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LETTER TO THE EDITOR

Evidence for a Fe-related defect centre in diamond

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Abstract
An undocumented photoluminescence centre at 1.789 eV has been characterized in diamonds grown by a high-pressure high-temperature technique. It could only be observed in nitrogen-free crystals grown in a Fe-containing chamber. The centre is unique for diamond due to its room-temperature linewidth, which can be as small as 1 meV. Polarization, temperature and time-resolved measurements reveal that the corresponding defect has trigonal symmetry, a 3.7 meV splitting in the ground state, vibronic modes of 30 and 48 meV, very weak electron–phonon coupling and a lifetime of 7 ms at room temperature. The centre is attributed to an interstitial Fe related defect.

Most synthetic diamond crystals are now grown by the high-pressure high-temperature (HPHT) technique with the use of a catalyst containing Ni, Co, Fe or Mn metal or one of their alloys. The catalyst material is always present in the grown crystal in the form of metallic or metal carbide inclusions. The question of whether it can incorporate into diamond as single atoms, thus forming point defects, was addressed several decades ago. It was found that Ni is responsible for more than 50 optical centres, which are relatively well characterized by now [1–3]. The incorporation of such a large atom as Ni into a rigid diamond lattice seemed unlikely, but it was further confirmed by electron spin resonance (ESR) results [2, 4]. Later, several Co-related centres have been characterized by optical and ESR techniques [5, 6] and recently a Mn-related defect has been detected by ESR in HPHT diamond [7]. Consequently, the presence of Fe-related defects in HPHT diamond is anticipated but, to the best of our knowledge, it has not been documented yet. In this letter we report the characterization of an undocumented photoluminescence (PL) centre, which may be attributed to an interstitial Fe-related defect.

More than one hundred HPHT diamond samples have been studied. The majority of them were crystals of 1–5 mm in size, having the shape of truncated octahedra with large, well-developed ⟨100⟩ and ⟨111⟩ faces, or were polished plates, cut from such crystals. The crystals were grown with catalysts containing Ni, Co, Fe, Mn or their alloys as the main component. In some samples the nitrogen content was reduced by adding Al or Zr getters into the growth chamber. In many samples the exact composition of the catalyst and getter

was unknown. It was determined with the x-ray fluorescence (XRF) technique using either an Oxford Instruments ED2000 system or the beamline L at the HASYLAB synchrotron.

An undocumented 1.789 eV PL centre was detected in 12 of the samples. Optical and XRF measurements show that 11 of them form a specific group: they were all grown with a Fe catalyst and Al getter and had extremely low defect content. No non-diamond inclusions could be detected in them by Raman scattering. All those crystals showed previously characterized [8] strong blue fluorescence and weak green broadband luminescence when excited by x-rays or UV light of above 4.8 eV energy. In a few samples a boron contamination of the level of a few ppb was revealed by IR absorption. A few crystals also exhibited weak PL associated with the negative nitrogen–vacancy centre ($[N–V]^-$). In order to roughly estimate the concentration of the defect centres, the PL intensity was normalized to the diamond Raman peak and compared with the PL intensity in samples, where the concentration of the specific PL centres was calibrated using optical absorption [1]. The results suggested that the concentration of the $[N–V]^-$ centres was of the order of a few ppb. No other optical centres could be detected in the 0.5–5.5 eV range from those samples by PL and optical absorption.

The twelfth sample showing the 1.789 eV centre was a polycrystal, spontaneously grown during the synthesis of an HPHT crystal using a pure Co catalyst. XRF measurements revealed that the polycrystal contained comparable amounts of Co and Fe, Fe probably being trapped from the material of the chamber. IR absorption revealed that the polycrystal contains less than 5 ppm of single substitutional nitrogen (N_S). The main crystal, grown in the same run, also contained Fe, but also about 50 ppm of nitrogen, and thus showed no 1.789 eV luminescence. The 1.789 eV centre was not detected in any other of the studied HPHT samples. Some of them were grown with Fe catalysts, but contained more than 40 ppm of N_S centres.

Despite the good morphology of those 11 crystals the 1.789 eV centre was not homogeneously distributed, but concentrated around a few black inclusions. The inclusions were magnetic and showed no Raman scattering signals. XRF measurements reveal that they consist of Fe or Fe carbides.

