

Correlation between optical absorption and EPR in high-pressure diamond grown from a nickel solvent catalyst

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Received 23 June 1997; accepted 4 September 1997

Abstract

There is a general tendency for the magnitude of the W8 electron paramagnetic resonance, attributed to substitutional negatively charged nickel, Ni_s^- , to increase in sympathy with the strengths of the 1.883 eV and 2.51 eV absorption bands in high-pressure synthetic diamond. The ratio of the intensities of the 1.883–2.51 eV bands is not constant, and is generally lower in diamonds with a low Ni_s^- concentration; a better correlation is obtained between the Ni_s^- concentration and the 2.51 eV absorption than with the 1.883 eV absorption. Concentrations of Ni_s^- up to 70 ppm are detected in some diamonds, and the relatively weak absorption in the 2.51 eV system suggests that either the oscillator strength is very low or that the optical transition occurs at a minor defect with a concentration which increases approximately in direct proportion to the concentration of W8 centres. The 1332 cm^{-1} absorption induced by nickel, but attributed to N^+ , does not correlate with Ni_s^- in diamonds with low nitrogen concentrations, in which the concentration of Ni_s^- is also small, and the charge compensation mechanism proposed in earlier investigations needs to be reconsidered for such specimens. © 1998 Elsevier Science S.A.

Keywords: HPHT diamond; Nickel centres; Optical absorption; EPR

1. Introduction

In this paper we present the first attempt to relate the optical absorption bands produced by nickel in synthetic diamond to the W8 electron paramagnetic resonance (EPR) attributed to substitutional negatively charged nickel.

1.1. Optical properties of nickel in diamond

In a study of synthetic diamond abrasive grit, Collins and Spear [1,2] observed a number of absorption and luminescence bands that occurred only in specimens grown using nickel, or a nickel alloy, as the solvent. In particular, there were vibronic absorption bands with zero-phonon lines at 1.40, 1.883 and 2.51 eV, and a broad featureless band with a maximum near 1.4 eV.

These authors also reported that the use of nickel, as the solvent catalyst for diamond growth, activated absorption at the Raman frequency (1332 cm^{-1}), and that there was a tendency for this absorption to be strong when the 2.51 and 1.883 eV absorption bands were strong.

In addition, Collins and Spear noted that the dominant cathodoluminescence (CL) in the visible region was a vibronic band with a zero-phonon region at 2.56 eV. The 1.40 eV system observed using CL, was also very intense in these diamonds. The 2.56 and 1.40 eV CL systems had first been observed [3] in synthetic diamond grit many years previously, but the association with the presence of nickel had not been established.

In a later investigation [4], these optical bands were studied in specimens grown using different concentrations of nitrogen. It was found that the 1.883 and 2.51 eV absorption bands were dominant, and the 1.40 eV absorption was very weak in diamonds with a high nitrogen concentration (~ 250 ppm); the broad

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1.4 eV band was the major absorption at intermediate nitrogen concentrations (~ 30 ppm) and at lower nitrogen concentrations (~ 5 to 10 ppm) the 1.40 eV vibronic absorption band was very strong and the 1.883 and 2.51 eV systems were very weak. These measurements suggested that the different absorption bands were associated with different charge states of the nickel impurity. Collins et al. [4] observed a further series of absorption lines at around 3.1 eV in diamonds with low nitrogen concentration, and Lawson and Kanda [5] have shown that these lines are not present in diamonds containing high (~ 250 ppm) concentrations of nitrogen.

Vishnevskiy et al. [6] and Lang [7] had shown, respectively, that the 2.56 and 1.40 eV CL systems are produced only in the $\{111\}$ growth sectors of synthetic diamond. Collins et al. [4] showed further that all the absorption and luminescence bands that they attributed to nickel occurred exclusively in the $\{111\}$ growth regions.

When virtually all the nitrogen is eliminated from a synthetic diamond, grown using nickel, the diamond has a brown colour because of a continuum absorption, which increases with increasing energy throughout the visible spectral region [8]. In addition to the 1.40 eV absorption there is a complex zero-phonon region between 1.21 and 1.24 eV. Like the 1.40 eV absorption, this structure is detected only in the $\{111\}$ growth regions. Furthermore, this absorption and the 1.40 eV absorption show related photochromic effects. Lawson et al. [8] therefore proposed that the 1.21 eV centre is a different charge state of the 1.40 eV centre.

