'Natural' and 'man-made' platelets in type-Ia diamonds

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Abstract

'Natural' platelets are planar defects in {001} planes found in natural type-IaA/B diamonds. 'Man-made' platelets are platelets formed in the laboratory by annealing type-IaA diamonds at temperatures over 2500°C. Careful study shows that the infrared (IR) spectra of the 'man-made' platelets are different from the IR spectra of 'natural' platelets. High-temperature (T ≥ 2000°C) annealing of platelets containing type-IaA/B diamonds modifies the IR absorption spectrum owing to the 'natural' platelets and makes it similar to the IR spectrum of the 'man-made' platelets. It is suggested that such high-temperature annealing changes the structure of the 'natural' platelets. The changes are too subtle to be detected by electron microscopy techniques. Topographic electron-energy-loss spectroscopy shows that platelets contain nitrogen at an average density of 0.7 atoms per a02; however, high-temperature annealing does not seem to affect the concentration of the nitrogen in the platelets.

§1. Introduction

Type-Ia diamonds contain small aggregates of nitrogen; in type IaA the nitrogen is aggregated in pairs at adjacent substitutional sites, A centres (Davies 1976, Jones et al. 1992, Mainwood 1994), while type-IaB diamonds contain B centres, which are four neighbouring nitrogen atoms and a vacancy (Loubser and van Wyk 1981, Jones et al. 1992, Mainwood 1994). Most natural diamonds, however, are type IaA/B which contain both A and B centres. Diamonds containing nitrogen in its different forms of aggregation have characteristic infrared (IR) absorption; the different shapes of the spectra of such diamonds can be found in a review article by Evans (1992).

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Type-IaA/B and some of type-IaB diamonds contain planar defects, or platelets, in {001} planes. Platelets also introduce characteristic IR absorption, namely a lattice mode, the D band (Clark and Davey 1984, Woods 1986), a low-frequency mode at 328 cm\(^{-1}\) (Sobolev et al. 1969, Woods 1989), which was attributed by Woods (1989) to a bending vibration of atomic bonds in the platelets, and by Bridgen et al. (1991) to a N–C vibration of atoms in the platelets and local modes with a major peak, the B'–platelet peak, found at various positions between 1359 and 1375 cm\(^{-1}\), and a smaller peak at 1430 cm\(^{-1}\). Evans et al. (1995) demonstrated by comparing the results of IR spectroscopy, X-ray diffraction and transmission electron microscopy (TEM) that these IR features are caused by the platelets.

Various pieces of information about the platelets can be obtained from studying the B' peak. The position of the B' peak depends on the size of the platelets, a higher energy corresponding to smaller platelets (Sobolev et al. 1968, Clackson et al. 1990). The integrated intensity of the peak gives a measure of the area of the platelets per unit volume (Sumida and Lang 1988). The symmetry of the B' peak varies according to its energy; higher-energy peaks (smaller platelets) are less symmetrical (Woods 1986). Woods (1986) also found that in most type-IaA/B diamonds, termed regular, there is a correlation between the intensity of the B' peak and the absorption due to the B centres. On the basis of this fact, he suggested a mechanism by which platelets are formed by the precipitation of the C atoms released when A centres aggregate to form B centres. Platelets can be formed in the laboratory by annealing type-IaA diamonds at temperatures over 2500°C (Evans and Qi 1982). Annealing these diamonds at such temperatures cause the A centres to aggregate to form B centres and platelets. We shall refer to platelets formed by this process as 'man-made' platelets.

Woods et al. (1993) studied the change in the position of the B' peak by changing the nitrogen and the carbon isotopes. They found no change in the peak position when\(^{15}\)N replaced \(^{14}\)N and concluded that nitrogen is not involved in producing this absorption. Recent electron–energy-loss spectroscopy (EELS) results (Bruley 1992, Fallon et al. 1995) gave evidence that the platelets do contain a certain amount of nitrogen. They also found that the concentration of nitrogen in the 'man-made' platelets is about one third of that of the natural platelets. The question remains whether this nitrogen is part of the structure of the platelets, whether it is there as an impurity, or whether it is only decorating the periphery of the platelets. Also, can high-temperature annealing introduce changes in the structure and the nitrogen content of the 'natural' platelets, making them similar to the 'man-made' platelets.

