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Optical detection of magnetic resonance of nitrogen and nickel in high-pressure synthetic diamond

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Diamonds grown by the temperature gradient method using a nickel catalyst exhibit a luminescence spectrum that is dominated by a broad band with sharp lines around 2.56 eV. We report optical detection of magnetic resonance of substitutional N^0 and substitutional Ni^- in this luminescence system. The results indicate that the luminescence arises from two overlapping bands, one resulting from distant deep nitrogen donor to shallow acceptor recombination, the other a localized transition involving the nickel that accounts for the sharp structure.

I. INTRODUCTION

Unless deliberate action is taken to eliminate it from the growth environment, nitrogen is normally the major impurity in synthetic diamond grown by the high temperature, high-pressure method.[1] Most of the nitrogen is present on single substitutional lattice sites and is known to introduce a donor level which, from photoconductivity is estimated to be at about 2.0 eV below the conduction band.[2–4] In its neutral charge state, it gives rise to a well studied EPR signal at $g = 2.0024$, with well resolved anisotropic hyperfine structure from its 100% ^{14}N isotope, reflecting a $\langle 111 \rangle$ off-center distortion of the atom.[5,6]

Single substitutional nitrogen also causes typical absorption in the infrared, visible, and ultraviolet regions.[7] The infrared absorption is vibrational in origin with the maximum at 1130 cm^{-1}. The absorption coefficient, α_s, at 1130 cm^{-1}, correlates with the paramagnetic nitrogen concentration $[N_s]$ (in parts per million) measured from the EPR spectrum, providing the calibration[8]

$$[N_s] = 25\alpha_s(1130\ \mathrm{cm}^{-1}). \qquad (1)$$

In the high-pressure synthesis method, transition metals are used as solvent catalysts. When nickel is used, the luminescence and absorption spectra of the particular crystal will exhibit typical bands with sharp transitions at 1.402 eV, 1.885 eV, 2.510 eV, 2.56 eV, and 3.1 eV. The bands at 2.510 eV and 3.1 eV are observed only in absorption, while the band at 2.56 eV is only detected in luminescence. The EPR spectra of such crystals may also show resonances that have been identified with Ni ions in different charge states.[9,10] In particular, an isotropic signal with $g = 2.0319$ has been identified with the negative charge state of isolated substitutional nickel (Ni_s^-)[10].

From all the optical features that are typical of high-pressure synthetic diamond grown in the presence of nickel, only for the 1.402 (1.404) eV doublet system is there unambiguous evidence of Ni being directly involved.[11,12] The optical defect is thought to be a trigonally distorted interstitial Ni^+ ion (Ni_i^+). The strength of the absorption can be used to estimate the concentration of Ni_i^+ in those centers. By detailed balance arguments, the concentration is given by[13]

$$[Ni_i^+] = \{90n^2E^2\tau g_f/\pi^2h^3(n^2+2)^2c^2g_i\}\int \alpha(\nu)d\nu, \qquad (2)$$

where $n = 2.5$ is the refractive index of diamond, $\tau = 33 \times 10^{-9}$ sec is the decay time of the 1.40 eV luminescence,[14] E is the approximate mean photon energy of the luminescence band, and where g_f and g_i are the degeneracies of the ground and excited states, respectively, of the 1.40 eV system. In addition, there have been reports that the concentration of single substitutional nitrogen in diamond is relevant to the strength of some of the optical features that are present in nickel-containing synthetic diamond. Again, however, there has been no clear evidence of what its role might be. In the work reported in this paper, we concentrate on the 2.56 eV photoluminescence (PL) band, and, using optically detected magnetic resonance (ODMR), show that neutral isolated substitutional nitrogen (N_s^0) and Ni_s^- are both participating in spin-dependent processes associated with the luminescence.

II. EXPERIMENTAL DETAILS

The sample used for this work was grown at the National Institute for Research in Inorganic Materials by the high-pressure method, using a nickel-containing solvent catalyst and was polished as a 1 mm edge cuboid with axes [110], $[1\bar{1}0]$, and [001]. From the absorption at 1130 cm^{-1}, we estimate using Eq. (1) a concentration of neutral single substitutional nitrogen of about 10^{19} cm^{-3}. From the strength of the absorption in the 1.40 eV band,

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we estimate using Eq. (2) the concentration of Ni_i^+ in the corresponding defect to be about 5.6×10^{12} cm^{-3}, but we have no direct measure of the total Ni concentration.