1.2. EPR properties of nickel in diamond

More than 30 years ago, Loubser and Van Ryneveld [9] detected an electron paramagnetic resonance (EPR) with $g=2.0310 \pm 0.0005$ in polycrystalline synthetic diamond, and noted that this resonance was absent if nickel was not used in the synthesis. They called the centre producing this signal "W8". The involvement of nickel in the W8 centre was confirmed by Samoilovich et al. [10], who observed a 0.65 ± 0.05 mT hyperfine splitting from ^{61}Ni in powdered specimens in which the proportion of this isotope had been increased to 86% from its natural abundance of 1.2%. Twenty years later, the availability of large (several mm) single crystals of synthetic diamond, grown by the temperature gradient method, enabled Isoya et al. [11] to study the W8 centre in more detail, using the pulsed Fourier transform EPR technique. They showed that the $g=2.0319$ EPR signal in synthetic diamonds arises from a substitutional Ni^- centre with an effective spin of $S=3/2$ and an electronic configuration $3d^7$. We will refer to the centre as Ni_s^- in this paper.

Two further EPR signals have been detected in synthetic diamonds with low nitrogen concentrations,

grown using nickel [12]. NIRIM-1 has $g=2.0112$ and is attributed to Ni^+ in an interstitial site with $3d^9$ configuration. NIRIM-2 is found at low temperatures (4 K) and is trigonal with $g_{\parallel}=2.3285 \pm 0.0050$ and $g_{\perp}=0$. This resonance has been associated tentatively with a nickel–vacancy complex Ni^+-V [12].

1.3. Correlations between optical absorption and EPR

With at least six different absorption bands and three different EPR signals attributed to the use of nickel in the synthesis of diamond, it is interesting to see whether there are any correlations between the intensity of an absorption band and the concentration of nickel determined by EPR. In this paper we draw together a number of previously unpublished pieces of work, which show that there is a general tendency for the magnitude of the W8 resonance to increase in sympathy with the strengths of the 1.883 and 2.51 eV absorption bands. Compared with other vibronic absorption bands in diamond the absorption in both of these optical systems is weak in relation to the W8 concentrations measured (up to around 70 ppm). This suggests that the absorption is due to transitions at minor defects having concentrations which increase approximately in direct proportion to the concentration of W8 centres.

2. Experimental procedures

In this investigation we have examined abrasive grit with dimensions around 0.5 mm, grown by General Electric, using either Ni or Ni/Fe as the solvent catalyst, De Beers diamonds with dimensions around 1 mm grown using Ni/Fe, and a range of specimens grown at NIRIM. The latter specimens, typically with dimensions 2–3 mm, were grown by the temperature-gradient method, generally using pure nickel as the solvent catalyst and various nitrogen getters (Ti, Zr, Al) to reduce the nitrogen concentrations. Three additional crystals were grown using Ni–10% Mn, Ni–20% Fe and 29% Ni–16% Co–55% Fe. Absorption spectra in the visible region were measured using a Spex model 1702 monochromator and the infra-red spectra were recorded using a Fourier Transform infra-red spectrometer (either a Bomem Michelson-110 or a Biorad FTS 40). The EPR measurements were carried out using a Bruker ESP300 X-band spectrometer for data shown in Figs. 1 and 3, a Varian E-Line Century Series X-band spectrometer for data shown in Fig. 4 and a superheterodyne spectrometer for the data shown in Fig. 5.

For the 1.883 and 2.51 eV systems the absorption spectra were measured at 77 K. Infra-red spectra were recorded with the specimens at room temperature. The intensity of the absorption in the defect-induced one-phonon region was determined by scaling the absorp-

bance plots, using the known absorption coefficient at 2000 cm^{-1} in the intrinsic two-phonon region. For all the optical measurements the light entered and left the crystals by a pair of opposite as-grown faces.

EPR spectra are normally obtained in a derivative form, and the intensity is obtained by a double integration of the signal. For quantitative studies, the numbers of each paramagnetic impurity within a given crystal were obtained by comparing the signal intensities with that from a standard sample — for example, a crystal of copper sulphate.

