, the optical transitions at 1.40 eV, typically observed by PL and absorption spectroscopy in HPHT diamonds with low nitrogen concentration, turned out to be rather stable against annealing at temperatures higher than 2000 °C [17]. In the PL spectra of annealed nickel- and nitrogen-containing diamonds, the S3, S2, and 2.369 eV systems dominate [17–19]. Additionally, PL bands with ZPLs at 1.413, 1.563, 1.648, 1.660, 1.704, 1.940, 1.991, and 2.071 eV are also produced through the annealing of such diamonds [17]. Among these systems only the S2, S3,

1.563, and 1.648 eV persist after annealing at temperatures  $T_a > 2000$  °C. It is widely accepted that the emerging features are due to the formation of nickel–nitrogen complexes [16, 17, 19]. An annealing study of nitrogen-containing diamonds grown in the presence of cobalt gives some evidence that nitrogen forms optically active complexes with cobalt in a similar way to with nickel [20]. The formation of nickel–nitrogen complexes is strongly suggested by the EPR studies of Nadolinny and co-workers on annealed HPHT crystals [10]. They observed a group of spin-half defects, namely NE1–NE3, NE5, and NE8 (assigned here as NE defects), with EPR spectra showing a multi-line structure due to the interaction of the unpaired electron with up to four nitrogen atoms. The observed deviations of the  $g$ -values from the free electron value  $g_e$  strongly suggest that they contain nickel. The S3, S2, and 2.369 eV vibronic systems have been tentatively correlated with the NE1, NE2, and NE3 paramagnetic centres, respectively [17, 18]. The authors think that all these centres are formed upon annealing through the capture of mobile nitrogen atoms by the NE4 centre. This defect is considered as the common fragment of the nickel–nitrogen complexes NE1–NE3, NE5, and NE8, which differ only in the number and in the positions of the nitrogen atoms in the coordination shell of nickel. They assume that during the early stages of heat treatments the NE4 defect is formed through the release of a self-interstitial by a substitutional  $\text{Ni}^-$ . In this process the nickel ion becomes positioned in the centre of two semi-vacancies, yielding a defect with  $D_{3d}$  point symmetry. The model for this centre has not been unambiguously established yet. Very recently, it was shown that the NE4 EPR spectrum was described with faulty  $g$ -values and corresponds in fact to the spectrum of the AB1 defect [21].

The incorporation of solvent metal atoms during the growth of HPHT samples affects the process of nitrogen aggregation upon high-temperature heat treatments [22, 23]. Topographic IR absorption measurements of diamonds grown from a nickel solvent system have shown a Ni-induced enhancement of the nitrogen aggregation [24]. The nickel concentration was estimated in this study by the concentration of the positively charged nitrogen defect determined through the absorption coefficient of the sharp peak at  $1332\text{ cm}^{-1}$  [10]. This seems to be justified because in such samples the position of the Fermi level is determined by the high nitrogen concentration, and recharging of a neutral nitrogen centre is mainly due to the transfer of its unpaired electron to nickel. In contradiction to previously published results [22, 23], it was found that the conversion of  $N_S$  defects into A aggregates does not follow second-order kinetics [24]. Fisher and Lawson observed a similar deviation from simple second-order kinetics for Ni- and Co-catalysed HPHT diamonds [25]. Several reasons for the observed deviation were discussed:

- (a) the nitrogen migration rate depends on the nitrogen charge state;
- (b) nitrogen forms A defects as well as nickel–nitrogen complexes; or
- (c) the nitrogen migration is assisted by vacancies and/or carbon interstitials generated by nickel impurities [24].