This work reports the results of a more detailed study of the formation and the characteristics of 'man-made' platelets produced by annealing type-IaA diamonds, and the effect of high-temperature treatment on the 'natural' platelets found in type-IaA/B diamonds. IR spectroscopy, TEM and EELS studies of platelets in their natural state and after annealing will be presented.

§2. EXPERIMENTAL DETAILS

To produce 'man-made' platelets, natural type-IaA diamonds were annealed at temperatures around 2650°C under a stabilizing pressure of 9–10 GPa, using the set-up described by Evans and Qi (1982). All the temperatures quoted in this work are accurate to within ±100°C or −50°C. (The measured temperature at the thermocouple is accurate to within ±50°C; however, since the thermocouple is an escape route for heat, the actual temperature of the specimen depends also on its distance from the tip of the thermocouple and can be higher by about another 50°C, and
therefore the temperature of the specimen is known to within +100°C or -50°C.) To study the effect of annealing on 'natural' platelets, natural type-IaA/B diamonds containing platelets were annealed at temperatures between 1900 and 2650°C. The values of the IR absorption before and after treatment were measured at room temperature using a Nicolet 5PC Fourier transform IR spectrometer at a resolution of 2 cm\(^{-1}\). The spectra at energies below 400 cm\(^{-1}\) were taken using a Perkin-Elmer PE580B spectrometer. The amounts of nitrogen in A and B centres were determined by decomposing the IR spectra in the one-phonon region, establishing the absorption coefficient at 1282 cm\(^{-1}\) caused by the A and B centres, and using the conversion factors of 16.5 atm ppm cm for the A centres and 80 atm ppm cm for the B centres (Boyd et al. 1994, 1995). Since specimens have to be thinned for TEM and EELS studies, it is not possible to study the effect of annealing on the same specimen. Therefore, pairs of specimens cut from the same diamonds and having virtually the same initial IR absorption were used. One slice from each pair was heat treated and the other slice was kept as a control. Both specimens were then polished to a thickness of 0.1 mm and their IR spectra re-examined for inhomogeneity. All specimens were then ion beam thinned until holes appeared. Three pairs of treated as well as untreated type-IaA/B diamonds were examined using TEM and EELS. Electron microscopy measurements were done using a JEOL 4000 EX electron microscope operating at 400 kV and a Philips CM20 operating at 200 kV.

EELS was used to compare the nitrogen contents of the platelets in the annealed specimens and the unannealed control. For these measurements, the specimens were examined in a VG Microscopes' model HB501 dedicated field emission gun scanning transmission electron microscope fitted with a Gatan model 666 parallel electron-energy-loss spectrometer. The microscope was operated at 100 keV using standard condenser lens conditions to optimize the current density incident on the sample. The probe diameter is assumed to be 1 nm and the electron beam about 0.5 nA.

Platelets were viewed edge on along either [100] or [110] directions. In regions thin enough for the platelet to cross the specimen thickness completely, the platelet is visible through phase contrast. Using the annular dark-field detector, necessary for EELS data collection, the image contrast is barely visible. The strategy adopted therefore is first to identify a platelet using the bright-field phase-contrast detector. Then the EELS experiment is carried out, after which the bright-field detector is reinserted to monitor the specimen drift.

Two types of experiment were performed. The first involved acquiring the spectra whilst the beam is simultaneously scanning across a small rectangular area by the line of the edge-on oriented platelet. Although this method compromises the optimum detection sensitivity, it does ensure that the platelet area is fully sampled through the specimen thickness. If one used a stationary probe, a slightly misplaced trajectory of the electron path or a tilted platelet would lead to a significant underestimation of the nitrogen content. The second experiment involved a line scan perpendicular to the platelet plane which also samples the full area of the platelet. In this case the beam is stepped digitally across the region of interest (the beam position is under computer control using Gatan's Digiscan system) and a spectrum is recorded at each pixel. The resultant spectrum-line profile data set is processed using MATLAB (Mathworks, Inc.). The total nitrogen in the platelet plane is given by the integrated nitrogen intensity over the profile. In the subsequent data analysis it is assumed that the platelet completely transects the specimen thickness. If this is not the case, the derived nitrogen density on the platelet plane is underestimated.
3.1. Annealing of type-IaA diamonds