There are problems with trying to correlate EPR signals and optical absorption spectra in specimens for which the defect distribution is inhomogeneous. The EPR measurement determines the total number of “spins” in the crystal, and is unaffected by the inhomogeneity, whereas the absorption measurement can be grossly affected by the lack of homogeneity. We have noted in Section 1 that the nickel-related centres are present only in the $\{111\}$ growth sectors of the diamonds; an absorption measurement which interrogates predominantly a $\{111\}$ region will therefore appear quite different to one where the light passes mainly through a $\{100\}$ growth sector [4]. In practice, for a typical cubo-octahedral synthetic diamond, some sort of average value is obtained, and repeated measurements on the same crystal, using different pairs of faces, yield absorption coefficients which agree to around $\pm 25\%$.

The data reported in this paper therefore indicate trends, rather than absolute correlations. To pursue the investigation further would require large diamonds to be grown, with similar defect concentrations to those investigated here, from which specimens containing only the $\{111\}$ growth sectors could be cut.

3. Results and discussion

The absorption spectra from these diamonds are similar to those reported previously [1,2,4], and here we show how the intensities of the 1.883 eV, 2.51 eV and 1332 cm^{-1} absorptions are related to each other, and to the concentrations of Ni_s^- , as determined from the strength of the W8 ($g=2.0319$) EPR signal.

For the 1.883 and 2.51 eV centres the concentration of the corresponding defect has been assumed to be proportional to the intensity of the zero-phonon line. Where the widths of the peaks were different in different specimens we have used the integrated absorption (i.e., the area under the absorption peak), expressed in units of meV cm^{-1} , as a measure of the defect concentration; where the peak widths remained sensibly constant over the range of diamonds investigated, the absorption coefficient in cm^{-1} has been used. The width of the 1332 cm^{-1} peak was approximately the same in all

samples, and here, too, the absorption coefficient has been used.

Fig. 1 shows the EPR signal plotted against the integrated absorption of the 2.51 and the 1.883 eV band for crystals grown at NIRIM. We see that there is a general trend indicating that when either absorption is strong the concentration of Ni_s^- is high. There are several crystals in which both the EPR signal and the optical absorption are too weak to detect, and this justifies plotting the straight lines through the data as least-squares fits through the origin. The apparent correlation is rather better for the 2.51 eV absorption (Fig. 1a), than for the 1.883 eV absorption (Fig. 1b), for which the data are more scattered. The standard deviations in the gradients are around 10% for the 2.51 eV absorption and around 21% for the 1.883 eV absorption.

