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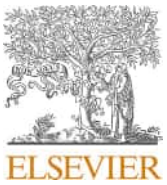

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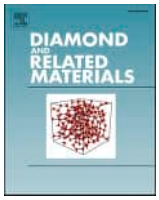

Twins separated at birth: Identifying pairs of polished diamonds with irradiation-related color from the same rough by fingerprinting using imaging and spectroscopy

Thomas Hainschwang [a,*], Franck Notari [b], Gianna Hainschwang [a], Michael Shara [c]

[a] GGTL Laboratories Liechtenstein, Gnetsch 42, 9496 Balzers, Liechtenstein
[b] GGTL Laboratories Switzerland, 4bis route des Jeunes, 1227 Geneva, Switzerland
[c] American Museum of Natural History, CPW & 79th street, New York, NY 10024, USA

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ABSTRACT

Some of the most famous diamonds of historical significance display beautiful and rare colors such as pink, blue and green. Many have been recut one or more times, either in attempts to improve their appearances, or to disguise their provenance. Given the major advances in instrumentation for characterizing diamonds in the past two decades, we pose the question: can one devise a methodology to create an analytical fingerprint of a diamond to identify it even after recutting, or to identify two polished diamonds of unknown provenance as having been cut from the same rough or polished diamond? To determine if this is feasible, we carried out an in-depth study of two pairs of polished diamonds colored mainly by the GR1 absorption, one pair known to have been cut from the same rough crystal, and one pair of diamonds of unknown provenance for which it was possible to prove that they originated from the same piece of rough. The data obtained by a combination of absorption spectroscopy from the UV to the mid-infrared, photoluminescence spectroscopy with various lasers from the UV to the NIR and luminescence imaging with a range of excitations was found to establish, beyond any doubt, that each of the two diamond pairs shared a common progenitor.

Nevertheless, for each of the diamond pairs only one diamond was identified as naturally colored while for the other one the color origin was given as "undetermined" by a prominent *gem* testing laboratory. The methodologies described herein can prevent such inconsistencies regarding diamonds of previously unknown provenance; they show spectroscopically how and why the color of some natural color origin green diamonds is enhanced by polishing, especially when removing surface radiation "stains"; further, such methodologies will identify "diamond twins separated at birth".

1. Introduction

Some of the most famous historical diamonds are those that have been either bought and sold several times, or stolen from their owners or looted from government treasuries one or more times. The 67 carat "French Blue" sold by Jean-Baptiste Tavernier to Louis XIV and looted in 1792 during the French revolution has almost certainly been recut into the 45 carat Hope diamond, now located in the Smithsonian Institution [1]. If there are other pieces of the French Blue still in existence [2], could they be identified as such? In addition to the Hope diamond, other infamous examples include the Sancy diamond, the Great Table diamond and the Orloff [3]. Each of these diamonds (and doubtless many others) may have been recut and/or repolished multiple times, to improve their appearance, obscure their provenance, or both. It would be of great interest for historians of the world's great diamonds to identify pieces cut from some of the world's most famous gems.

Even in the case of relatively anonymous diamonds, being able to identify two or more pieces sawn from the same rough material could be of significant gemological or financial interest. In particular, while trying to establish that certain rare, fancy-colored diamonds are of natural color origin, it might be useful to be able to "link" two polished stones to the same piece of rough material. We are unaware of any published attempt to establish a methodology for carrying out such an identification. The opportunity to do this presented itself to the authors serendipitously when they were requested to examine, characterize, and issue fingerprint reports for two pairs of polished diamonds colored

* Corresponding author.
E-mail address: thomas.hainschwang@ggtl-lab.org (T. Hainschwang).

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mainly by the GR1 defect. One of these pairs of unknown origin was first analyzed in 2014 and then again in more details in 2023, and the other pair of known origin was characterized recently only, in 2023.

The goal of this paper is to describe the results of imaging and spectrographic analyses to create a unique data fingerprint for a diamond. With this study we have established, beyond any reasonable doubt, that the two pairs of colored diamonds, one pair of unknown origin and one pair with known origin from the same rough, did indeed have a common origin for each pair. The same methodology can be used to test whether other purported "twins separated at birth" have a common origin. The diamond fingerprinting procedure to create a dataset with which a diamond can be identified at any time - even after recutting (within certain limitations) - has been developed by one of the authors (TH) from 2017 to 2019 and has been introduced in the market in collaboration with Mark Cullinan as the "Cullinan Reports" [4]. One of the motivations for the current paper is to encourage other labs to adopt, and perhaps improve on the methodology described in detail in what follows. An additional benefit of this methodology is that we are able to demonstrate the spectroscopic changes that some green diamonds undergo, during polishing, that enhances these diamonds' green colors.

1.1. Background on the color origin of diamonds with radiation-related color and the testing thereof: a true conundrum

Naturally colored diamonds are rare, especially those with violet, pink to red, orange, blue and green colors [5]. The color of diamonds can be changed by a range of treatment methods, including electron and neutron irradiation [6], high temperature treatment [7], high pressure/high temperature and combinations thereof [8,9]. Since virtually any color except violet can be produced by treatment, and since treated diamonds are of much lower value than naturally colored diamonds, it is of utmost importance to the market that competent *gem* testing laboratories can conclusively distinguish untreated colored diamonds from their treated counterparts. For an experienced diamond expert with the right analytical equipment, the identification of the color origin is usually rather straight forward. This is not true for diamonds colored by irradiation-induced defects. Here we approach the limit of the analytical capacities for any lab, because both natural and artificial irradiation have the same effect on diamond: they knock out carbon atoms to create vacancies and interstitials [10]. Simple irradiation creates neutral vacancies known as GR1 (V^0) and negatively charged vacancies known as ND1 (V^-) and a series of interstitial-related defects [11 and references therein]. Further, irradiation results in accumulations of vacancies similar to what is known in brown diamonds as "vacancy clusters". Of these defects created by irradiation, the neutral vacancy induces color-causing absorption from about 745 to 510 nm which results in a greenish blue color when the diamonds were colorless before irradiation. The vacancy clusters are generally the result of higher incident energies of irradiating particles or photons and add an absorption continuum to the GR1 and ND1 absorptions, known as the "UV band" [12]. As the UV band increases linearly with increased irradiation energy and dose (in the experience of the authors), and as it is not created by low doses of low energy electrons (e.g., 0.5 to 1.5 MeV) it is clearly not linked to simple vacancies. As the continuum of the UV band needs significantly higher annealing temperature to be annealed out than the GR1 (plus all other GR bands in the UV to violet spectral domain) and ND1 defects, it appears reasonable to speculate that the defect is of similar structure as other "brown-causing" continua such as known in natural and CVD synthetic diamond; therefore the authors tentatively assign the UV band continuum being linked to a cluster-like vacancy defect.

With this added continuum, the color turns from a dominantly blue hue to a dominantly green hue. There are other ways of obtaining green instead of blue colors, such as the use of yellowish diamond as a starting material. Vacancies and especially interstitials are mobile at rather low temperatures, with interstitials starting to move in the lattice from temperatures as low as 100 °C and vacancies from about 500 °C; these temperatures vary from diamond to diamond, mostly depending on the presence of other defects. At temperatures above 500 °C vacancies migrate rapidly to join whatever nitrogen impurities are present in a diamond to form nitrogen-vacancy defects such as NV^0, NV^-, H2, H3 and H4 [13], while the GR1 and ND1 defects anneal out. In type Ia diamonds the defects that influence the color most after such annealing are H3 and H4; they are the reason for yellow bodycolor and green luminescence (most pronounced in so-called "green emitter" diamonds) [14]. Hence there is a range of diamond colors that are related to natural or artificial radiation [15].