Theoretical modelling suggests mechanisms that involve both vacancies and carbon interstitials [24]. The observation of the W15 and W33 vacancy-containing paramagnetic centres in annealed diamonds grown from nickel and cobalt solvents is considered as an indication of the generation of vacancies during the heat treatments [26]. Other authors suggested that the interstitial-assisted aggregation process might be more effective than the vacancy-assisted mechanism [24, 25]. This is supported by the optical detection of the  $1450\text{ cm}^{-1}$  absorption peak related to interstitial nitrogen in intermediate annealing stages [27]. Nickel being larger than carbon may be a centre of generation of carbon interstitials, which create nitrogen interstitials by exchanging places with substitutional nitrogen. Interstitial nitrogen is more mobile than substitutional nitrogen, so the aggregation rate is increased.

### 3. Experimental details

The crystals used in this work were synthesized at NIRIM (Japan) by the temperature gradient method at  $\approx 6$  GPa and temperatures of about 1450 °C using Ni-containing solvents/catalysts. In order to monitor the formation of the nickel-related defects, we selected two crystals with different nickel concentrations. The latter is quantified by the as-grown concentration of W8 centres measured by means of EPR. The crystals do not exhibit any sign of pre-annealing during growth since we did not detect other nickel-related EPR lines, which are known to appear for annealed crystals. The diamonds were grown using the alloys Ni–2 wt% Ti (sample A) and Ni–20 wt% Fe (sample B) as solvents/catalysts. These samples were subjected to an isochronal annealing sequence in the temperature range between 1550 and 2000 °C. Heat treatments were carried out for 4 h using the same apparatus as was used for growing the crystals. EPR spectra were measured after each annealing step at suitable temperatures in the range from 4.2 to 100 K, depending on which paramagnetic centre was detected.

EPR measurements were carried out on a Bruker ESP 300E spectrometer. This equipment was mounted with X- and Q-band microwave bridges and corresponding cylindrical TE<sub>011</sub> microwave resonators. For measuring EPR at low temperatures we used a helium gas-flow cryostat for the X-band and a helium bath cryostat for the Q-band. Samples were oriented with respect to the external magnetic field  $B$  by using either the {111} and {100} growth facets or faces polished parallel to the main crystallographic planes. In order to guarantee thermal equilibrium in the occupation of the different defect states the samples were cooled down slowly in the dark and EPR measurements performed also keeping the crystals in the dark.

IR absorption spectra from the as-grown samples and after each anneal were also measured, so that the concentrations of the substitutional nitrogen defects N<sup>0</sup> could be determined throughout the annealing sequence. IR spectra were obtained with a Bruker IFS66V Fourier-transform spectrometer at room temperature. This system is equipped with a KBr beam splitter, a Globar as light source and a DTGS detector. All spectra were recorded at room temperature. The intensities of the spectra were calibrated through the absorption value at 2000 cm<sup>-1</sup>, which is known to be 12.3 cm<sup>-1</sup> for all diamonds [28].

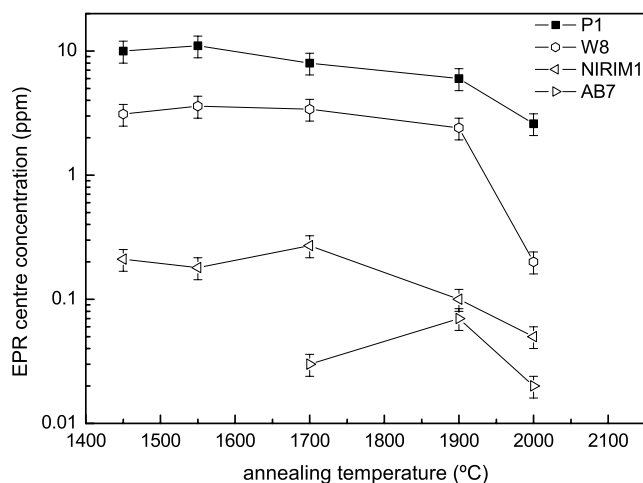
### 4. Results and discussion

Nitrogen present in diamond induces absorption in the one-phonon region. The different forms of incorporated nitrogen give rise to characteristic spectra. Reconstructing the experimental IR absorption spectra as a mixture of the well-known A, B, N<sup>0</sup>, and N<sup>+</sup> components we estimate their respective concentrations using the calibration factors connecting their different IR absorption coefficients and the nitrogen concentration reviewed in [6]. Since substitutional N<sup>0</sup> centres are detectable also by means of EPR (P1 centre), concentrations measured by means of IR absorption were used for calibration in the determination of the concentrations of other paramagnetic centres.