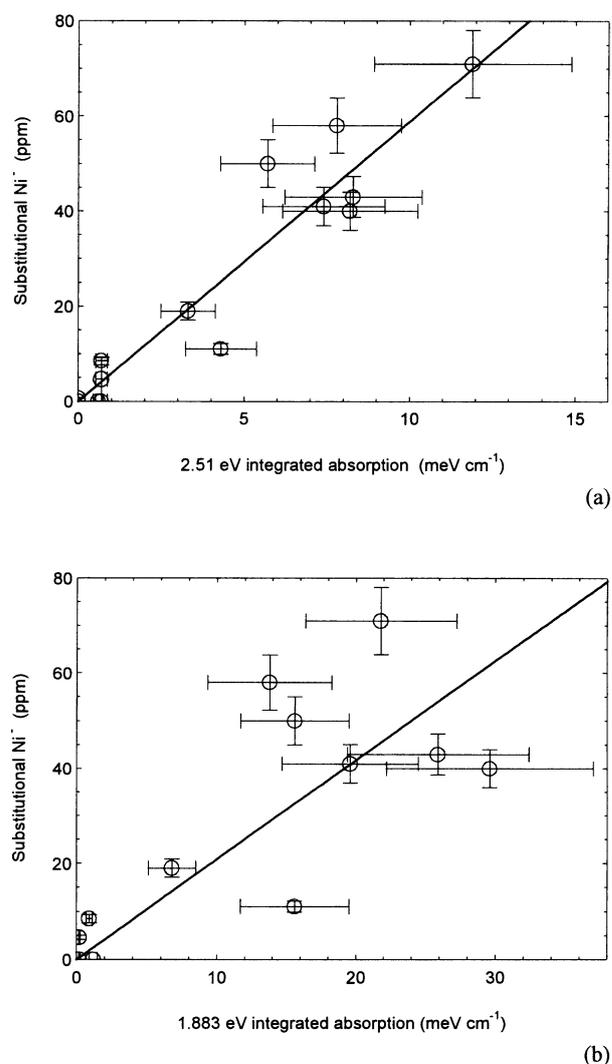


Fig. 1. The concentration of negatively charged substitutional nickel centres, determined from EPR measurements, plotted against the integrated absorption of: (a) the 2.51 eV zero-phonon line; and (b) the 1.883 eV zero-phonon line, for diamonds grown at NIRIM. The straight lines are unweighted least squares fits to the data, of the form $y = ax$.

Many of the diamonds with data points near the origin have a low concentration of 1.883 and 2.51 eV defects because the nitrogen concentration is low and the other nickel-related absorption bands at 1.4 eV (broad) and 1.40 eV (sharp doublet) dominate the spectrum [4]. By contrast, the diamond grown from the Ni alloy (Ni/Co/Fe) still has an appreciable nitrogen concentration and the only nickel-related absorption peaks it contains are those at 1.883 and 2.51 eV; because these are of low intensity the datum point for this specimen is also near the origin. The trends shown in Fig. 1 therefore appear to be independent of the nitrogen concentration in the crystal, or the presence of other nickel-related absorptions.

The large error bars on the absorption axes in Fig. 1 arise because the nickel centres are not homogeneously distributed in the diamonds, and repeated measurements, using different faces of the crystals, give a typical spread of $\pm 25\%$. In any one spectrum the area under the peak can be measured with a precision of better than $\pm 7\%$.

The reason why the 1.883 and 2.51 eV absorptions do not behave identically in Fig. 1 is illustrated in Fig. 2, which shows the ratio of these absorptions, plotted as a function of the 2.51 eV absorption. Again the data are very scattered, and this is a genuine variability from sample to sample, since the two absorption systems were measured simultaneously for a given crystal and the uncertainty in the ratios is therefore no more than $\pm 10\%$. We see that this ratio is around 3 for high values of the absorption and drops below unity at low values.

Fig. 3a shows the absorption at 1332 cm^{-1} plotted against the absorption at 2.51 eV. Collins and Spear [1] noted that these absorptions showed an approximate correlation, but this clearly breaks down at low values, where several specimens show appreciable absorption at 1332 cm^{-1} , but very little at 1.883 or 2.51 eV. Fig. 3b

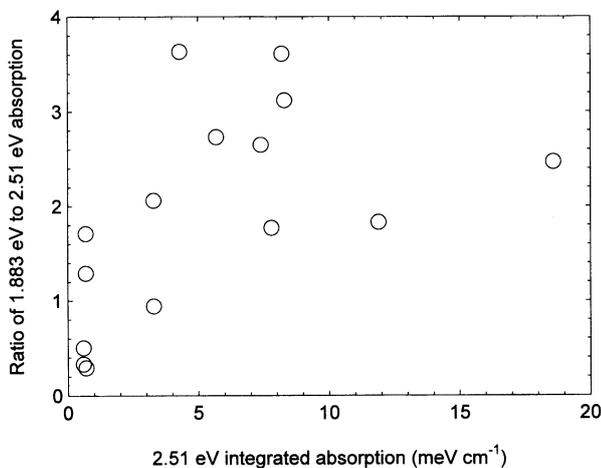


Fig. 2. The ratio of the absorption strengths of the 1.883–2.51 eV zero-phonon lines plotted against the intensity of the 2.51 eV zero-phonon line, for diamonds grown at NIRIM.