The extreme similarity of diamonds colored by artificial irradiation and diamonds colored by natural radiation has led to the situation that such diamonds often obtain an "undetermined" color origin by a *gem* testing laboratory, meaning that the laboratory cannot identify the color origin as natural or treated. In the authors' experience the procedure of identifying the color origin is a very detailed and complex procedure combining the observation of color distribution, spectroscopic analysis by absorption and luminescence spectroscopy and luminescence imaging. The exact procedure used is usually unpublished and part of any lab's internal confidential procedures of how to approach this problem. This results in the unfortunate situation that apparently random conclusions for such diamonds are not rare, and that contradictory conclusions reached by the same lab on the same stone, with no apparent nor justified reason, occur. This work is part of the research project on this topic by the authors that has been ongoing since 2009. Based on an important database of historical green to greenish blue diamonds predating the 1940's (and hence of unambiguous natural color origin) and a large database of treated diamonds that we have assembled through a significant diamond treatment research project, we are currently in the position to accurately identify the color corigin of the vast majority of diamonds colored by artificial or natural radiation.

2. Materials and methods

Four individual diamonds comprising two pairs, and individually weighing 0.76 to 7.74 ct were analyzed in detail for this study (Fig. 1). See Section 2.1 (sample table) for details on the diamonds. The color distributions and strain patterns of the diamonds were analyzed using a Leica M205C Trinocular Microscope, equipped with a Leica DFC450 CCD camera. The color distribution was checked with the diamonds immersed in ethanol alcohol ($n = 1.36$) or diiodomethane ($n = 1.74$). The strain patterns were analyzed with the stones immersed and between crossed polariser and analyser. Infrared spectra of all the samples were recorded with a resolution of 4 cm^{-1}, and for some also 1 cm^{-1}, on a Perkin Elmer Spectrum 100S and on a Perkin Elmer Frontier FTIR spectrometer, both equipped with a thermoelectrically cooled DTGS detector, using a diffuse reflectance accessory as a beam condenser and a 5× beam condenser. The spectra were recorded over the range of 8500 to 400 cm^{-1}, with 50 to 200 scans for each diamond averaged to improve the signal-to-noise ratio of the final spectrum. The nitrogen concentration was determined by progressive spectral decomposition via spectral calculations ("progressive decomposition"). It was calculated based on the known average absorbance of the intrinsic diamond infrared feature at 1995 cm^{-1}, which has been defined by others as 12.3 absorbance units per cm of optical path [16].

Fig. 1. The two pairs of diamonds that were analyzed for this study. Left: pair (hereafter called "pair 1") - 7.74 ct and 2.91 ct; right: (hereafter called "pair 2") - 0.96 ct and 0.76 ct. Photos: T. Hainschwang.

All diamond spectra were normalized before the concentration calculation could be reliably conducted. This normalization was performed by spectral calculation, for which the absorbance value of the intrinsic diamond absorption on the Y axis at 1995 cm^{-1} was measured and then a multiplying factor was applied in order to obtain a value of 12.3 cm^{-1}. The spectrum was then multiplied by this factor. Normalization of the diamond infrared spectra cannot only be performed using this method – but actually any desired intrinsic diamond absorption maximum between 4000 and 1550 cm^{-1} can be chosen since these maxima are constants just like the point at 1995 cm^{-1}. This way, even a spectrum not fully resolved at 1995 cm^{-1} can still be properly normalized for the calculation of nitrogen concentrations.

For the "pair 2", nitrogen calculation was performed by progressive spectral decomposition in which the individual components (A and B centers) were subtracted from a given spectrum, using reference spectra of pure signals of the respective centers. For the "pair 1" the nitrogen absorption was too strong and could not be fully resolved; therefore the calculation of the A and B center nitrogen concentrations were obtained based on the formula defined by the authors for nitrogen content calculations based on the secondary nitrogen peaks at 482 cm^{-1} (A centers) and 1010 cm^{-1} (B center). Near infrared spectra in the range 11′200 to 4000 cm^{-1} (900 to 2500 nm) were recorded using a custom-built GGTL NIR spectrometer system using a thermoelectrically cooled InGaAs detector, in a 15 cm integrating sphere using a 150-Watt NIR light source. Spectra were recorded with 50 scans for each diamond, at a resolution of 4 cm^{-1}, at room temperature and with the samples cooled to 77 K using a special custom-built low temperature accessory.

Photoluminescence spectra were recorded on a GGTL Photoluminator RS6 system using 360, 402, 473, 532 and 635 nm laser excitations, and a high-resolution Echelle spectrograph by Catalina Scientific equipped with an Andor Neo CMOS camera, thermoelectrically cooled down to −30 °C. The system was set up to record spectra in the range of 350 to 1150 nm with an average resolution of 0.06 nm. All photoluminescence spectra were recorded with the diamonds cooled to 77 K by direct immersion in liquid nitrogen. Diamond positioning and mapping on this system is achieved using computer controlled motorized XYZ platforms. PL and Raman signal is collected using our own optical design focussing the signal into an optical fiber connected to the spectrometers used. As diamond can be a notoriously non-homogenous material, particularly concerning its defect distribution in PL, samples were scanned and mapped carefully using the lasers and system described above with a lower resolution but high-throughput Avantes Avantspec ULS-RS TEC CCD spectrometer covering the range of 240 to 1040 nm to record the most representative spectrum rather than one of a small area with concentrated defects that are non-representative of the average sample; the defect distribution was also verified by luminescence imaging prior to PL spectroscopy (see below). UV–Vis-NIR spectra were recorded on a GGTL D—C 3 spectrometer system using a combined xenon, halogen and LED light source; a quadruple channel spectrometer with a Czerny-Turner monochromator and a thermoelectrically cooled CCD detector was employed, with an average resolution of 0.3 nm. The spectra were measured with the samples cooled down to 77 K and placed in an integrating sphere of 15 cm diameter.

Luminescence imaging was performed using a prototype GGTL Mega DFI luminescence imaging and spectroscopy system which is based on a 1500-Watt deep UV enhanced xenon light source properly filtered to create a broad emission band from 200 to 430 nm while suppressing all other visible and near infrared wavelengths. The broad UV band is then subdivided into 6 different UV excitations centered at wavelengths of choice between 215 nm to 380 nm using high-quality band pass, and short pass filters. The excitation bands chosen for these diamonds were the following:

1) a narrow band centred at 214 nm with FWHM of 10 nm.
2) a broader band with FWHM of 20 nm centred at 220 nm.
3) a relatively narrow band centred at 265 nm of FWHM of 10 nm.
4) a relatively broad band centred at 280 nm with a FWHM of 30 nm.
5) a broad band centred at 320 nm with FWHM of 70 nm.
6) a broad band of a FWHM of 65 nm centred at 350 nm.