Eight pure type-IaA specimens were annealed at a temperature of 2650°C. Annealing such a specimen, having initially 1100 ppm N in A centres, for 9 h caused about 80% of the A centres to aggregate into B centres and the accompanying formation of platelets (figure 1(a)). Although the results, as far as the production of B centres and platelets are concerned, are similar to those observed by Evans and

![Graph](image)

Figure 1. (a) The spectrum of a type-IaA/B diamond obtained after annealing a pure type-IaA diamond at 2650°C for 9 h, showing the formation of the B centres and the platelets. (b) The local-mode region of the spectrum of (a) before (---) and after (-----) annealing, showing the appearance, after annealing, of the new bands at 1488 cm⁻¹ and 1425 cm⁻¹ and the single nitrogen peak at 1344 cm⁻¹. The peak at 1405 cm⁻¹ is due to hydrogen.
Qi (1982), we would like to report the results of a more detailed study of the local modes associated with the 'man-made' platelets. Figure 1(b) shows the local mode region of the spectra before and after annealing. The main features are the appearance of a new additional broad local band at 1488 ± 3 cm⁻¹, a band at 1425 ± 3 cm⁻¹ which is thought to be the equivalent to the 1430 cm⁻¹ peak associated with 'natural' platelets and the introduction of the local mode at 1344 cm⁻¹ due to single substitutional nitrogen atoms, caused by the breaking up of some of the A centres (Evans and Rainey 1975). The peak at 1405 cm⁻¹, seen in figure 1(b), is due to hydrogen in the diamond and is not associated with the platelets. An indication that these new peaks are caused by the platelets was obtained by examining their position in two ¹³C diamonds. All the peaks, including the B' peak, were shifted by a factor of 0.98. This is the same factor found by Woods et al. (1993) for the shift in the B' peak for ¹³C diamonds. Also we could not form these peaks by annealing pure type-IaB diamonds that do not contain platelets.

The shape of the B' platelet peaks produced by annealing these type-IaA diamonds is broader than the B' peaks associated with 'natural' platelets; for example the width at half-height of a B' peak with an integrated intensity of 480 cm⁻² produced by 'man-made' platelets is 29 cm⁻¹ compared with 19 cm⁻¹ for a peak with the same integrated intensity and similar position produced by 'natural' platelets. Since the position of the B' peak depends on the size of the platelets, broadening can be caused if the 'man-made' platelets have a wide range of sizes. Figure 2 shows a TEM image of a typical region showing the platelets formed in a type-IaA diamond.

Figure 2. A dark-field electron micrograph of 'man-made' platelets. The incident electron beam was parallel to the (001) direction. The width of the image is 1.5 μm.
annealed at 2650°C for 3.5 h, producing a B' platelet peak at 1363 cm⁻¹, having an absorption coefficient of 12.5 cm⁻¹ and width at half-height of 33 cm⁻¹. The size of the platelets is fairly uniform at about 300 ± 45 Å. We would like to mention that the relationship between the position of the B' peak and the size of the platelets follows the same relationship found by Clackson et al. (1990) for 'natural' platelets.

The B' peak positions of the man-made platelets varied between 1370 and 1362 cm⁻¹. Successive annealing of the same specimen at the same temperature caused the B' peak to shift towards lower energies, showing an increase in the size of the platelets. In all cases the peak was symmetrical irrespective of the size of the platelets. As in the case of the regular natural diamonds, a correlation was found between the integrated intensity of the B' peak produced by the treatment and the B absorption at 1282 cm⁻¹, the solid line shown in figure 3. The broken line in figure 3 is the relationship found by Woods (1986) for regular natural diamonds.

3.2. Annealing of type-IaA/B diamonds

3.2.1. Results of infrared spectroscopy

Annealing between 2000–2350 and 2650°C produced changes in the IR absorption due to platelets; these changes are summarized in table 1.