The various paramagnetic centres, which produce overlapping EPR lines in the X- and Q-band, were identified through their complete angular dependence upon the rotation of the external magnetic field  $B$  in a {110} crystallographic plane. These line positions were calculated using the spin Hamiltonian

$$H = \beta B \cdot \mathbf{g} \cdot S + S \cdot \mathbf{D} \cdot S + S \cdot \mathbf{A} \cdot I, \quad (1)$$

with parameters given in the corresponding references. The ratio between the concentration of these centres and that of the well-known P1 centre (substitutional N<sup>0</sup>) was determined by comparing their EPR intensity. In each case the saturation behaviour of the transitions



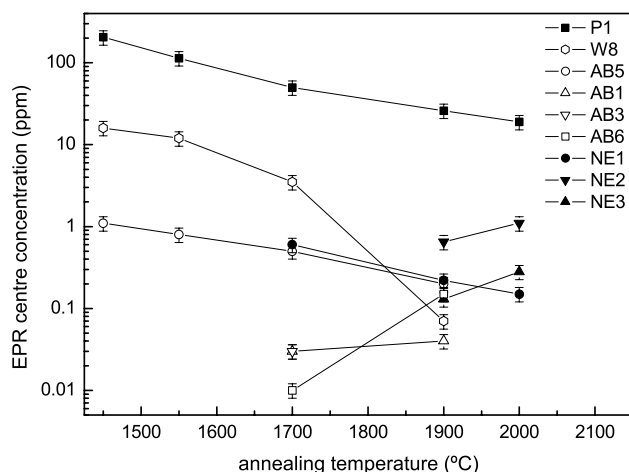
**Figure 1.** Concentrations of the paramagnetic centres measured in sample A after each annealing step of an isochronal (4 h) annealing sequence. Concentrations measured in the as-grown crystal correspond to the temperature of 1450 °C, since this is the temperature at which the crystal was grown.

was verified to avoid any errors resulting from saturation effects. Although the optimum experimental conditions for the detection of the P1 centre are different from those of the other defects, we have carefully chosen the acquisition parameters (e.g. temperature, modulation amplitude, modulation frequency, magnetic field direction) which permitted the simultaneous observation of the P1 centre and of the defects with unknown concentration. The concentration of the W8 signal was determined assuming that the line at  $g = 2.0319$  corresponds only to the transition  $M_S = -1/2 \leftrightarrow +1/2$  of an  $S = 3/2$  system with a zero-field splitting parameter  $D \approx 0$ , where the  $M_S = \pm 1/2 \leftrightarrow \pm 3/2$  transitions are broadened beyond detection [9].

#### 4.1. Annealing sequence: sample A

Prior to annealing, sample A exhibited a green colour that changed to brown upon annealing at a temperature as high as 2000 °C. It is believed that the formation of nickel–nitrogen centres during heat treatments is responsible for this colour change. In figure 1, the concentrations of the paramagnetic centres detected in sample A are plotted throughout a sequence of isochronal heat treatments at temperatures in the range 1550–2000 °C. At all annealing stages the EPR measurements of sample A show the spectra of the P1, W8, NIRIM1, and NIRIM2 centres. The concentrations of the defects P1, W8, and NIRIM1 revealed a significant decrease only after the heat treatment at 1900 °C.

