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A contribution to the understanding of pink color in diamond: The unique, historical «Grand Condé»

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Abstract

We recorded properties of a historical 9.01 ct pink diamond, the Grand Condé. It is a type IIa diamond that shows very weak absorptions at 860, 960, 1050, 1115 and 1156 cm^{-1} that had not been reported yet. It shows an homogeneous fancy pink coloration with a subtle orangey component, and no discernable colored graining. However, we recorded an absorption band at 550 nm (2.2 eV), usually typical of pink diamonds with colored graining due to plastic deformation: this is the first time that these two properties are reported together for a single diamond. This shows that there is no direct connection between pink graining and the absorption at 2.2 eV.

Second, we recorded a series of sharp absorptions at 573, 586, 594, 600 and 609 nm. We name it the 609 nm system. This system, probably related to the pink coloration, had only once been partially documented before, in three dark pink to red-brown diamonds. The 609 nm system is not related to the intensity of the pink coloration. Although this system might be vibronic in nature, it does not show the typical pattern for a simple vibronic structure.

Keywords: Natural type IIa diamond; Pink coloration; Plastic deformation

1. Introduction

The origin of color in pink diamonds is still a subject of debate. The most common variety of pink diamond displays "pink graining", that is lamellae of pink coloration parallel to {111} [1]. The color itself is due to a broad absorption centered around 550 nm or about 560 nm (about 2.2 eV), depending on the authors [2–5]. This feature is classically attributed to plastic deformation [6,1]. However, the details at the atomic level of the defect responsible for this absorption are still unknown. Some other pink diamonds are known as "Golconda pinks" [1]. These type IIa diamonds show an homogeneous light pink, slightly orangey coloration, due to a strong $N–V^-$ absorption at 637 nm and its associated vibronic structure; this is always associated with an orange luminescence, due to the $N–V^0$ center (zero-phonon line at 575 nm approximately).

Further, high pressure–high temperature treatment of pinkish brown diamond may produce pink diamonds on rare occasions, by removing the brown component of the coloration [7].

In this context, we examined a historical 9.01 ct faceted pink diamond known as the "Grand Condé" diamond (Fig. 1). It has been kept since 1862 in the Château de Chantilly, Oise, France, and catalogued as pink, thus proving its color to be natural. Although well-known and often mentioned, this diamond had not been studied yet because of technical difficulties: it cannot leave the castle for any reason, as is stated in the testament of the Duke of Aumale, descendant of the Prince of Condé and last private owner of the diamond. For this study, we used only transportable instruments and measurements were conducted inside the castle of Chantilly (for details of the gemological properties and colorful history of the stone, see Refs. [8,9]). We encountered some unexpected physical and gemological properties which are unique

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Fig. 1. The historical "Grand Condé" pink diamond, 9.01 ct. Note the subtle orangey hue (for color, the reader is referred to the web version of this article).

compared to published data for pink diamonds. In particular, the unique absorption spectrum is reported here, and we discuss its implications for the origin of the pink color.

2. Methods

We examined the internal characteristics of the stone using a GIA Gem Instruments portable microscope, equipped with an immersion cell with liquid diiodomethane to reduce internal reflections; we also used polarizing filters in order to observe the anomalous double refringence of the diamond. The ultraviolet (UV) luminescence was observed under a Kruss UV240 UV lamp emitting short wave (254 nm) and long wave (365 nm) radiation. Infrared absorption spectra were acquired using a Nicolet 5700 spectrometer brought by Thermo Electron Corporation. Each spectrum is an accumulation of 100 scans at a resolution of 4 cm^{-1} or 0.5 cm^{-1}, acquired in transmission mode, in the range 400–5000 cm^{-1}.

Visible–near infrared (Vis–NIR) absorption spectra in the 400–1000 nm range were recorded with a custom-made system, equipped with an Ocean Optics SD2000 dual channel spectrometer with a resolution of 1.5 nm. A 2048-element linear silicon CCD detector was employed; samples were analyzed using an integration sphere as a light collector.

Photoluminescence (PL) spectra were recorded using a semiconductor laser emitting at 532 nm and a power of 50 mW, with the same spectrometer and CCD detector as described above, at a resolution of 1.5 nm. The diamond was cooled at 77 K in liquid nitrogen for the Vis/NIR and PL spectra.

3. Results

3.1. Physical description

The Grand Condé diamond is faceted as a somewhat irregular, flat pear-shape measuring approximately 20 × 14 × 5 mm.

Under the microscope, the pink coloration appears to be distributed homogeneously. No colored zoning or graining is observed, despite careful examination in immersion liquid. An intense anomalous double refringence is observed between crossed polarizers (Fig. 2): large areas of first and second order colors and coarse black bands crossing over the stone are superimposed on a discrete "tatami graining", deemed typical of type II diamonds [10,11].