3.2.1.1. The B' peak and associated higher-energy peaks. In all the treatments the height of the peak was reduced while the width at half-height increased (figure 4). Also, in all cases the peak becomes more symmetrical (last column of table 1).
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Temperature* (°C)</th>
<th>Time (h)</th>
<th>Absorption coefficient (cm⁻¹) ±0.2 cm⁻¹</th>
<th>Position (cm⁻¹) ±0.2 cm⁻¹</th>
<th>Area (cm⁻¹) ±3%</th>
<th>A (cm⁻¹) ±0.5 cm⁻¹</th>
<th>B (cm⁻¹) ±0.5 cm⁻¹</th>
<th>D (cm⁻¹) ±0.5 cm⁻¹</th>
<th>B' symmetry* (±0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P47</td>
<td>T₁: 1900</td>
<td>6</td>
<td>22.2</td>
<td>1365.5</td>
<td>354</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>T₂: 2100</td>
<td>4</td>
<td>22.1</td>
<td>1366.4</td>
<td>350</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>1.52</td>
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<tr>
<td>KW6</td>
<td>T₁: 2300</td>
<td>1</td>
<td>26.6</td>
<td>1370.2</td>
<td>700</td>
<td>35</td>
<td>14.2</td>
<td>5.2</td>
<td>1.27</td>
</tr>
<tr>
<td>P25</td>
<td>T₁: 2300</td>
<td>3</td>
<td>19.5</td>
<td>1373.0</td>
<td>730</td>
<td>35.2</td>
<td>14.0</td>
<td>5.5</td>
<td>1.0</td>
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<td>20</td>
<td>1368</td>
<td>350</td>
<td>14.5</td>
<td>7</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
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<td>3</td>
<td>20</td>
<td>1369</td>
<td>330</td>
<td>14.7</td>
<td>6.9</td>
<td>2.7</td>
<td>1.0</td>
</tr>
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<td>KW5</td>
<td>T₁: 2000</td>
<td>2</td>
<td>31.2</td>
<td>1370.3</td>
<td>595</td>
<td>38.9</td>
<td>11.0</td>
<td>3.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>T₂: 2350</td>
<td>2</td>
<td>17.3</td>
<td>1371.4</td>
<td>599</td>
<td>37.4</td>
<td>11.5</td>
<td>3.7</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
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<td>2</td>
<td>27.9</td>
<td>1370.0</td>
<td>566</td>
<td>28.8</td>
<td>10.7</td>
<td>4.1</td>
<td>1.80</td>
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<tr>
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<td>15.9</td>
<td>1371.7</td>
<td>545</td>
<td>28.0</td>
<td>10.1</td>
<td>3.4</td>
<td>1.08</td>
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<td>2.75</td>
<td>29.4</td>
<td>1370.6</td>
<td>573</td>
<td>35.8</td>
<td>11.2</td>
<td>4.4</td>
<td>1.09</td>
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<td>17.9</td>
<td>1368.7</td>
<td>625</td>
<td>23.6</td>
<td>13.7</td>
<td>3.6</td>
<td>1.5</td>
</tr>
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<td>T₁: 2650</td>
<td>3</td>
<td>23.3</td>
<td>1365.7</td>
<td>440</td>
<td>12.9</td>
<td>8</td>
<td>3</td>
<td>1.35</td>
</tr>
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<td>P67</td>
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<td>0.6</td>
<td>23</td>
<td>1364.4</td>
<td>205</td>
<td>18</td>
<td>5.5</td>
<td>2.0</td>
<td>1.00</td>
</tr>
<tr>
<td>B9-2</td>
<td>T₁: 2650</td>
<td>2</td>
<td>20.4</td>
<td>1370.0</td>
<td>210</td>
<td>17</td>
<td>5.5</td>
<td>1.8</td>
<td>1.50</td>
</tr>
<tr>
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<td>2</td>
<td>26</td>
<td>1362.3</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>e</td>
<td>e</td>
</tr>
</tbody>
</table>

* Tᵣ is the rth anneal.
* Defined as the ratio of the distance from the center line of the peak to the left slope over the distance to the right slope, measured at half-height; 1 means a fully symmetrical peak.
* Not measured.
* Small concentration of A centers; most of the placelets are converted to dislocation loops.
Figure 4. The change in the B'-platelet peak in a type-IaA/B diamond before (-----) and after (----) heat treatment. Also the appearance, after treatment, of the 1490 cm\(^{-1}\) band is shown.

Figure 4 also shows the changes in the region of the spectrum at higher energy than the B' peak. There is no apparent change in the 1430 cm\(^{-1}\) peak; however, a new broad absorption band at 1490 ± 3 cm\(^{-1}\) was introduced. This is probably the same band as that at 1488 ± 3 cm\(^{-1}\) obtained when annealing type-IaA diamonds to form platelets as shown in figure 1(b).