In accordance with previous observations [14], we were not able to measure the NIRIM2 EPR lines in slow-passage conditions. Therefore, the determination of the concentration is hindered. However, we observed no drastic changes of the NIRIM2 intensity after each annealing step up to 2000 °C. This behaviour supports the suggestion that the NIRIM2 defect consists of a nickel atom associated with another defect producing a very stable structure. The centre was tentatively assigned as an interstitial  $\text{Ni}^+$  ion with a vacancy or impurity at a neighbouring position responsible for the defect's trigonal ( $C_{3v}$ ) crystal field [14]. It was argued that the optical transitions at 1.40 eV with zero-phonon lines at 1.401 and 1.404 eV and the NIRIM2 EPR spectrum are caused by the same centre [14, 29]. Strong evidence for this assignment was obtained by studies of the Zeeman splitting behaviour of the 1.40 eV feature through the magnetic circular dichroism of the optical absorption (MCDA) [30]. PL studies



**Figure 2.** Concentrations of the EPR centres measured in sample B throughout an isochronal (4 h) annealing sequence. Concentrations measured in the as-grown crystal correspond to the crystal temperature of growth (1450 °C).

of annealed diamonds grown at HPHT from nickel-containing systems also revealed that the 1.4 eV vibronic system is still present in the optical spectra of crystals that underwent heat treatments at temperatures as high as 2200 and 2500 °C [17].

After annealing sample A at 1700 °C, the lines related to another centre labelled AB7 appeared in the EPR spectrum. The angular dependence of the AB7 EPR lines reveals that this spectrum is produced by a paramagnetic defect with orthorhombic-I symmetry and spin  $S = 1/2$  [13]. The departures of the principal  $g$ -values from the free electron value  $g_e$  found for this centre indicate that the centre probably contains a transition metal ion as a constituent [13]. The AB7 centre exhibits a transitory behaviour: its EPR intensity increases upon annealing at 1900 °C but decreases upon heat treatment at 2000 °C. The AB7 centre is formed at early annealing stages before nitrogen shows a significant aggregation. Since vacancies and interstitials become mobile at much lower temperatures than nitrogen, the AB7 defect may be produced through the capture of mobile vacancies and/or interstitials by a nickel-related defect.

#### 4.2. Annealing sequence: sample B

The as-grown sample B exhibited the yellow colour typical of nitrogen-rich diamond. Like that of sample A, the colour of sample B changed progressively to brown as the sample was sequentially annealed. In addition to the P1 centre, the as-grown sample B showed the presence of W8 and AB5 defects. Heating this sample to 1550 °C caused a decrease of the P1 signal (see figure 2), as opposed to the case for sample A where a significant change in the P1 signal intensity was detected only after annealing at 1900 °C. A similar behaviour was observed for the W8 signal intensity. A decrease in the P1 concentration is always accompanied by a decrease in the W8 signal intensity in both samples A and B, regardless of their differences in initial nitrogen concentration. This is an indication that the main mechanism of nitrogen aggregation in such diamonds should also involve the W8 defect.

After annealing sample B at 1700 °C we were able to detect the EPR spectra of the centres AB1 [12], AB3 [12], AB6 [13], and NE1. The EPR spectra of the centres AB1, AB3, and AB6 disappear upon heat treatment at 2000 °C. Although the AB1 and AB3 lines appeared in

the EPR spectra of sample B only upon annealing at 1700 °C, we observed these lines also in some as-grown samples. Our EPR measurements on a set of HPHT samples grown with nickel reveal that the AB1 and AB3 centres are present in detectable amounts in as-grown samples that contain high concentrations of W8 centres (>40 ppm). In contrast to the AB1 and AB3 defects, the AB6 centre has never been detected in as-grown samples.