Figure 1(a) shows a room-temperature PL spectrum from one of the eleven described HPHT stones under 2.410 eV excitation. The excitation was provided by a CW Ar^+ laser. Looking from the high-energy part the following features are seen: the first- and second-order diamond Raman peaks at 2.245 and 2.1 eV, respectively, a doublet centred at 1.789 eV and two vibronic replicas, red-shifted from it by 30 and 48 meV. All those features are superimposed on the previously characterized broad PL band [8]. When excited at 2.410 eV the maximum amplitude of the 1.789 eV doublet was one fifth of the first-order diamond Raman peak.

A high-resolution spectrum of the doublet at 77 and 300 K is shown in figure 1(b). P marks the laser plasma lines, which were not suppressed by a filter for calibration purposes. The doublet components have positions of 1.7869(3) and 1.7906 eV at 300 K and 1.7893 and 1.7930 eV at 77 K. As customary, the centre is further classified by the position of the strongest line at 77 K. The halfwidth of the lines is 2.4 meV at 300 K and 2.0 meV at 77 K. When focusing the excitation light further from a metallic inclusion the intensity of the doublet and its linewidth decrease, indicating that the latter is determined by the inclusion-induced strain. The smallest observed linewidth was 1 meV at room temperature and it did not change significantly when cooling the sample down to 77 K. The ratio of integrated intensities of the doublet lines is constant in the temperature range 77–300 K, indicating a splitting of 3.7 meV in the ground state.

The relaxation time of the PL doublet was measured by two techniques: by direct registration of the PL transient under 3 ns 2.255 eV pulsed excitation and by fitting the frequency dependence of the doublet intensity in the range 4–1130 Hz, measured under chopped Ar^+ laser excitation at 2.410 eV. The pulsed excitation was provided by an N_2 laser coupled to a tunable
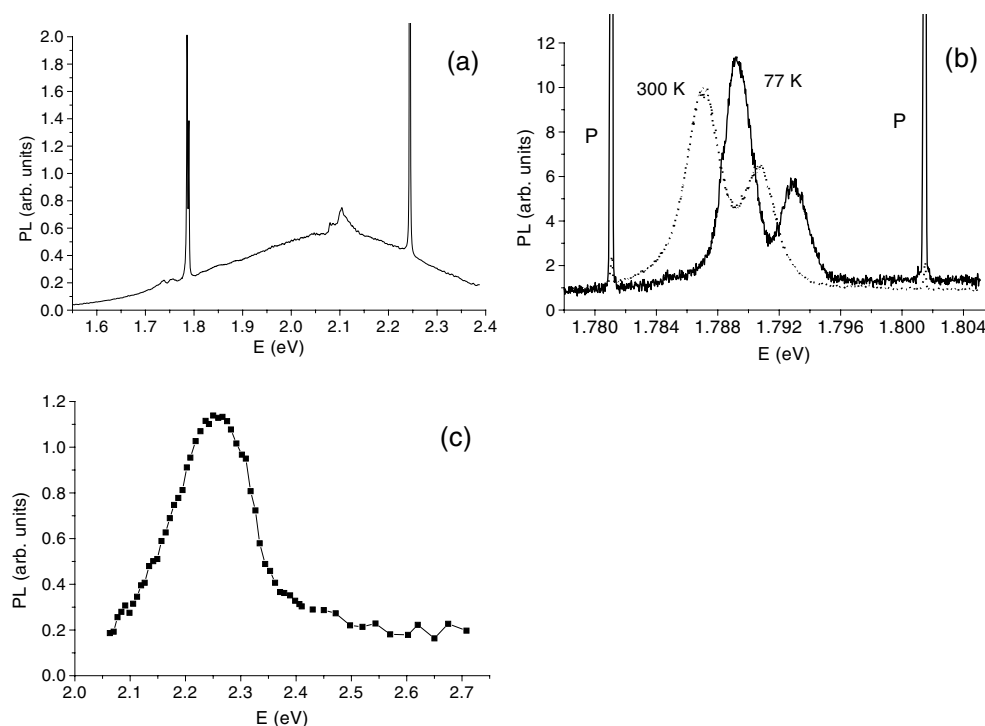
Figure 1. (a) A room-temperature PL spectrum from an HPHT diamond under 2.410 eV excitation. (b) A high-resolution spectrum of the c doublet from (a) at 77 and 300 K. P marks the laser plasma lines. (c) A room-temperature PLE spectrum of the 1.789 eV doublet.