For luminescence observations the system uses both a Leica 495 camera for long exposure imaging and an Optica SZP fluorescence microscope for direct observation. For luminescence and Raman spectroscopy the microscope is coupled to an Avantes double channel spectrometer with a thermoelectrically cooled CCD detector and a resolution of 0.7 nm over the spectral range of 240 to 1060 nm; in addition, a 300 mW 405 nm laser is coupled through its optics as additional excitation for luminescence imaging and for both luminescence and Raman spectroscopy.

2.1. Sample table

	Sample #	Color	Weight	Cut	Type	Nitrogen content (±5 %)	Comments
Pair 1	23-D-12621-a	Yellowish green	7.74_2 ct	Rectangular cushion modified brilliant	IaA ≫ B	A: 1200 ppm B: 140 ppm	None
	23-D-12621-b	Brownish greenish yellow	2.91_0 ct	Partially faceted cushion	IaA ≫ B	A: 1200 ppm B: 140 ppm	Color modified by brown radiation stains
Pair 2	23-D-12631-a	Green	0.96_5 ct	Pear rose cut	IaA ≫ B	A: 940 ppm B: 140 ppm	Old cut – originally mounted in antique earrings
	23-D-12631-b	Green	0.76_1 ct	Pear rose cut	IaA ≫ B	A: 940 ppm B: 140 ppm	Old cut – originally mounted in antique earrings

3. Results and discussion

3.1. Fingerprinting of diamond pair 1

3.1.1. Visual characterization

The first pair of diamonds visually appeared noticeably different from each other, since the smaller stone presented a brownish greenish yellow color when face up while the larger stone was yellowish green in color (see Fig. 1). Hence by simple visual observation their relationship was not apparent. Their origin from the same rough was claimed by the owner of the two diamonds. Under the optical microscope both stones showed mostly brown and a few green radiation stains from natural alpha particle irradiation [17]. The smaller stone was only partially finished with less-than-ideal proportions. In addition, it had large, indented naturals and many more brown radiation stains than the fully facetted and well-proportioned larger diamond.

When immersed in methylene iodide (n = 1.74) both diamonds exhibited a homogenous color besides the only shallowly penetrating irradiation stains. Under crossed polarizing filters both stones showed modest strain-related double refraction but since the smaller diamond was only partially faceted, we were unable to create a meaningful comparison of the extinction patterns.

3.1.2. Luminescence imaging

Luminescence imaging was performed for the two diamonds with all 6 excitations of the Mega DFI Instrument, from 380 to 215 nm. The luminescence of the diamonds was very weak, particularly under shorter

Fig. 3. The details of the very fine growth structure of the two diamonds, reminiscent of a barcode, as revealed by short wave UV excitation of the Mega DFI luminescence system. Part of the image taken from the 7.74 ct diamond (inside the rectangle labeled "a") was superimposed on the image recorded from the 2.91 ct diamond (the rest of the image labeled "b"); a 100 % perfect match of the two growth structures in the two directions was obtained. This "fingerprint matching" is proof that the stones originate from the same rough and demonstrates that the tables of each stone lie in the plane where the stones were connected, hence corresponding to the plane where the diamonds were laser-sawn. Micrograph: T. Hainschwang.

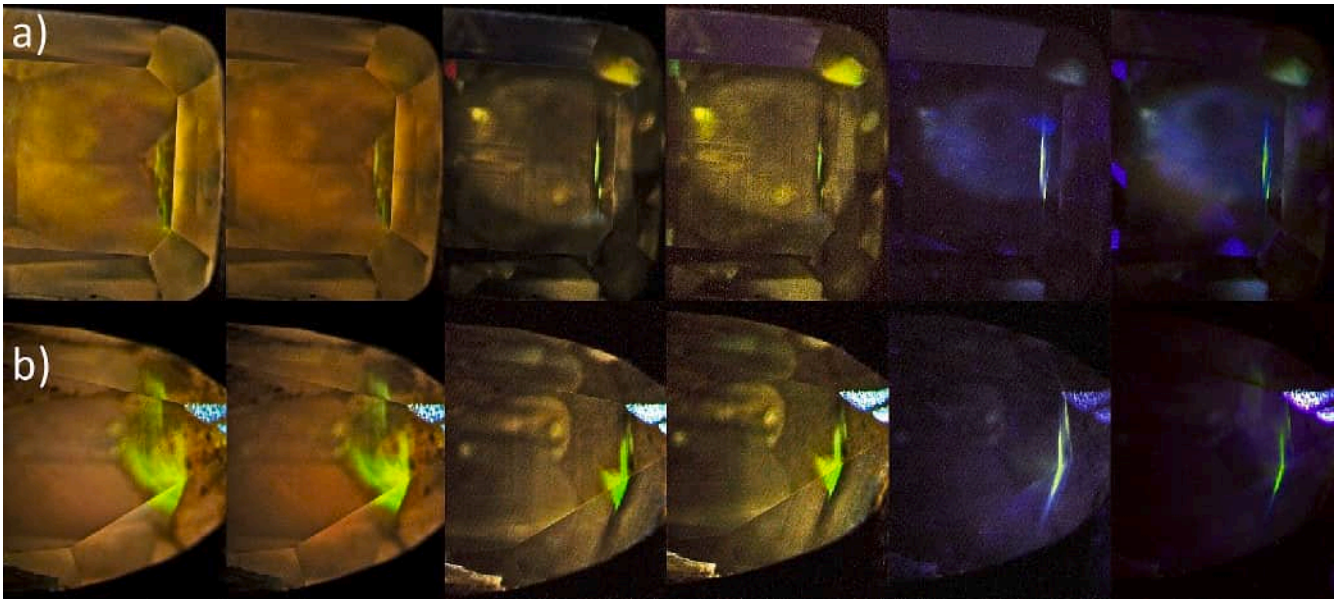

Fig. 2. The luminescence images of the two diamonds, recorded using a Mega DFI system at 6 different wavelengths from 380 to 215 nm (left to right), demonstrate the extreme similarity of the two diamonds. Both the general luminescence as well as the presence of localized green luminescence from the H3 center at the same position of the diamonds make it highly likely that the stones originate from the same rough. Photos: T. Hainschwang.

UV wavelengths, but nevertheless the similarities of the two diamonds when analyzed through the table were striking: in Fig. 2 one clearly sees that both stones exhibited the exact same general luminescence and that both show a localized zone of green fluorescence from the H3 center at the corresponding edges of their table facets. These images alone are by themselves a very strong indication that the two stones originate from the same rough.

To further exploit the power of these luminescence images we took the images recorded under short wave UV that most clearly showed the diamonds' growth sectoring and superimposed the image of the 7.74 ct diamond onto the image of the 2.91 ct diamond; the result was remarkable, with a 100 % match between the growth sectors; the exact same quantity of and spacing between the growth lamellae can be seen (Fig. 3). This more detailed analysis of the luminescence unambiguously proves the origin of the two diamonds from the same rough, and further demonstrates that the diamonds were originally joined where the diamonds' table facets have been placed, hence they were laser sawn parallel to the plane that was then used to polish the table facets.

3.1.3. *Infrared spectroscopy*

The infrared spectra of the two diamonds identified each as type IaA ≫ B with the same nitrogen speciation and content of 1200 ppm A centers and 140 ppm B centers (±5 %) (Fig. 4). Even though the spectrum of the much larger 7.74 ct diamond could not be as well resolved as the spectrum of the smaller sample (because of the much longer pathlength that the IR light travels through the diamond), after normalization at the available fully resolved intrinsic diamond bands all spectral features except the hydrogen peaks at 3107 and 1405 cm^{-1} matched at nearly 100 %.