At annealing temperatures higher than 1700 °C we observed the appearance of the NE2 and NE3 spectra, as well as a slight decrease in the concentration of NE1 centres. These centres seem to be produced by aggregation of mobile nitrogen atoms to a nickel defect during the annealing of nickel-containing diamond [10]. The detection of the NE1 centre after annealing at 1700 °C supports this suggestion. Additionally, we observed that this signal decreases progressively as we anneal the sample B at increasing temperatures. Simultaneously, the NE2 and NE3 EPR lines appear upon annealing at 1900 °C and rise in intensity with the heat treatment at 2000 °C. Thus, the observed changes of the NE1 and NE2 intensity agree with the proposal that the NE1 defect gives rise to the NE2 centre by the capture of a third nitrogen atom. Regarding the NE3 defect, it is believed that this centre is generated by the aggregation of a nitrogen atom to the NE5 defect [10]. Although the NE3 centre was detected after annealing at 1900 °C, we have not measured the NE5 EPR lines at any stage of the annealing. It is likely that in this sample the NE5 centre exists in another charge state that is undetectable by means of EPR. In fact, the first detection of the NE5 paramagnetic centre was performed upon illumination of the samples [31]. Such observations indicate that the most stable charge state of this defect in this type of diamond is non-paramagnetic.

The enhancement of nitrogen aggregation in nickel-containing diamonds is proposed to be due to the generation of carbon interstitials by nickel defects [24, 25]. The proposed process occurs when a substitutional Ni<sup>-</sup> ion displaces a neighbouring carbon atom, creating a nickel–vacancy defect. The carbon interstitials formed migrate to substitutional N atoms and exchange sites, creating highly mobile N interstitials. These nitrogen atoms can then migrate to form A centres. The AB1, AB3, and AB6 defects are obvious candidates for being by-products of the transformation of the W8 centres into other more stable defects, such as the NE1–NE3 and NE5 nickel–nitrogen complexes, since we have shown that they are produced upon annealing at intermediate temperatures and anneal out at higher temperatures. Studies of the <sup>13</sup>C hyperfine structure of the NE1–NE3 and NE5 centres show that their common structure is a nickel ion positioned in the centre of a double semi-vacancy (NiVC<sub>6</sub>) [10]. Moreover, it is proposed that the AB1/NE4 trigonal centre is a paramagnetic charge state of the NiVC<sub>6</sub> defect [10, 21]. Such assignment is supported here due to the detection of the AB1 EPR spectrum in the annealing sequence prior to the nickel–nitrogen defects and due to the observation that it anneals out at temperatures where the concentration of NE2 and NE3 centres increases. Further, we believe that such NiVC<sub>6</sub> structure can exist in more than one charge state, which may not be obliged to have a non-zero spin.

Another proposed mechanism for the increase of the formation rate of nitrogen pairs is based on the release of vacancies from a nickel-related complex. These vacancies would be trapped by nitrogen and in this way would assist in the migration of nitrogen [24, 26]. In contrast to previous observations of Nadolinny *et al* [26], our studies did not detect any EPR signal of the W15 and W33 vacancy-related centres through the annealing of both samples A and B.

The annealing data summarized in figures 1 and 2 provide evidence that the decrease in the concentration of W8 defects is not accompanied by an equal increase of the concentration of the nickel–nitrogen defects NE1, NE2, and NE3. There is a large discrepancy between the as-grown concentration of W8 centres and the sum of the concentrations of the NE2 and NE3 defects measured after annealing at 2000 °C. The concentrations of the different centres



determined clearly prove that not all W8 centres transform into the established paramagnetic NE centres as has been proposed [10]. Obviously, most of the substitutional  $\text{Ni}^-$  defects generate other centres that are non-paramagnetic or were not detected by means of EPR up to now. These may be NE defects in another charge state or defects with other structures. Alternatively, the strong decrease of the  $\text{Ni}^-$  centre concentration may be due to a shift of the Fermi level, which converts some  $\text{Ni}_5^-$  into  $\text{Ni}_5^0$  that has not been observed by means of EPR.