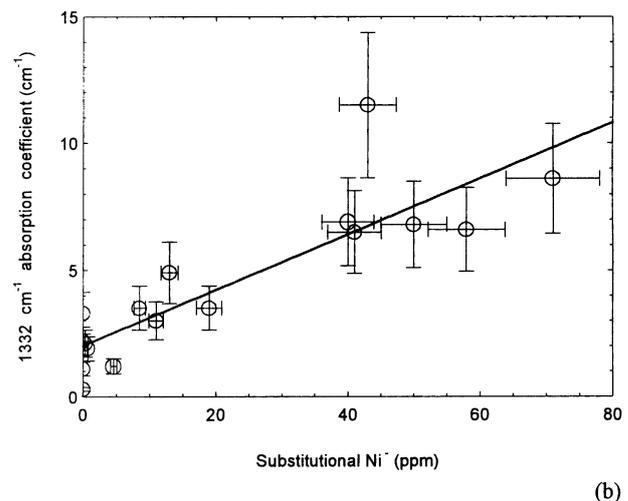
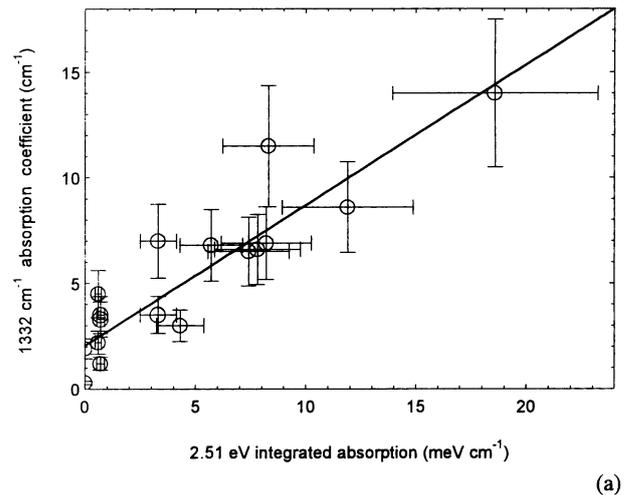


Fig. 3. The intensity of the 1332 cm^{-1} peak, plotted against: (a) the integrated absorption of the 2.51 eV peak; and (b) the concentration of negatively charged substitutional nickel centres, for diamonds grown at NIRIM. The straight lines are unweighted least squares fits to the data, of the form $y = ax + b$.

shows the 1332 cm^{-1} absorption plotted against the concentration of Ni_s^- , and again the trend breaks down at low values. Lawson and Kanda [5] have proposed that the absorption at 1332 cm^{-1} is produced by nitrogen which has become positively charged, by donating an electron to produce the negatively charged Ni centres. The proposal that the 1332 cm^{-1} absorption is due to N^+ is also supported by EPR measurements on diamonds that have been annealed in the dark [13]. However, Fig. 3 illustrates that these conclusions are not completely consistent in diamonds grown using nickel; there must be another centre, accepting an electron from the nitrogen, and which is not detected in the optical absorption spectrum, or by EPR, in order to explain these results.

Fig. 4 shows the Ni_s^- concentration plotted against the 2.51 eV absorption for the De Beers diamonds grown

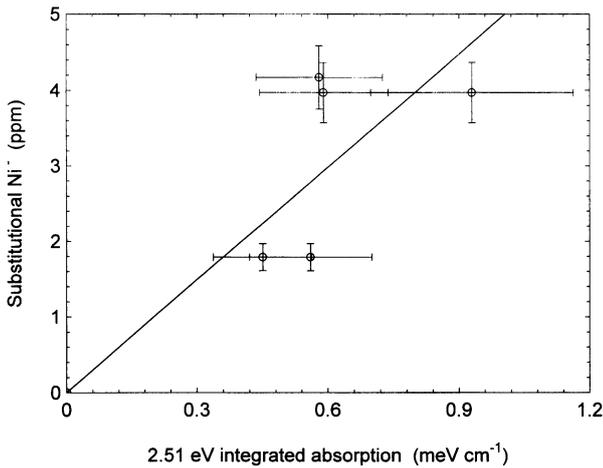


Fig. 4. The concentration of negatively charged substitutional nickel centres, plotted against the integrated absorption of the 2.51 eV zero-phonon line, for diamonds grown by De Beers. The straight line is an unweighted least squares fit to the data, of the form $y=ax$.

from Ni/Fe. Again the same trend is noted as in Fig. 1a, and the gradient of the plot is similar. As with Fig. 1, there is more scatter if the Ni_s^- data are plotted against the strength of the 1.883 eV absorption. The use of a Ni alloy gives low values of absorption and Ni_s^- concentration, and, in agreement with Fig. 2, the ratio of the 1.883–2.51 eV absorption is substantially less than unity for each of the five diamonds.