A proper residual trace could not be elaborated for these two spectra as there were too many unresolved spectral bands (due to some of the intrinsic diamond absorptions and the main nitrogen-related one-phonon absorption band). A minor spectral difference was visible for the intensity of the hydrogen absorptions at 3107 and 1405 wavenumbers, which is easily explained as a slightly inhomogeneous distribution of hydrogen in the progenitor rough stone. Such inhomogeneities are common and well-documented [18].

In the inset in Fig. 3 the perfect match not only in intensity but also Full Width at Half Maximum (FWHM) of all spectral features, including the platelet peak at 1373 cm^{-1} with FWHM of 22 cm^{-1}, is demonstrated. To find two diamonds with such identical platelet peak absorptions is virtually impossible unless the two stones originate from the same rough.

3.1.4. *UV–Vis-NIR spectroscopy*

A surprise to anyone only visually seeing these two diamonds – one appearing predominantly green and one predominantly yellow – the UV–Vis-NIR spectra (recorded at 77 K) exhibited near identical spectra dominated by radiation-related absorption bands caused by the ND1, GR1, 594.2 nm and H3 defects as well as the N3 center absorption. For details on these defects refer to [11] and references therein. In Fig. 5 the two spectra and the residual trace (after subtraction of the spectrum of the 7.74 ct diamond (labeled a) from the spectrum of the 2.91 ct diamond (labeled b)) are shown, shifted vertically for enhanced clarity. It is apparent that all spectral bands are virtually identical in both intensity and FWHM, and that the only significant difference between the spectra is an absorption continuum increasing from 750 to 325 nm. The barely visible weak nickel-nitrogen defect related absorptions in the NIR portion of the spectra are not elaborated further but consist of the many complex bands described by the authors in an earlier publication [19]. This absorption continuum is the explanation of why the smaller diamond appears brownish greenish yellow and not yellowish green like its bigger "twin": The continuum adds a yellow brown color to the smaller diamond which, in combination with its much smaller size and far-from-ideal proportions, results in its different and less attractive color. The absorption continuum is the result of the multitude of brown irradiation stains and their reflections within the diamond. If properly recut, thereby removing the brown radiation stains, the visual color of the 2.91 ct diamond would doubtless become significantly greener, resembling its "twin".

The luminescence imaging and absorption spectroscopy results presented above have demonstrated that the 7.74 and 2.92 carat diamonds, with very different visual appearances in Fig. 1, must be "twins" derived from the same rough stone. As shown in Fig. 5, the removal of most of

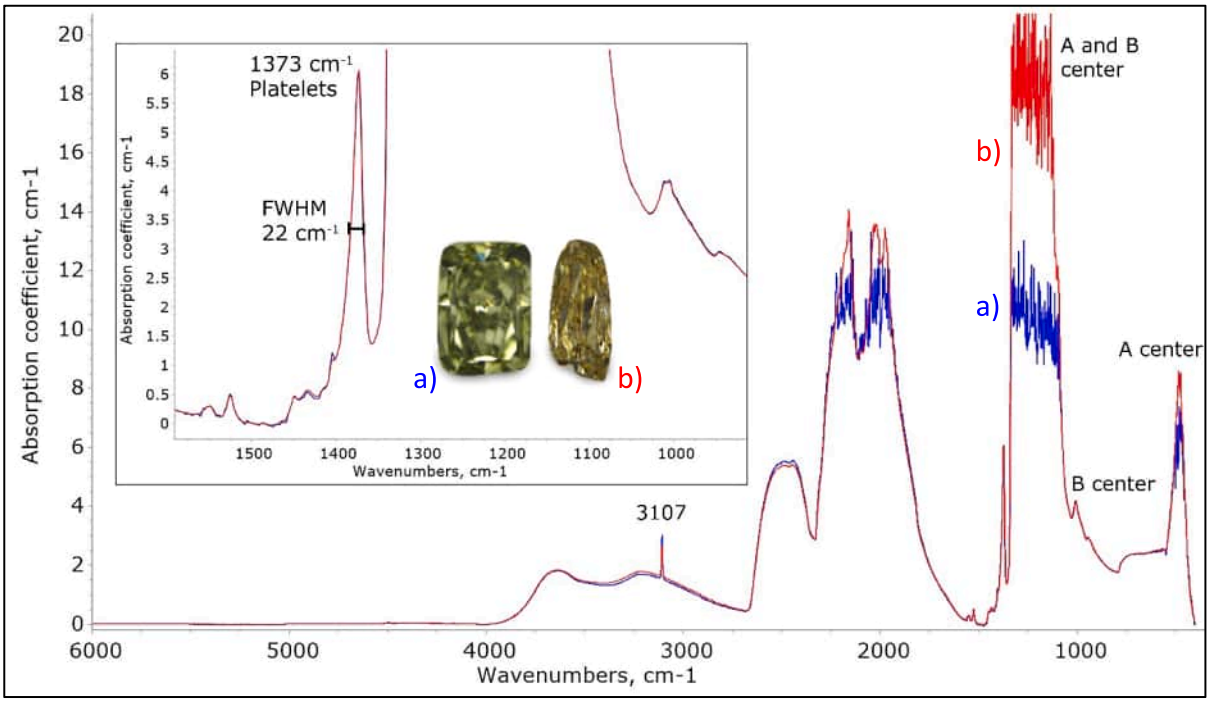

Fig. 4. The infrared spectra of the 7.74 and 2.91 carat diamonds, normalized and superimposed. The extremely close match of the two spectra is apparent, with only the 3107 and 1405 cm^{-1}H-related absorptions showing a slight intensity difference.