The ODMR experiments were performed at pumped-liquid-helium temperatures (1.7 K) in an Oxford Instruments SM-4 superconducting magnet optical cryostat. The sample was mounted in a 35 GHz TE_{011} cavity allowing for optical excitation and detection of the emitted light, and could be rotated to measure the angular dependence of the ODMR spectrum. A Gunn oscillator provided microwave power to the cavity of up to 70 mW (0 dB), which was on-off modulated with a frequency up to 10 kHz. To excite the luminescence, 15 mW radiation at 325 nm from a He-Cd laser was used. The emitted light was detected by a Si photodiode, with subsequent lock-in detection at the microwave modulation frequency. For the spectral dependence of the ODMR signals, the emitted light was dispersed prior to detection by a 1/4 m Jarrel-Ash monochromator.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Luminescence and angular dependence of the ODMR

The PL spectrum at 1.7 K for the 2.56 eV system is shown in Fig. 1(a). In Fig. 2(a), we show the ODMR spectrum, measured by monitoring the change of the total PL intensity with the static magnetic field applied along [001], with full microwave power and a microwave modulation frequency of 500 Hz. Two positive ODMR signals are observed, a sharp isotropic resonance at 1.225 T with a width at half height of 1.5 G and an isotropic value of $g = 2.0324(5)$, and a broad band centered at $g \sim 2.00$.

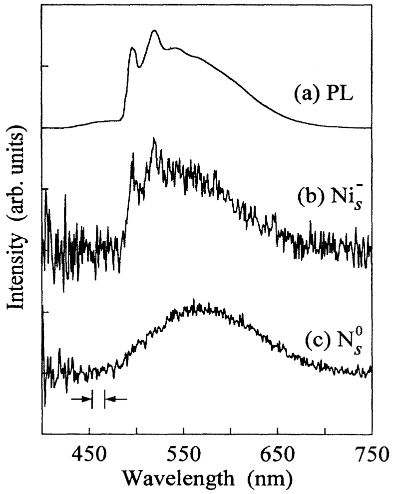

FIG. 1. Spectral dependence of (a) the photoluminescence, (b) the Ni_s^- ODMR, and (c) the N_s^0 ODMR at $T = 1.7$ K. The spectra have been corrected for monochromator and detector sensitivity.

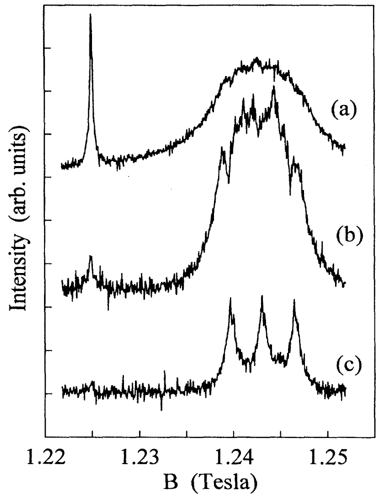

FIG. 2. ODMR spectra, **B** || [001], for the following modulation frequencies and microwave powers: (a) 500 Hz, 0 dB; (b) 20 Hz, 0 dB; (c) 20 Hz, −20 dB.

A g value of 2.0319 has been identified in diamond, using straight EPR, as arising from the negative charge state of isolated substitutional nickel (Ni_s^-).[10] No other EPR signals have been reported near this g value.[6] Accepting this identification, we identify the isotropic line at $g = 2.032$ that we observe as that of Ni_s^-.

Upon reduction of the microwave power, and at lower modulation frequency, the broad resonance is observed to display well defined structure, Fig. 2(c). The angular dependence of this structure is illustrated in Fig. 3. The spectrum can be described by the spin Hamiltonian,

$$\mathcal{H} = g\mu_B \mathbf{B} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} \ , \qquad (3)$$

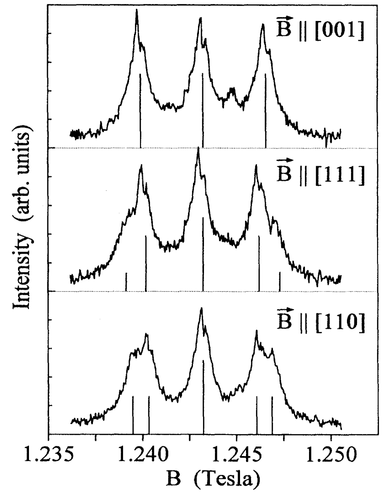

FIG. 3. ODMR of the $g \sim 2$ spectrum at three orientations of **B**. Indicated below the spectra are the amplitudes and positions of the hyperfine lines for N_s^0 (Refs. 5, 6).

where the first and second terms describe the Zeeman and the hyperfine interaction, respectively, for an electronic spin $S = 1/2$ interacting with a 100% nuclear spin $I = 1$. The established values for neutral isolated substitutional nitrogen (N_s^0), $g = 2.0024$, $A_{\|} = 114$ MHz, and $A_{\perp} = 81$ MHz, with the hyperfine axis along $\langle 111 \rangle$,[5,6] match the results within accuracy as shown in the figure, unambiguously identifying the defect as N_s^0.