3.2.1.2. Other changes caused by the treatment. These are as follows.

On annealing at 2000–2350°C, the integrated intensity of the B' peak remained unchanged. In the couple of cases where there seem to be a small reduction (table 1), the change is within experimental error. The position of the peak moved slightly (1–2 cm\(^{-1}\)) to higher energies (smaller platelets?).

On annealing at 2650°C, in some cases, when the annealing caused A centres to aggregate to form B centres, the integrated intensity of the B' peak increased. This increase was always coupled with corresponding changes in the absorption due to the nitrogen in the A and B centres and the D band; namely the absorption due to the A centres decreased, the absorption due to the B centres increased and the absorption due to the D band, the band associated with the platelets, increased (for quantitative values see table 1). These changes are in line with Woods' (1986) proposal that the platelets are formed by the carbon interstitials liberated when A centres aggregate to form B centres. The position of the peak moved slightly (1 or 2 cm\(^{-1}\)) to lower energies (larger platelets?).
3.2.1.3. The 328 cm\(^{-1}\) peak. The strength of this peak, and the associated higher-energy shoulder, for two specimens KW6 and P25 was measured before and after treatment at 2300°C. In both cases the peak and the associated shoulder disappeared, as shown in figure 5. Also, no such peak was found in specimens P01 and KW5 after treatments at 2650°C. However, treatments at temperatures up to 2200°C did not affect the intensity of this peak. No such peak was observed in any type-IaA/B diamonds formed by annealing pure type-IaA diamonds at 2650°C.

In an effort to differentiate between the various phenomena, some of the samples were annealed at lower temperatures. No change was observed after annealing for 6 h at 1900°C. The changes in the shape of the B\(^{\prime}\)-platelet peak and the appearance of the broad band at 1490 cm\(^{-1}\) start to take place after annealing at 2000°C. The elimination of the 328 cm\(^{-1}\) bond could only be achieved after annealing at 2300°C.

In summary, the annealing process changes the characteristic IR absorption associated with the 'natural' platelets and makes them similar to that observed for the 'man-made' platelets; namely, a broader and more symmetrical B\(^{\prime}\) peak and the introduction of the additional broad absorption bands at 1490 cm\(^{-1}\). These changes, coupled with the disappearance of the 328 cm\(^{-1}\) peak, thought to be associated with nitrogen in the platelets (Bridden et al. 1991), and the lower value of the concentration of nitrogen in the man-made platelets (Fallon et al. 1995), beg the question of whether the nitrogen can be made to diffuse away from the platelets as a consequence of the high-temperature annealing. It was thought that TEM and EELS might give an answer.

![Figure 5](image_url)

Figure 5. The spectra of a type-IaA/B diamond before and after treatment at 2300°C for 2 h showing the disappearance of the 328 cm\(^{-1}\) peak as a consequence of the heat treatment.
3.2.2. Transmission electron microscopy results

3.2.2.1. 'Man-made' platelets. We examined several 'man-made' platelets in three specimens using high-resolution transmission electron microscopy (HRTEM). No differences were detected between the contrast from these platelets and the contrast from the 'natural' platelets, confirming the results of Fallon et al. (1995) obtained from examining one of these specimens.

3.2.2.2. Annealed 'natural' platelets. Using TEM, HRTEM and phase contrast we found that the high-temperature annealing did not introduce any microscopically detectable changes in the shape or the contrast of the 'natural' platelets found in type-IaA/B diamonds. Three pairs of specimens, the annealed and their control, were examined. No significant changes were detected in the specimens annealed at 2300°C. However, small changes were observed in specimens annealed at 2650°C. A more detailed study was conducted on a pair of specimens, one of which was annealed at 2650°C for 2 h and its control. Statistical analysis of 250 platelets showed that the platelet size in the treated specimen is slightly smaller (a decrease of about 10%) than in its control untreated specimen, and the area of platelets per unit volume is slightly higher by about 17% ± 5%. IR results of the same treated specimen (table 1, specimen P67) show that the position of the B' peak in the treated specimen shifted after treatment by -1.5 cm⁻¹ (larger platelets) and the area of the peak increased by 26% ± 5%.