The EPR signal of the AB5 centre in sample B decreases throughout the annealing sequence and disappears upon heat treatment at 2000 °C. This centre was detected in all as-grown samples synthesized without the addition of nitrogen getters to the nickel-containing solvent/catalyst. A model consisting of a nickel–nitrogen pair in the negative charge state was proposed for its structure [11]. For such a defect structure we expect that during annealing it will behave similarly to the one proposed for the single-substitutional  $\text{Ni}^-$  defect [10]. Hence, nickel would release one of its four nearest neighbours, possibly the nitrogen atom, forming a defect with the same structure as that suggested for the AB1/NE4 centre. The creation of nitrogen interstitials in this process would also contribute to the enhancement of the A centre formation rate.

The reason for the deviation from second-order kinetics observed in the aggregation of nitrogen upon annealing of nickel-containing diamond at high temperature is still unknown. Among the proposed explanations, one is based on the possibility that in such samples nitrogen is also being trapped by nickel defects [25]. This would lead to the formation of nickel–nitrogen complexes, along with the A aggregates. However, in comparison to the initial concentration of substitutional  $\text{N}^0$  defects, the concentration of nickel–nitrogen centres, which involve two or three nitrogen atoms, produced upon annealing is not significant (see figure 2). Therefore, it is unlikely that the formation of the well-known paramagnetic nickel–nitrogen complexes plays a fundamental role in the kinetics of the nitrogen aggregation.

## 5. Conclusions

The formation and annealing out of EPR defects in HPHT diamond were comprehensively investigated through an annealing study. It is found that substitutional  $\text{N}^0$  and  $\text{Ni}^-$  defects show similar behaviours when diamond samples are subjected to high-temperature heat treatments. NIRIM1 defects reveal a significant decrease in concentration upon annealing at temperatures higher than 1900 °C, whereas the NIRIM2 EPR spectrum is shown to be rather insensitive to the heat treatments. Unlike the NIRIM1 centre, the NIRIM2 defect seems to correspond to a rather stable configuration of nickel in the diamond lattice.

The detection of the NE1, NE2, and NE3 paramagnetic defects after annealing of a HPHT diamond with high nitrogen content agrees with the observations [10] that these nickel–nitrogen complexes are produced upon annealing of such crystals.

The concentration of nickel-related defects measured throughout the annealing sequence shows that not all W8 defects transform into the NE1–NE3 and NE5 defects, with the subsequent generation of carbon interstitials. In fact, most of the substitutional nickel is transformed into other defects that are non-paramagnetic or have not yet been detected by means of EPR. The behaviour of the concentration of the AB1, AB3, and AB6 centres suggests that these defects are by-products of the creation of carbon interstitials by as-grown nickel defects (e.g., the W8 centre), which is supposed to enhance the nitrogen aggregation. The assignment of the AB1/NE4 EPR centre to the  $\text{NiVC}_6$  model is supported due to the detection of its EPR spectrum at intermediate annealing stages.

The AB5 centres occur in as-grown HPHT diamonds rich in nitrogen and their concentration is decreased upon heat treatments. A mechanism similar to that proposed

previously to explain the behaviour of the substitutional Ni<sup>-</sup> defects upon annealing [10] explains the decrease of the concentration of AB5 centres upon heat treatments.

It is shown that the formation of nickel–nitrogen paramagnetic defects during high-temperature heat treatments of HPHT diamond cannot be responsible for the deviation of the nitrogen aggregation from the second-order kinetics.

### Acknowledgments

The work was supported in part by ‘Acções Integradas Luso-Alemãs’, Project No A-13/99. RNP acknowledges the financial support from ‘Fundação para a Ciência e a Tecnologia’ under contract PRAXIS XXI/BD/18405/98.