B. Polarization dependence of the ODMR

By inserting a Polaroid linear filter between the sample and detector, we have investigated the dependence of the ODMR signal on the polarization of the luminescence. Figure 4 shows the result with **B** $\|$ [110] and light polarized along $[1\bar{1}0]$ or [001]. The clear difference between the relative intensities of the N_s^0 hyperfine satellites (which arise from the two different sets of equivalent $\langle 111 \rangle$ defect orientations, as shown in the inset), provides unambiguous proof of the direct involvement of the nitrogen in the luminescence. The sense of the effect reveals that the transition moment is along the defect $\langle 111 \rangle$ axis (π dipole).

C. Microwave power and frequency dependence of the ODMR

As pointed out earlier in this section, the N_s^0 resonance sharpens up revealing the hyperfine structure at lower microwave power and modulation frequency, as depicted in Fig. 2. This can be understood if the luminescence band associated with the nitrogen resonance is due to distant donor-acceptor (DA) pair recombination. Each pair can be described by a spin Hamiltonian that is the sum of the isolated donor (nitrogen) and acceptor Hamiltonians, plus an exchange interaction whose magnitude depends upon the pair separation. For pairs at large separation, the resonances of the isolated donor and acceptor are expected (exchange interaction ~ 0), but for those at closer separations, the lines are broadened due to exchange splittings of each resonance, which must be averaged over the pairs at all of the closer distances.[15,16]

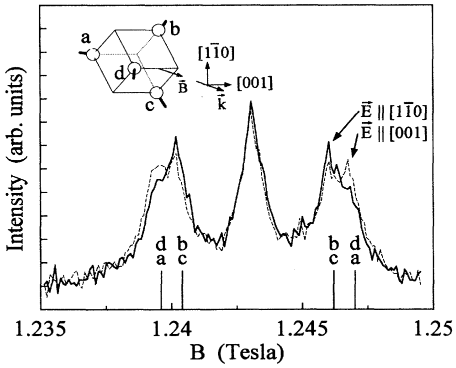

FIG. 4. Dependence of the N_s^0 ODMR spectrum upon the polarization of the detected light. The geometry of the experiment is shown in the inset and the positions of the hyperfine satellites for the four different $\langle 111 \rangle$-oriented defects are indicated below the spectra.

Spectra obtained for high microwave power and modulation frequency will be most sensitive to the closer pairs with the shorter radiative lifetimes and will tend, therefore, to be broad. Lower modulation frequency and power preferentially tend to select the longer radiative lifetimes associated with the distant pairs, giving prominence to their sharp isolated resonances. The Ni_s^- line at $g = 2.032$ also sharpens by a factor ~ 2 at lower microwave power, but disappears too rapidly vs reduced modulation frequency, see Fig. 2(b), to determine its modulation frequency dependence.

D. ODMR spectral dependence

The spectral dependence of the ODMR signals was investigated by setting the magnetic field to resonance and scanning through the luminescence. The results are shown in Figs. 1(b) and (c). In the case of the Ni_s^- resonance, the spectral dependence exhibits all the fine structure present in the luminescence spectrum, Fig. 1(a), while that of the N_s^0 resonance is a structureless band with the maximum shifted slightly to lower energies. This indicates the existence of two different processes giving rise to the luminescence. One, involving the Ni_s^- resonance, gives rise to the structured luminescence band. The other is the result of radiative recombination between a substitutional nitrogen donor and an unknown acceptor (not observed in the resonance).

IV. DISCUSSION

The observation of the isotropic $g = 2.032$ resonance and of the nitrogen donor signal, as enhancement of the 2.56 eV luminescence shows that the luminescence occurs through processes involving both Ni_s^- and N_s^0. However, the nickel and nitrogen resonances display significant differences in their spectral dependences. The spectral dependence of the N_s^0 resonance is broad and extends somewhat further into the red than that of the Ni_s^- resonance, which is also broad, but in addition shows the same sharp structure as the luminescence band. We interpret this as evidence for the existence of two recombination processes contributing to the luminescence, the "2.56 eV band" being the overlap of the two emission spectra.