3.2.3. Electron-energy-loss spectroscopy results

The nitrogen contents in 56 platelets in six specimens were measured using EELS. A typical spectrum showing the intense carbon edge at 290 eV and a weak, barely visible N K edge at 400 eV is illustrated in figure 6. The integrated counts in the edge are proportional to the number of atoms illuminated by the probe. A simple geometrical model was used to convert the measured intensity ratios \( I_N/I_C \) of the nitrogen counts to the carbon counts, to the amount of nitrogen in the platelet. The illuminated volume of material is taken to be the thickness multiplied by the irradiated area \( d^2 \), where \( d \) is the larger of the beam raster dimension or the probe size. The area of the platelet illuminated is taken to be equal to \( d \) multiplied by the foil thickness. The nitrogen excess, \( \Gamma_N \) in units of atoms per unit cell area \( a_0^2 \), is then given by

\[
\Gamma_N = \frac{\sigma_C}{\sigma_N} \frac{I_N}{I_C} \rho_C a_0^2 d,
\]

where \( \rho_C \) is the atomic density of carbon in diamond, \( \sigma_i \) is the partial ionization cross-section for element \( i \) and \( a_0 \) is the unit-cell dimension for diamond. The nitrogen excess \( \Gamma_N \) would be equal to four if the platelets were composed from sheets of substitutional and interstitial nitrogen as predicted for example by the 'Lang platelet model'. To extract the integrated counts from the spectrum, a power-law background is first removed from the carbon edge and fitted in the region immediately preceding the edge. It must be pointed out that, owing to the very low signal-to-background ratio (\( S/B < 0.05 \)), the visibility of the N K edge is very poor in the raw data even though its signal-to-noise ratio is sufficient for accurate quantification (\( S/N \geq 30 \)). As a consequence of the low \( S/B \) ratios it is not possible in this case to use conventional procedures, such as power-law fitting, to remove the background under the nitrogen edge. In order to view and determine the integrated counts in the
Figure 6. Overlapping EELS data taken from the platelets and neighbouring diamond matrix. The C K edge from 290 eV dominates the spectrum. The presence of nitrogen is indicated by its K edge at 400 eV which can be detected only by using the standard difference. The dominance of the carbon edge in the raw data is a result of the beam diameter which overlaps with the neighbouring matrix. The near-edge structure on the carbon edge is characteristic of diamond.

The EELS results from the 56 platelets are listed in table 2. The average nitrogen content in the three control untreated samples (P26, B9–1 and B3–5) was found to be 0.7 atoms per $a_0^2$. Upon heat treatment, the nitrogen level in two of the samples, P25 and B9–2, increases to 0.9 atom per $a_0^2$, an apparent ‘increase’ of 30%, whilst in a
Table 2. EELS results.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Annealing temperature (°C)</th>
<th>Annealing time (h)</th>
<th>Number of platelets measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>2300</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>P26</td>
<td>2650</td>
<td>None</td>
<td>11</td>
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<tr>
<td>B9-2</td>
<td>2600</td>
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<td>B9-1</td>
<td>2700</td>
<td>None</td>
<td>8</td>
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<td>B3-2</td>
<td>2700</td>
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<td>8</td>
</tr>
<tr>
<td>B3-5</td>
<td>2700</td>
<td>None</td>
<td>20</td>
</tr>
</tbody>
</table>

N concentration $\Gamma_N$ (atoms per $a_0^2$)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
<th>Standard error</th>
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<tbody>
<tr>
<td>P25</td>
<td>0.60</td>
<td>1.19</td>
<td>0.9</td>
<td>0.17</td>
</tr>
<tr>
<td>P26</td>
<td>0.46</td>
<td>1.14</td>
<td>0.66</td>
<td>0.07</td>
</tr>
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<td>1.57</td>
<td>0.93</td>
<td>0.21</td>
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<td>B9-1</td>
<td>0.26</td>
<td>0.99</td>
<td>0.64</td>
<td>0.12</td>
</tr>
<tr>
<td>B3-2</td>
<td>0.56</td>
<td>0.72</td>
<td>0.65</td>
<td>0.05</td>
</tr>
<tr>
<td>B3-5</td>
<td>0.38</td>
<td>1.17</td>
<td>0.71</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*a Below detection level.