Under ultraviolet radiation, the Grand Condé diamond emits a weak yellowish-green fluorescence under long wave, and a weaker whitish-yellow under short wave. Using a "Type IIa Diamond Spotter®", the stone appears transparent to short wave radiation, which is typical for type IIa diamonds. However we did not observe any pink color vanishing after short wave irradiation, although the color of type IIa pink diamonds is commonly unstable under short wave UV radiation (e.g., [12]).

3.2. Mid-infrared absorption

The infrared absorption spectrum of the Grand Condé diamond is shown in Fig. 3. This is typical of a type II diamond as no nitrogen-related absorption is observed in the defect-induced region. Weak absorptions are present at 860, 960, 1050, 1115 and 1156 cm^{-1}. From the various spectra taken, they appear to be true absorption features, but they have never been reported before. We also observe a very weak but true absorption at 1341 cm^{-1} which has been described only once before, in type IIa synthetic CVD diamonds [13]. We acquired spectra at high resolution (0.5 cm^{-1}) in order to establish that this peak is clearly distinct from the classical 1344 cm^{-1} nitrogen peak, as well as water vapor peak (the 1341 cm^{-1} peak we observe is too broad and not at the right position for water). The origin of this peak remains also unknown.

3.3. Visible–near infrared absorption

The visible–near infrared absorption spectrum of the Grand Condé diamond is shown in Fig. 4. We observe a large absorption band centered at about 550 nm, typical for pink diamonds that show pink colored graining.

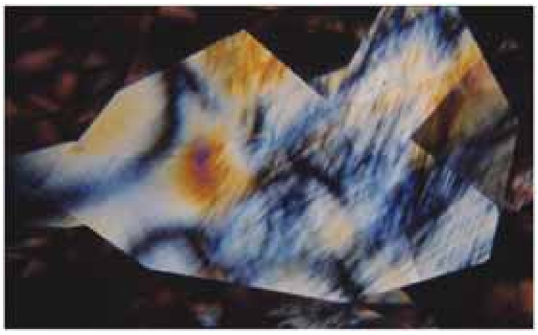

Fig. 2. Anomalous double refringence of the Grand Condé diamond observed between crossed polarizers. Broad bands of first order interference colors are superimposed on a discrete "tatami graining" typical for type IIa diamonds, suggesting significant strain.

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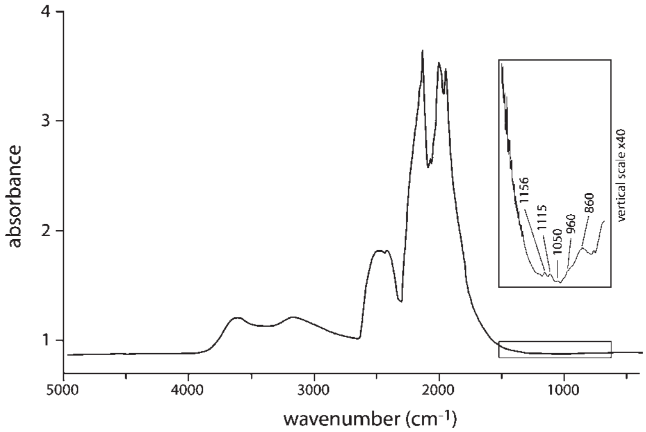

Fig. 3. Infrared absorption spectrum of the Grand Condé diamond in the range 480–5000 cm^{-1}, at a resolution of 4 cm^{-1}. The diamond is clearly type IIa and has minor, unknown absorptions in the defect-induced region.

Table 1
Peaks belonging to the 609 nm system: peak position shows that they are not equidistant in energy, thus it is unlikely to be a vibronic system

a)	b)	c)	d)
573	2,164	48	22
586	2,116	30	14
594	2,088	21	11
600	2,067	31	10
609	2,036		18

a) Peak position (nm); b) peak position (meV); c) energy difference between two successive peaks (meV); d) peak width (meV).

In addition to the main, large band, we observe a series of superimposed weaker and sharper absorptions at 573, 586, 594, 600 and 609 nm approximately. For commodity, we propose to call this series the 609 nm system, as the 609 nm band is that of lowest energy. The main three were once before reported in three pink to red-brown diamonds [3], at 590, 605 and 610 nm; because of the weakness of the system in this case, the positions were rounded to the closest 0 or 5 nm position, and the two weakest peaks were not visible. Note that the 609 nm system was much weaker in this case, even if the diamonds were much darker. The peaks of the 609 nm system are not equidistant in energy (Table 1). Neither do they show the classic progression of a vibronic structure, with the lowest energy absorption being sharp and intense, and the phonon sidebands becoming broader and less intense with increasing absorption energy. Hence, this feature is not a simple vibronic structure, as originally suggested [3]. If vibronic, it must involve several systems.