Fig. 5 shows data for three different batches of GE abrasive grit, two batches grown using Ni, and one using Ni/Fe. Here, too, there is a general tendency for the strength of the W8 EPR signal to increase as the absorption increases. Despite the severe scatter on this

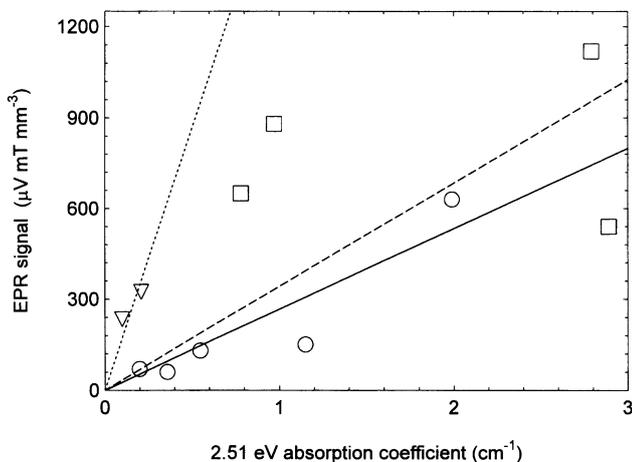


Fig. 5. The EPR signal due to negatively charged substitutional nickel centres, plotted against the absorption coefficient of the 2.51 eV zero-phonon line, for three batches of synthetic diamond abrasive grit grown by GE. (□, dashed line; and ○, continuous line; Ni solvent catalyst. ▽, dotted line; Ni/Fe solvent catalyst). The straight lines are unweighted least squares fits to the data, of the form $y=ax$. Uncertainties in the data are around $\pm 10\%$ for the EPR measurements and $\pm 30\%$ for the absorption coefficients.

diagram, and the limited amount of data, there is an indication that the gradient of the line for the Ni/Fe diamonds is significantly higher than for either set of the Ni diamonds. The two Ni/Fe diamonds had 1.883–2.51 eV ratios of less than unity, while, for the remaining diamonds used for Fig. 5, this ratio lay between 1.7 and 6, and varied in a random way.

4. Conclusions

Measurements on synthetic diamonds produced by three different laboratories show that there is a general tendency for the magnitude of the W8 EPR resonance, with $g=2.0139$ and attributed to negatively charged substitutional nickel, to increase in sympathy with the absorption bands at 1.883 and 2.51 eV. The ratio of the intensities of the 1.883–2.51 eV bands is not constant, and is generally lower in diamonds with a low Ni_s^- concentration; a better correlation is obtained between the Ni_s^- concentration and the 2.51 eV absorption than with the 1.883 eV absorption. However, the apparent correlation is likely to be indirect. A typical oscillator strength for a zero-phonon line in diamond [14] is $f=2 \times 10^{-15} \text{ meV cm}^2$. From Fig. 1, for an integrated absorption of 10 meV cm^{-1} , this would suggest a concentration of $\sim 5 \times 10^{15} \text{ cm}^{-3}$ for the 2.51 eV centre, compared with 10^{19} cm^{-3} actually measured for the concentration of Ni_s^- . Unless the oscillator strengths of the nickel-related centres are uncharacteristically low, it is probable that the 2.51 eV absorption is produced by an electronic transition at a minor defect, with a concentration which increases approximately in direct proportion to the concentration of W8 centres.

The intensity of the vibrational transition at 1332 cm^{-1} induced by the Ni is of the order of magnitude expected for the nickel concentrations measured. The assignment of this absorption to positively charged nitrogen [5] neatly explains why nickel is present in the negative charge state in diamonds with high nitrogen concentrations. This model needs to be refined, however, to account for the significant intensity observed for the 1332 cm^{-1} absorption in diamonds with very low nitrogen concentrations, for which the W8 EPR signal is undetectably weak.

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