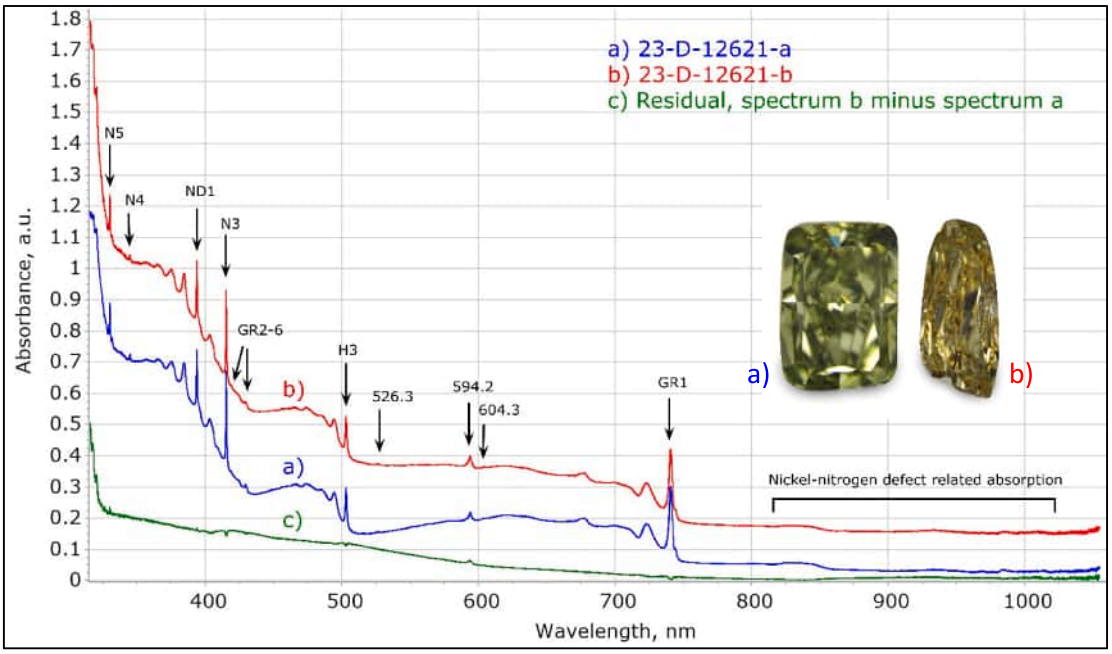

Fig. 5. The UV–Vis-NIR spectra of the 7.74 and 2.91 carat diamonds and their residual after subtraction of spectrum a) from spectrum b) show that all spectral features are practically identical except for an underlying absorption continuum that ranges from 750 to 325 nm in the spectrum of the smaller diamond. This continuum – in addition to size and cut proportions – is responsible for the different color appearance compared to its bigger "twin". Since the path length through sample a) was distinctly longer than through sample b), the spectra had to be slightly adjusted to each other. This was obtained by normalization based on their N3 center absorption which can be considered to be of rather homogenous distribution in these specific diamonds. Spectra shifted vertically for enhanced clarity. See text for further details.

the radiation staining from one of these "twins", but not the other, resulted in only apparently insignificant changes to the absorption spectrum but modified the visual color of the "more polished" diamond dramatically, enhancing its visual green color. The UV–Vis-NIR absorption spectroscopy in Fig. 5 shows that the only change that must have happened to the 7.74 ct diamond is the removal of the "brown continuum" that originates from the brown radiation stains. A diamond's color can be dramatically modified through the polishing process, and

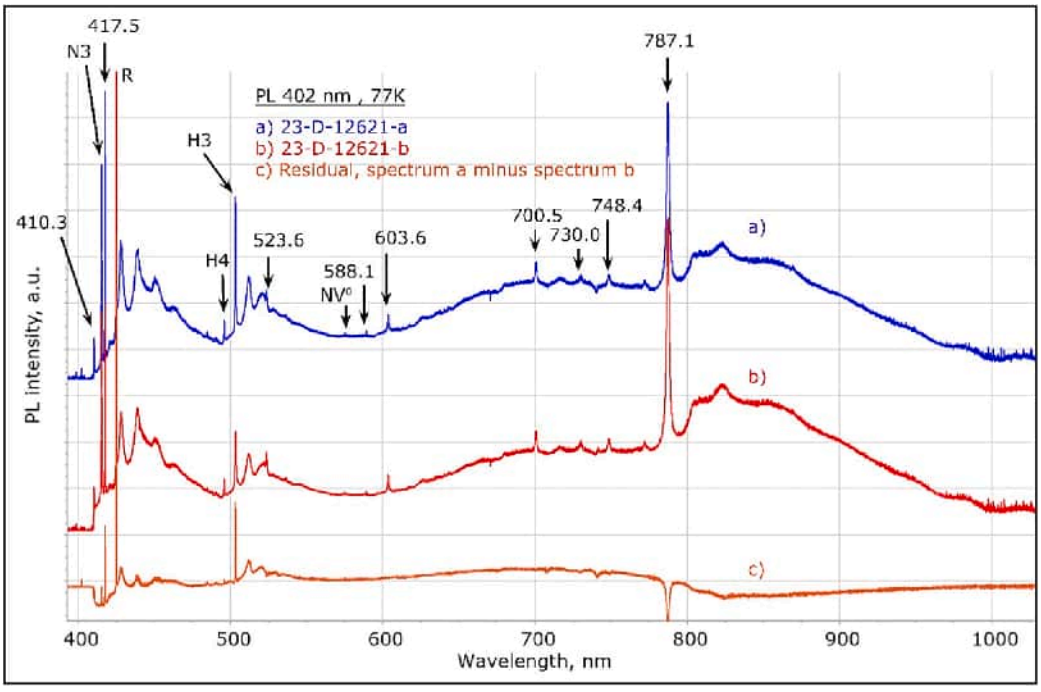

Fig. 6. The 402 nm laser PL spectra of the 7.74 and 2.91 carat diamonds cooled to 77 K and their residual trace show that every spectral feature seen in one of the pair is also present in the other: not a single PL peak found in sample a) is absent in sample b) and vice-versa. The only apparent difference between the spectra of the two diamonds is the intensity of some of the spectral features. Such intensity differences are due to heterogenous distribution of defects throughout the mass of the original rough diamond, and the influence of different sizes and cut proportions of the two diamonds on the fluorescence. The spectra are shifted vertically for enhanced clarity.

these two stones are outstanding examples to demonstrate this. Supporting this statement is the observation that "cape" type yellow diamonds typically look rather pale when cut as a regular brilliant cut, while the color of such diamonds with a rather pale bodycolor can be strongly intensified by the use of other cutting styles such as cushion or cut-cornered modified brilliant cuts (i.e. Radiant cut etc.). The same effect is no less true for individual green to greenish blue diamonds: as more and more of their radiation stains are removed, and well-placed facets are added or modified to increase the pathlengths (and concomitant selective absorption) of light, green diamonds can be made to appear more intensely green as polishing proceeds, without them having been irradiated or "treated" in any way. Gemological labs wishing to ensure against such treatment can and should measure and *quantitatively* compare spectra at various polishing stages to ensure that no irradiation treatment (which strengthens the GR1 absorption and induces other various vacancy and interstitial-related defects) has been used in between cutting steps. Conclusions about the common (or not) progenitor of a pair of diamonds, or by extension the color origin of an individual diamond, based on its visual appearance alone, *have no scientific validity*.

3.1.5. Photoluminescence spectroscopy

The 7.74 and 2.91 carat diamonds were characterized by PL spectroscopy using a range of lasers, of which the spectra using 402, 473 and 532 nm are presented here (Figs. 6, 7 and 8). Each diamond was exposed to the same laser excitation radiation for the same length of time. The spectra recorded with these three laser wavelengths all demonstrate that the defects within the lattices of these two diamonds are identical, and present in very similar concentrations. While PL is inherently not a quantitative method, the very similar emission intensities with identical PL exposure time is an effective measure to indicate similar defect contents obtained under identical acquisition conditions. While there are noticeable intensity differences observed for some of the spectral features, overall, the intensities of the pairs of spectra are extremely similar. Most telling is that, when examining PL peak by PL peak, it is obvious that *every* single peak present in the one diamond of the pair was *also* present in the other diamond, and that is true for every pair of PL spectra recorded.

The intensity differences between spectra are due to heterogenous distribution of defects through the mass of the original rough diamond [20,21], and the impossibility to avoid the influence of such zones when recording the PL of weakly luminescing diamonds. In addition, the masses and cuts of the tested diamonds likely play a role, as the area excited by the laser is larger in the bigger diamond and reflections of the luminescence within the diamond are more efficient in a well-cut diamond than in poorly cut stones. For these reasons an otherwise non-fluorescent, well-cut diamond with a small, strongly fluorescing area near the culet may appear overall strongly fluorescent when observed face-up under UV illumination. Therefore, we expect more intensity variations in PL spectra than in absorption spectra, particularly in diamonds of significant size difference and different cut proportions. The presence of all defects with similar overall PL intensity is hence more determining of "kinship" between two diamonds than exactly the same intensities of all individual PL features.