These features are superimposed on an absorption continuum rising towards the UV, which is likely responsible for the orange component of the color.

We also observe a weak, sharp absorption at 741 nm that corresponds to the well-known GR1 center. It is related to the presence of carbon vacancies due to a small amount of natural irradiation, as is commonly observed in natural diamonds.

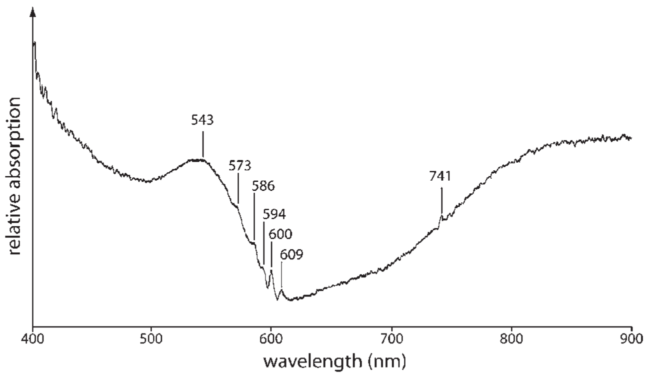

Fig. 4. Visible–near infrared absorption spectrum of the Grand Condé diamond in the range 400–900 nm, showing the 550 nm broad band as well as the superimposed 609 nm system, and a very weak GR1 absorption at 741 nm.

3.4. Photoluminescence

No luminescence is excited with a 532 nm laser. This is rather surprising for a colored type IIa diamond not to observe the emissions corresponding to absorptions in the visible range.

4. Discussion

The first unique character of the Grand Condé diamond is that it does not show any pink colored graining, yet it is colored by the broad 550 nm absorption band. This is the first time such properties are recorded together in a pink diamond. One other such stone has been recently observed in the trade [14]. One could argue that the pink graining is so thin that it cannot be observed using a binocular microscope only. However, the intense pink coloration of the diamond would imply a strong pink graining. Further, the observation between crossed polarizers did not reveal any planar features correlating to colored graining, as it always does when it is present, even very thin.

The disconnection of pink graining from the 550 nm band is still consistent with the pink color being related to plastic deformation. As a matter of fact, the anomalous double refringence of the Grand Condé is high compared to that of a classical type IIa diamond (even if it does not underline lamellae of colored graining). It is comparable to that of many type Ia diamonds, and the so-called “tatami graining” is not dominant here. This is sometimes observed in type IIa stones, irrelevant of their color [14]. This is suggestive of a high amount of strain in this crystal, and the coloration could be related to this strain, even if somewhat different from that observed in graining.

Secondly, the Grand Condé shows the best example recorded so far of what we propose to call the 609 nm system, with five

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intense peaks (instead of the three recorded earlier). This series has only been documented in type Ia pink to red diamonds so far [3], suggesting that it is somehow related to the pink coloration. Alone, this system is not a strong absorber and probably does not participate in the coloration process. Further, among the published examples, the intensity of this series of absorptions is not related to the intensity of the 550 nm band, or even to the intensity of the pink color. Neither can it be, as originally suggested, the vibronic structure associated with the 550 nm band, even if this band is known to be of a vibronic nature [2]. The fact that the 609 nm system has been observed in type I and type II pink diamonds suggests that nitrogen is most likely not involved in the associated defect, as it is strong in type IIa diamond and weaker in type Ia diamond.

Thirdly, in general, most type IIa diamonds fluoresce blue, and some orange [5]. Hence, the observed greenish to white UV-excited PL is also very unusual.

Finally, the absence of 532 nm laser excited PL is a rare fact even among type IIa stones, in particular colored ones. This further illustrates the uniqueness of this stone, together with the highly unusual UV luminescence color.

5. Conclusion

The Grand Condé diamond displays optical properties that had never been described together. First, most importantly, it demonstrates for the first time that there is no direct connection between pink graining and the 2.2 eV absorption. Yet, this is not inconsistent with this last band being related to plastic deformation. Second, this diamond displays the best known example of a rare group of absorption features we propose to call the 609 nm system. This cannot be the vibronic structure of the 2.2 eV band, as suggested earlier, although there is probably a connection to the pink color. The origin of this absorption at the atomic level is still unknown. Third, the luminescence behavior is highly unusual for a pink type IIa diamond: greenish white PL emission under UV lamps, and no PL emission excited with a 532 nm laser. Fourth, the Grand Condé displays some very weak IR absorptions at 860, 960, 1050, 1115 and 1156 cm^{-1} that had not been reported yet, but remain unexplained.

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