third treated sample, B3-2, the nitrogen content was 0.65, that is virtually no change. The 30% increase in P25 and B9-2 exceeds the standard error for the measurement. However, owing to the small number of platelets per specimen examined, the spread of values in the nitrogen concentration in the platelets within the same specimen, and the conflicting results of the three annealed specimens lead us to conclude that more data are needed before we can draw a conclusion about whether high-temperature annealing produces any change in the nitrogen content in the platelets. However, for specimen B3-2 which received a severe treatment, where most of the platelets were transformed to dislocation loops (Evans et al. 1995), the fact that the nitrogen concentration in the remaining platelets of specimen B3-2 is comparable with the nitrogen concentration in its untreated control, specimen B3-5, indicates strongly that the high-temperature annealing does not change the concentration of nitrogen in the platelets.

Some insight into the chemical bond of the nitrogen in the platelet is found in the energy-loss near-edge structure (ELNES). The N K edge ELNES is proportional to the local unoccupied density of p states above the Fermi level. From figure 6 we observe that the ELNES of nitrogen is very similar to that of carbon in diamond, suggesting that nitrogen is substitutional. By further careful subtraction of the matrix carbon edge from the carbon edge recorded at the boundary, a platelet-sensitive component is extracted and represents the local electronic structure of the carbon bound within the platelet structure itself. This is shown in figure 7. It is interesting to note that it is very similar to the nitrogen ELNES from the platelet. This supports the notion of substitutional nitrogen. The ELNES of nitrogen is the same as reported in earlier work (Bruley 1992, Fallon et al. 1995). The difference between the carbon structural modifications of the platelet and that of bulk diamond presumably represents the structural modifications of the platelet itself. The interpretation of this shape awaits electronic structure calculations of platelet structure
models. We note that the heat treatment does not appear to influence the ELNES (figure 8). Comparing the nitrogen edge spectra in figure 8 suggests that there may exist a slight increase in the signal at the edge threshold for sample 9-2 relative to sample 9-1. Unfortunately the signal-to-noise ratio in the data is too poor to discern unambiguously whether this change is due to a difference in the energy resolution in the two spectra or whether it reflects ELNES and hence bonding of the nitrogen. Such a difference, if it were to be confirmed, is consistent with an increasing fraction of molecular nitrogen species. However, with adequate counting statistics, it is safer to assume that the local platelet structure is not grossly affected by the heat treatment.

§4. DISCUSSION

If we assume, following the results of Sumida and Lang (1988) for 'natural' platelets, that the integrated intensity of the B' peak does give the area of platelets per unit volume also in the case of the 'man-made' platelets, then the results shown in figure 3 suggest that, when the platelets are formed in the laboratory at the high temperature of 2650°C, the area per unit volume of platelets formed per number of B centres aggregated is smaller than the area per unit volume of 'natural' platelets formed in nature at temperatures ranging between 1000 and 1200°C. This can be caused by the higher mobility of the carbon interstitial at the higher temperatures, causing more to be trapped by competing traps.
The TEM results on specimen P67 and its control P68 show that annealing introduces an increase (17% ± 5%) in the area of platelets per unit volume; this result is in line with the increase of the area of the B'-platelet peak (26% ± 5%) which also measures the area of platelets per unit volume. However, if we accept that the average size of the platelets, after annealing is given by the position of the B' peak, then the TEM results on specimen P67 and its control P68 seem to contradict the IR observation, where the shift to lower energies of the position of the B peak indicates an increase in the average size of the platelets. However, it is difficult to say whether these changes, being so small, are meaningful. Also, the TEM results are taken from two different specimens; the treated specimen and the control. Although these samples were cut from the same diamond and had the same initial IR spectra, this does not necessarily mean that the small changes observed in microscopic volumes sampled by the electron beam in the TEM fully represent what happens everywhere in the specimen. It can be concluded that the changes, if any, in the shape and the size of the platelets caused by the annealing process are too subtle to be detected conclusively by electron microscopy.