3.2. Fingerprinting of diamond pair 2

3.2.1. Visual characterization

The second pair of pear rose cut diamonds that was originally mounted in a pair of antique earrings visually looked very similar as they both were green in color and of similar size and cut (see Fig. 1). The larger stone appeared of somewhat deeper green color, likely linked to its larger body mass and hence larger light pathlength and increased selective light absorption. When immersed in methylene iodide (n = 1.74) both diamonds exhibited a homogenous color, and no obvious zoning could be observed. Under crossed polarizing filters both stones exhibited distinct strain-related double refraction. Since the stones were of good cut and transparency the extinction patterns in each could be analyzed and compared meaningfully. It is important to note that strain patterns are not homogenous at all throughout the mass of a diamond and will be modified when a diamond is split into two or more stones. The comparison of strain can only be used to observe an overall similarity, not to find patterns that can actually be overlaid on top of each other. Fig. 9 displays extinction appearing like irregular curved black bands that intersect in the core of each of the diamonds with a roughly similar distribution. This kind of strain is likely caused by strain between growth sectors, visible in both diamonds (Fig. 9). Typically, such strain occurs when diamonds have both cube or cuboid and octahedral sectors [22]; since the tested stones are natural diamonds the strain is likely caused by cuboid octahedral mixed growth [23].

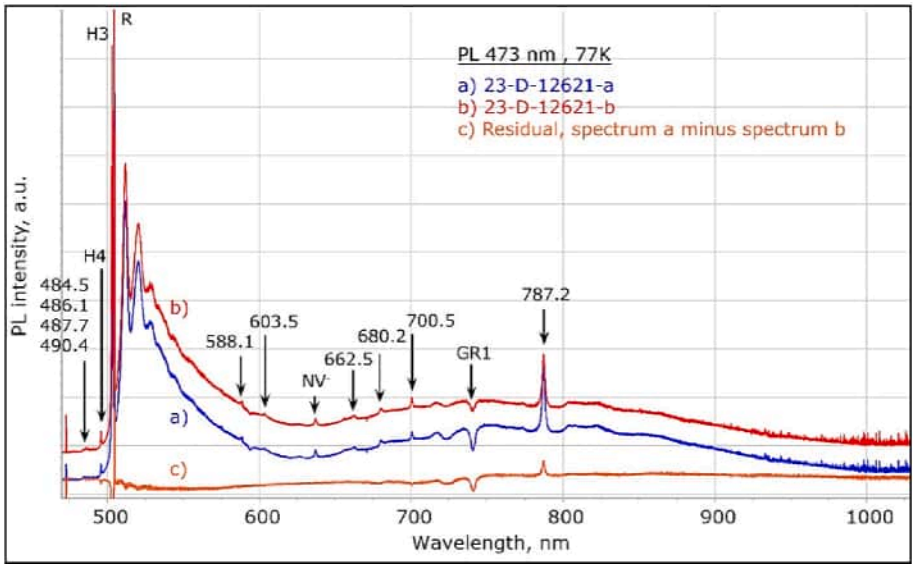

Fig. 7. The 473 nm laser PL spectra of the 7.74 carat and 2.91 carat diamonds cooled to 77 K and their residual trace show that the spectral features of the two diamonds are all identical; only slight intensity differences (due to different sizes and cuts of the two diamonds) can be seen. Spectra shifted vertically for enhanced clarity.

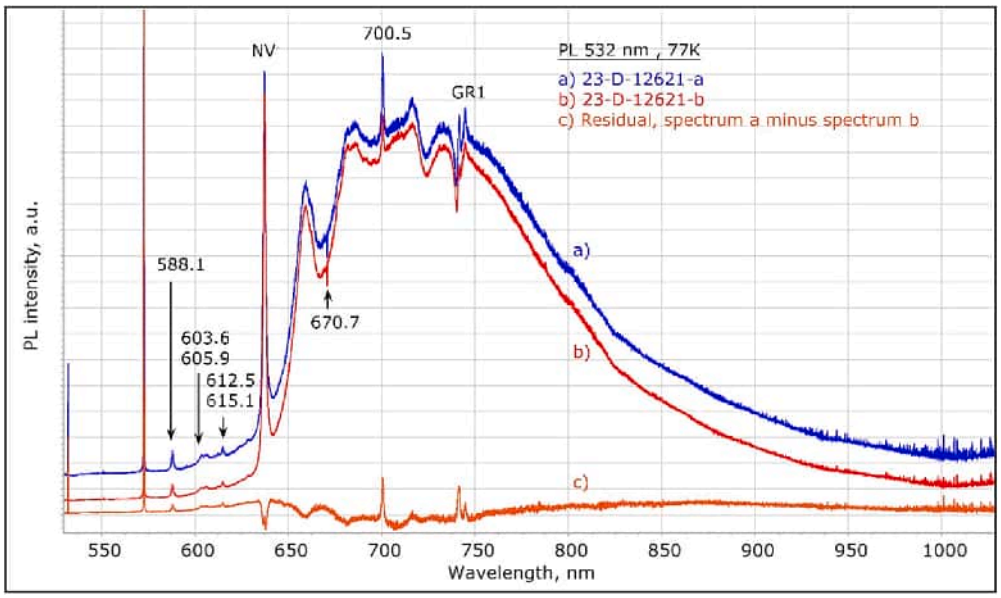

Fig. 8. The 532 nm laser PL spectra of the diamonds cooled to 77 K and their residual trace show that the spectral features of the two diamonds are all identical, only slight intensity differences (due to different sizes and cuts of the two diamonds) can be seen. Spectra shifted vertically for enhanced clarity.

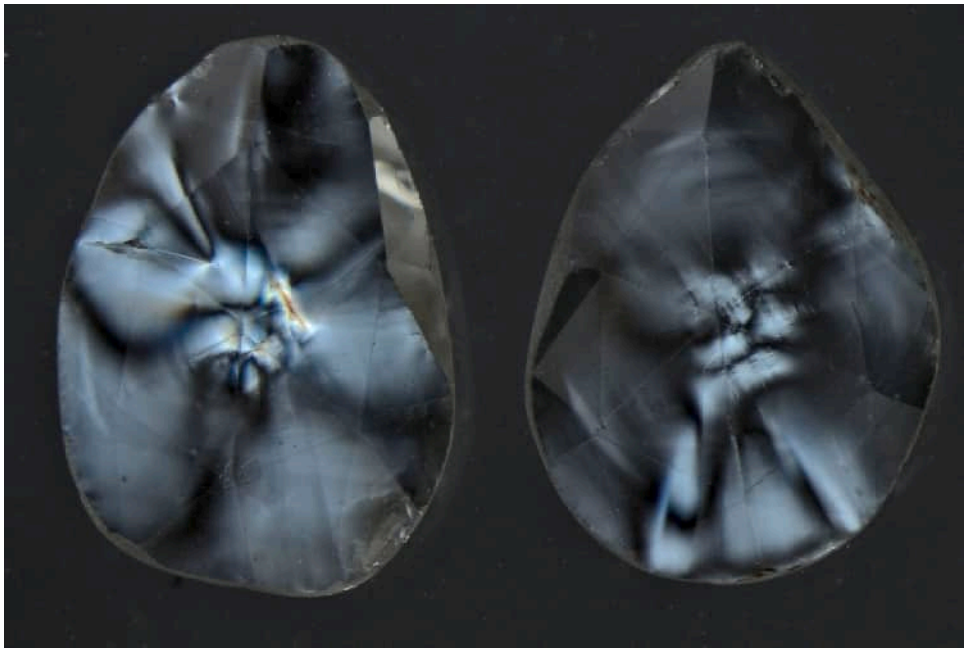

Fig. 9. Under crossed polarizing filters in immersion in methylene iodide, extinction with similar general distribution, likely from strain between cuboid and octahedral growth sectors, was visible in both diamonds of pair 2.
Photo T. Hainschwang