(2.06–2.75 eV) dye cell module. Both methods yielded a relaxation time of 7 ms at 300 K and 10 ms at 77 K.

A room-temperature PL excitation (PLE) spectrum of the doublet is presented in figure 1(c). Because of the weakness of the PL signals the PLE spectrum could only be measured at room temperature with the pulsed tunable laser system, which was used for PL relaxation measurements. The broad signal at 2.25 eV in figure 1(c) can be interpreted as a vibronic band of some weak zero-phonon line, which could not be resolved in this experiment either due to the high measurement temperature or because of insufficient pulse-to-pulse stability of our laser system. The doublet could not be excited at 1.960 or 1.837 eV using a CW He–Ne or a diode laser, respectively.

Figure 2 presents polar graphs for the strongest PL component of the doublet under polarized 2.410 eV Ar$^+$ laser excitation at room temperature. The polarization of the excitation was rotated in the [100] plane starting from the ⟨100⟩ and ⟨110⟩ directions, and the detection polarization was fixed in the ⟨100⟩ and ⟨110⟩ directions for figures 2(a) and (b), respectively. No significant changes in the relative intensities of the doublet components with polarization direction have been observed. The results could only be fitted with a trigonal XY dipole [9]. The fit is shown by dotted curves in figure 2.

The 1.789 eV PL doublet exhibits spectroscopic properties which are rather unusual for an intrinsic or a light-impurity-related defect in diamond, but may be considered as common for many Ni-related PL centres. Those properties include a relatively weak vibronic structure, low energy of the vibronic modes, long relaxation time and a characteristic excitation spectrum with strong electron–phonon coupling. Weak electron–phonon coupling of PL transition shows the
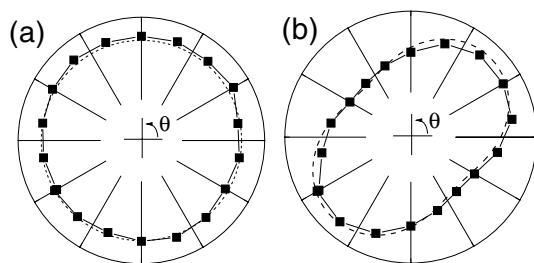
Figure 2. Polar graphs for the strongest PL component of the 1.789 eV doublet under polarized 2.410 eV Ar$^+$ laser excitation at room temperature. The polarization of the excitation was rotated in the [100] plane starting from the $\langle 100 \rangle$ (a) and $\langle 110 \rangle$ (b) directions, and the detection polarization was fixed in the $\langle 100 \rangle$ (a) and $\langle 110 \rangle$ (b) directions.

interstitial character of the corresponding defect centre [1]. Long relaxation indicates that the optical transition from the ground state to the first excited state, responsible for the 1.789 eV system, is forbidden. This fact is commonly interpreted as the corresponding energy levels originate from the d-shells of a transition metal element, optical transitions between those being forbidden. Efficient excitation of such PL is possible due to the presence of a higher-lying excited states (like the ones responsible for the 2.25 eV band in the PLE spectrum of figure 1(c)), for which some admixing of s- and p-shells occurs, thus making the transition allowed. Such a situation is typical for Ni and Co-related centres in diamond [3, 5, 10]. It may be visualized as the levels responsible for the PL transition originating from the electronic states of an isolated heavy ion, while significant coupling to the lattice phonons occurs in the electronic states responsible for the PL excitation transitions.

We interpret the correlation of the appearance of the 1.789 eV PL doublet with the presence of Fe in the growth chamber and in the produced crystals as evidence for the involvement of Fe atom(s) in the corresponding defect centre. Referring to the Ni centres, the trigonal symmetry is consistent with interstitial Fe or with Fe atom in the divacancy cite [1, 2, 4]. The observed quenching of the 1.789 eV doublet, even by a small amount of single substitutional nitrogen donors, can be interpreted as the observed defect being present in a positive charge state [1].

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