### References

- [1] Smith W V, Sorokin P P, Gelles I L and Lasher G J 1959 *Phys. Rev.* **115** 1546
- [2] Kiflawi I, Mayer A E, Spear P M, van Wyk J A and Woods G S 1994 *Phil. Mag.* **B 69** 1141
- [3] Lawson S C, Fisher D, Hunt D C and Newton M E 1998 *J. Phys.: Condens. Matter* **10** 6171
- [4] Zaitsev A M 2001 *Optical Properties of Diamond: a Data Handbook* (Berlin: Springer)
- [5] Ammerlaan C A J 2002 *Numerical Data and Functional Relationships in Science and Technology (Landolt–Börnstein New Series Group III, vol 41)* ed O Madelung, U Rössler and M Schulz (Berlin: Springer)
- [6] Davies G 1999 *Physica B* **273/274** 15
- [7] Samoilovich M I, Bezrukov G N and Butuzov V P 1971 *JETP Lett.* **14** 379
- [8] Twitchen D J, Baker J M, Newton M E and Johnston K 2000 *Phys. Rev. B* **61** 9
- [9] Isoya J, Kanda H, Norris J R, Tang J and Bowman M R 1990 *Phys. Rev. B* **41** 3905
- [10] Nadolinny V A, Yelisseyev A P, Baker J M, Newton M E, Twitchen D J, Lawson S C, Yuryeva O P and Feigelson B N 1999 *J. Phys.: Condens. Matter* **11** 7357
- [11] Neves A J, Pereira R, Sobolev N A, Nazaré M H, Gehlhoff W, Naeser A and Kanda H 2000 *Diamond Relat. Mater.* **9** 1057
- [12] Neves A J, Pereira R, Sobolev N A, Nazaré M H, Gehlhoff W, Naeser A and Kanda H 1999 *Physica B* **273/274** 651
- [13] Pereira R N, Gehlhoff W, Neves A J, Sobolev N A and Kanda H 2003 at press
- [14] Isoya J, Kanda H and Uchida Y 1990 *Phys. Rev. B* **42** 9843
- [15] Pereira R N, Neves A J, Gehlhoff W, Sobolev N A, Rino L and Kanda H 2002 *Diamond Relat. Mater.* **11** 623
- [16] Lawson S C and Kanda H 1993 *J. Appl. Phys.* **73** 3967
- [17] Kupriyanov I N, Gusev V A, Borzdov Yu M, Kalinin A A and Pal’yanov Yu N 1999 *Diamond Relat. Mater.* **8** 1301
- [18] Nadolinny V A and Yelisseyev A P 1993 *Diamond Relat. Mater.* **3** 17
- [19] Yelisseyev A P and Nadolinny V A 1995 *Diamond Relat. Mater.* **4** 177
- [20] Lawson S C and Kanda H 1996 *J. Appl. Phys.* **79** 4348
- [21] Gehlhoff W and Pereira R N 2002 *J. Phys.: Condens. Matter* **14** 13751
- [22] Satoh S and Sumiya H 1995 *High Pressure Research in Solids* ed M Senoo, K Suito, T Kayabashi and H Kubota (Japan: Elsevier Science and The Society of Material Science)
- [23] Kiflawi I, Kanda H, Lawson S C and Fisher D 1997 *Diamond Relat. Mater.* **6** 1649
- [24] Kiflawi I, Kanda H and Mainwood A 1998 *Diamond Relat. Mater.* **7** 327
- [25] Fisher D and Lawson S C 1998 *Diamond Relat. Mater.* **7** 299
- [26] Nadolinny V A, Yelisseyev A P, Baker J M, Twitchen D J, Newton M E, Feigelson B N and Yuryeva O P 2000 *Diamond Relat. Mater.* **9** 883
- [27] Kiflawi I, Mainwood A, Kanda H and Fisher D 1996 *Phys. Rev. B* **54** 16719
- [28] Davies G 1977 *Chemistry and Physics of Carbon* vol 13, ed P W Philips and P A Turner (New York: Dekker)
- [29] Nazaré M H, Neves A J and Davies G 1991 *Phys. Rev. B* **43** 14196
- [30] Mason P W, Ham F S and Watkins G D 1999 *Phys. Rev. B* **60** 5417
- [31] Nadolinny V A and Yelisseyev A P 1994 *Diamond Relat. Mater.* **3** 1196