3.2.2. Luminescence imaging

Luminescence imaging was performed for the 0.96 and 0.76 carat diamonds with all 6 excitations of the Mega DFI Instrument, from 380 to 215 nm. Just like for the other diamond pair, the luminescence of the diamonds was weak, particularly under shorter UV wavelengths. Nevertheless, the luminescence appearance of the two pear rose cut green diamonds, under the six different excitations, turned out to be extremely similar, with the stones showing precisely the same luminescence intensity, color and spatial distributions of color under every UV excitation (Fig. 10). Unlike the other diamond pair, for these stones we were unable to resolve a fine structure of fluorescence, because their luminescence under the shorter UV wavelengths was so weak.

While it is still remarkable to have two diamonds with exactly the same luminescence reaction under identical testing conditions, there is not the same irrefutable evidence of kinship in the luminescence of these two stones that point towards a common origin from the same rough, as in the 7.74 + 2.91 carat pair. The spectral data (next sections) were therefore of more importance to prove that the 0.96 and 0.76 carat stones had a common progenitor.

3.2.3. Infrared spectroscopy

When these two diamonds were first received in 2014, their infrared spectra immediately aimed the attention of the authors towards the possibility that the diamonds originated from the same rough. The

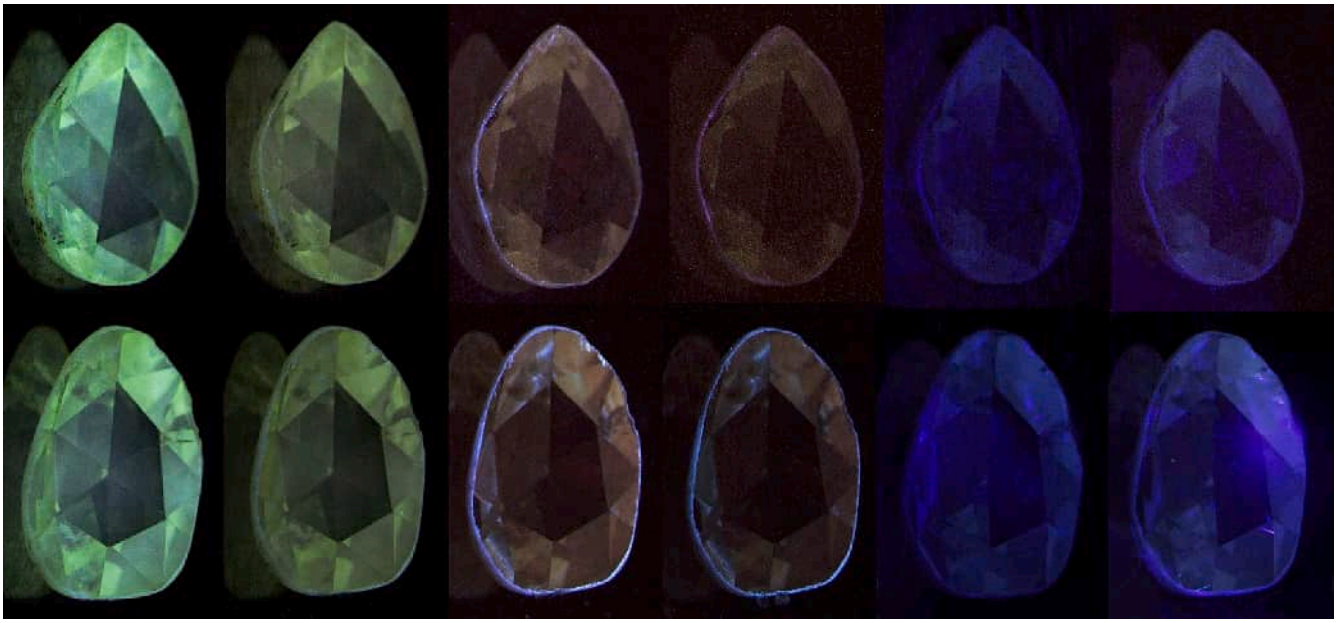

Fig. 10. The luminescence images of the 0.96 and 0.76 carat diamonds, recorded using a Mega DFI system at 6 different wavelengths from 380 to 215 nm (left to right), demonstrating the extreme similarity of the two diamonds. The overall luminescence colors and intensities are strong first indications showing a likely "kinship" of the two diamonds.
Photos: T. Hainschwang.

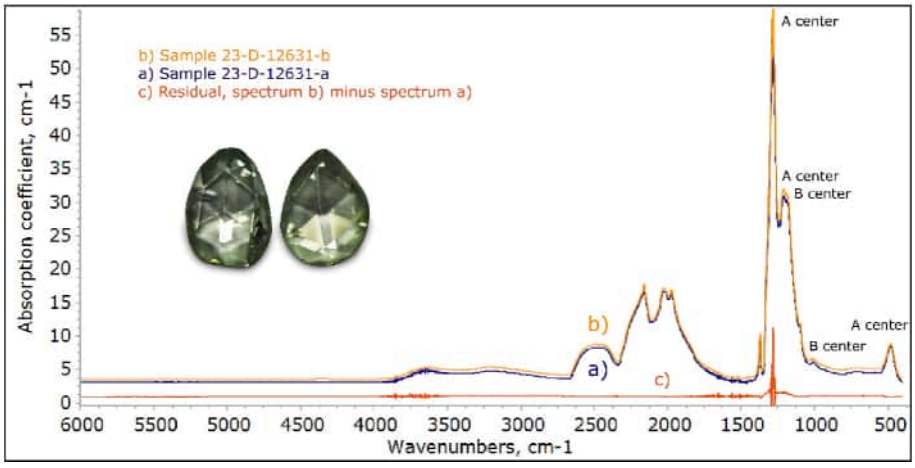

Fig. 11. The infrared spectra of the 0.96 and 0.76 carat diamonds, normalized to the intrinsic diamond absorption, and their residual trace after subtraction of spectrum a) from spectrum b). The extremely close match of the two spectra is apparent. There is virtually zero residual visible except in the area not fully resolved around 1282 cm^{-1} (A center nitrogen absorption). Spectra shifted vertically for enhanced clarity.

spectra were found to be a perfect match in every detail; no difference whatsoever could be detected. This was reconfirmed when the stones were fully characterized in 2023 (Fig. 11). For both stones a nitrogen content of 940 ppm A centers and 140 ppm B centers (±5 %) has been determined; the platelet peak absorption was found to be identical in position and shape, positioned at 1369 cm^{-1} with a FWHM of 13 cm^{-1}. Again, as mentioned earlier for the other diamond pair analyzed, such a perfect match in platelet peak position, intensity and FWHM alone is highly unlikely to occur unless one examines diamonds that originated from the same rough [24]. For the two diamonds of this pair, the infrared spectra alone are very indicative for their common origin. The "jump" in the residual trace when the two spectra are subtracted from each other (Fig. 11, trace c) is purely instrumental, since the A center nitrogen absorption at 1282 cm^{-1} could not be perfectly resolved, i.e. it is *not* due to an actual spectral difference.