IR results show an increase in the symmetry of the B'-platelet peak as a consequence of the heat treatment. The observed asymmetry of the B'-platelet peak is related to the size of the platelets: smaller platelets which have a larger number of atoms at their edge per unit area than the larger platelets have a more asymmetrical B' peak (Woods 1986). This asymmetry is thought to be due to the strain field around the edge of the platelets. This strain field can be reduced if nitrogen atoms diffuse away from the platelets. Contrary to the expectation expressed in §3.2.1
above, there is no evidence for weakly bound labile nitrogen atoms that would diffuse away from the platelet upon heat treatment. On the other hand, if platelets contain dangling bonds, as suggested by Fallon et al. (1995), the strain field can also be reduced if, for example, nitrogen atoms diffuse to the platelets, thereby satisfying dangling bonds, or by substituting highly stressed carbon sites within the structure of the platelet. According to this view, the diffusion of nitrogen atoms to the platelets will be energetically favoured owing to strain relaxation which stabilizes the platelet structure. Although the EELS results from two pairs of specimens show an apparent increase in the nitrogen concentration of the platelets, the results from the third pair of specimens for which the annealing was more severe, where a larger number of platelets were examined and the spread of values of the nitrogen concentration in the platelets of the same specimen is smaller, however, show no change in the nitrogen concentration in the platelets. This leads us to conclude that, if there is no detectable change in this case, then the annealing does not change the nitrogen concentration in the platelets.

We have no straightforward explanation for the broadening, reduction in height and unchanged integrated intensity of the B'-platelet peak. We can only speculate that the annealing might have caused changes in the structure of the platelets which also produce the changes in the shape of the B' peak and the appearance of the absorption at 1490 cm\(^{-1}\). The similarity of the IR spectra of the 'annealed' and the 'man-made' platelets, produced at high temperatures, give some credence to this assumption. If we accept this hypothesis, then we have to assume that the changes are either too small or not of the kind that can be detected by TEM. Another possibility would have been that these changes are caused by a change in the distribution of sizes of the platelets without changing the area of the platelets per unit volume. This assumes that some platelets grow in size while the size of others has been reduced, which is not very likely. Also, TEM results do not support this assumption. EELS results also do not show any change in the amount of nitrogen in the platelets. However, it is interesting to speculate that annealing is producing submicroscopic voidites at the platelets; we may be seeing evidence for this in the EELS data (figure 8). If this is taking place, TEM and HREM would not be able to resolve such a very small cluster of nitrogen; however, this might create some of the changes seen in the IR spectroscopy.

As mentioned above, the annealing at high temperatures can reduce the strain field surrounding the platelets, eliminating the asymmetry of the B'-platelet peak. The elimination of the strain field surrounding the platelets might also cause a change in the position of the B' peak to lower energies. If this is the case, it is tempting to think that the observed changes in position do not correspond to changes in the sizes of the platelets in line with the TEM results. However, the elimination of the strain field cannot explain the observed shift to higher energies when annealing in the lower-temperature range. Therefore we have to conclude that the observed shifts in the position of the B'-platelet peak do indicate a small change in the size of the platelets caused by the annealing process.

If we accept that the 328 cm\(^{-1}\) peak is caused by a C–N vibration, when the nitrogen atoms are in a certain configuration (Bridden et al. 1991), then the disappearance of this peak can be caused by a change in the configuration, or redistribution, of the nitrogen atoms in the platelets as a result of the anneal, such as the speculated formation of submicroscopic voidites. The difference between the temperature needed to anneal out this peak (at least 2300°C) and the temperature to
produce the changes in the B' peak and the formation of the 1490 cm\(^{-1}\) absorption band (2000°C) indicates that the two phenomena might not be directly related.

§ 5. CONCLUSIONS

The IR absorption of the ‘man-made’ platelets which is due to local modes differs from the comparable spectrum of the ‘natural’ platelets. Similar changes, namely the changes in the shape (broadening and higher symmetry) of the B’-platelet peak, the formation of the 1490 cm\(^{-1}\) absorption band and the elimination of the 328 cm\(^{-1}\) peak can be introduced in the spectra of the ‘natural’ platelets by high-temperature annealing. This indicates that high-temperature treatment can cause changes in the structure of the ‘natural’ platelets. Such changes are too subtle to be observed using electron microscopy.

EELS results support the finding by Fallon et al. (1995) that platelets contain nitrogen as an impurity. Our EELS results indicates that high-temperature treatment does not change the nitrogen concentration in the platelets. Both IR spectroscopy and TEM results show that annealing at 2650\(^0\), if accompanied by the aggregation of A centres to form B centres, increases the area of the platelets per unit volume.

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