Consider first the nitrogen-related emission. The characteristics of the N^0 ODMR spectrum vs microwave power and modulation frequency suggests radiative recombination between distant DA pairs:

$$N_s^0 + A^0 \longrightarrow N_s^+ + A^- + h\nu. \quad (4)$$

Consistent with this, the polarization of the luminescence is directly correlated with the orientation of the individual ⟨111⟩-distorted nitrogen donors. The fact that the acceptor resonance is not observed is as expected if it is effective-mass-like, the degeneracy of the top of the valence band causing its EPR signal to be strongly strain broadened and difficult to detect, as in all cubic semiconductors. (Only in high quality silicon, with very low internal strains, has the shallow acceptor resonance been observed.[17])

For DA pair recombination, the peak of the luminescence is given by

$$h\nu_{\max} = E_D - E_A + \langle e^2/\epsilon r\rangle - E_{\text{relax}}, \tag{5}$$

where E_D and E_A are the energy levels measured from the valence band for the donor and acceptor, respectively, r is their separation, and E_{relax} is the combined energies of relaxation for the two, as the electron makes the transition from the donor to the acceptor and their charge states change.

The off-center nitrogen distortion is generally believed to occur only for the neutral state, the result of a pseudo-Jahn-Teller distortion, which produces a deep highly localized state.[18,19] We expect, therefore, a substantial lattice relaxation contribution from it. This, in turn, requires that the acceptor be a shallow effective-mass-like with an extended wave function for efficient distant DA luminescence, and therefore its contribution to E_{relax} should be negligible. With the nitrogen donor level at $\sim$ 2 eV below the conduction band, the band gap of 5.5 eV, the luminescence maximum at 2.15 eV, and an acceptor level at 0.37 eV above the valence band,[20] we obtain $E_{\text{relax}} \sim 1.0 \text{ eV} + \langle e^2/\epsilon r\rangle$. In synthetic diamond, the donors and acceptors are expected to be reasonably uniformly distributed giving $\langle 1/r\rangle \sim N^{1/3}$, where N is the concentration of the pairs.[21,22] With $N \sim 10^{19}$ cm^{-3}, this leads to only $\langle e^2/\epsilon r\rangle \sim 0.03$ eV, a negligible value, and we conclude, therefore, that $E_{\text{relax}} \sim 1.0$ eV. This is a reasonable value, consistent with recent experimental estimates of the N_s^0 relaxation,[4,19] and roughly consistent also with the width of the band in Fig. 2(c). [A simple one-vibrational-mode treatment for lattice relaxation during an optical transition leads, in the limit that $E_{\text{relax}} \gg \hbar\omega$, to a Gaussian line shape with half width $W \cong \sqrt{8\ln 2 E_{\text{relax}}\hbar\omega}$ (Ref. 23). With a mode frequency $\omega \sim 700$ cm^{-1} (Ref. 24), this predicts a width of 0.7 eV. The observed value is 0.5 eV.]

It is interesting to note that a band, with identical spectral characteristics to that of Fig. 1(c), has been studied previously in synthetic diamond. This emission, labeled "A band," was ascribed by Dean[22] to DA recombination, suggesting that the donor is isolated nitrogen. Subsequently, the DA origin was confirmed by other workers.[25] Somewhat later, however, when experimental results indicated the nitrogen to be $\sim$ 2 eV from the conduction band,[2–4] it was argued that the energy of the transition implied a deeper donor level than that for nitrogen and it was concluded instead that the donor must be a nitrogen aggregate[26]. Our results now demonstrate conclusively that the donor is indeed isolated substitutional nitrogen. The reasoning that led to the dismissal of the isolated nitrogen donor apparently did not properly include its relaxation.

Now consider the Ni_s^--related luminescence, which alone displays the sharp structure associated with the 2.56 eV luminescence. This structure has been studied previously in considerable detail under higher resolution and was found to display the complexity characteristic of a localized transition at a defect.[27] It is, therefore, more difficult to come up with a unique model that explains the observation of the ground state EPR of Ni_s^- in the luminescence. One possibility is spin-dependent hole transfer from a distant acceptor to Ni_s^- producing an excited luminescent state of Ni_s^0. Alternatively, it could be observed via spin memory in the pumping cycle with the luminescence being that of an excited-to-ground-state transition of Ni_s^-. Further studies will be required to test these models.

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