3.2.4. UV–Vis-NIR spectroscopy

Just as with the infrared spectral data of Fig. 11, the UV–Vis-NIR spectra of these two green diamonds that were recorded with the diamonds cooled to 77 K were found to be so similar that one might initially think that they were recorded from the same stone (Fig. 12). Everything from the common absorption cut-off at 306 nm, the presence, intensity and FWHM of every single absorption feature to the identical type of absorption continuum demonstrated two things. First, the stones can only have originated from the same rough. Second, after confirming that the stones have a common origin, it can only be concluded that both stones have the same color origin. Given the identical absorption spectra in two stones originating from the same rough, any other conclusion about origin of color makes no sense.

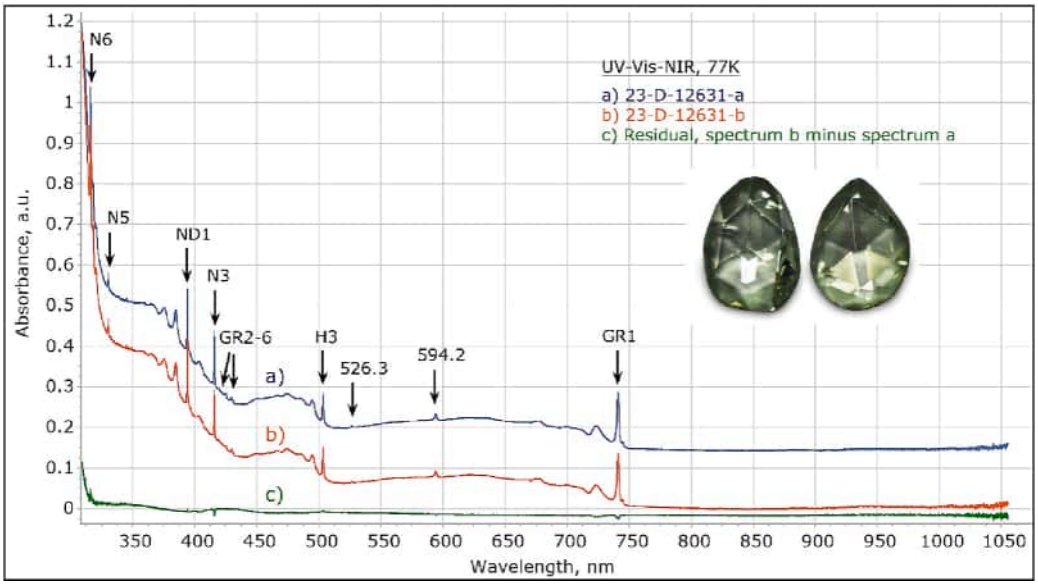

Fig. 12. The UV–Vis-NIR spectra of the two diamonds (recorded with the stones cooled to 77 K) and their residual after subtraction of spectrum a) from spectrum b) shows in a striking way that these spectra are practically identical. The match is perfect to a point that one might be inclined to claim that they were recorded from the same sample. Encountering such an extreme match between the low temperature UV–Vis-NIR spectra of two diamonds demonstrates beyond any reasonable doubt that: 1) the samples originate from the same rough diamond; and 2) since the two diamonds originate from the same piece of rough, and the relative strengths of the GR1 features are essentially identical, the color origins of the samples must be identical. As the samples show very similar depths hence the path length through the samples being very similar, the spectra were not normalized at all but are shown as recorded.

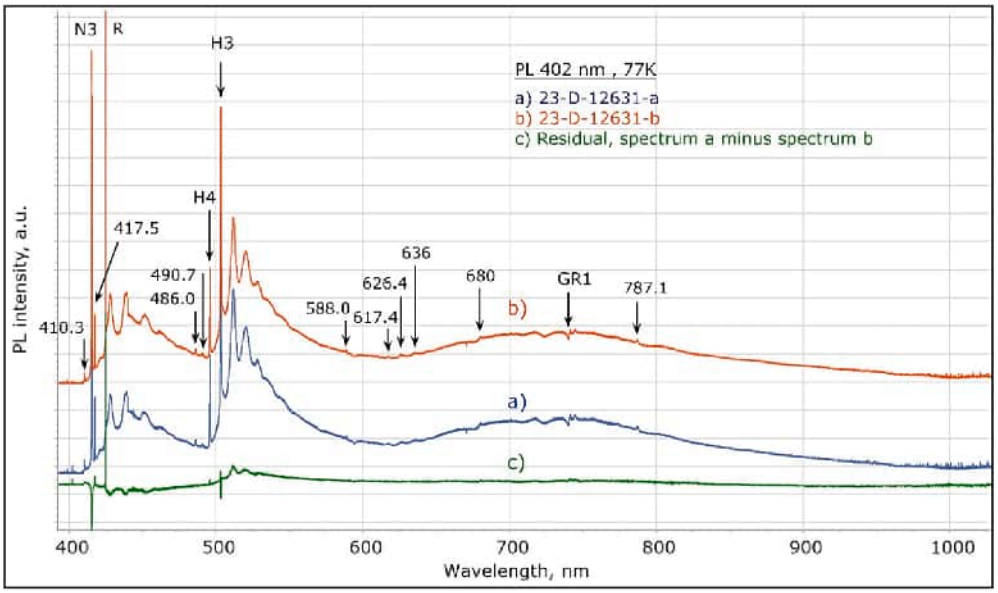

Fig. 13. The 402 nm laser PL spectra of the diamonds cooled to 77 K and their residual trace show that the spectral features are all present in the two diamonds; not a single PL peak found in sample a) is absent in sample b) and vice-versa. The only apparent differences of the spectra of the two diamonds are slight intensity variations of some of the spectral features such as N3 and H3. Such intensity differences are due to non-homogenous distribution of defects through the mass of the original rough diamond, and the influence of size and cut proportions on the fluorescence. Spectra shifted vertically for enhanced clarity.

3.2.5. Photoluminescence spectroscopy

Just as for the 7.74 + 2.91 carat diamond pair, the PL of the 0.96 and 0.76 carat diamonds was recorded with a range of lasers, from the UV to the NIR; for the sake of demonstrating their astonishing similarity in crystal defects, the spectra recorded using 402, 473, 532 and 635 nm are shown for these samples (Figs. 13, 14, 15 and 16). Besides some minor intensity variations of certain defects such as H3, the spectra under all excitations were practically identical for these two green diamonds: the presence of all spectral features with the same intensities and FWHM in each pair of spectra at each excitation is further evidence for the common origin of the two diamonds. If one would argue that the luminescence images, IR and UV–Vis-NIR spectra are not sufficient for such a conclusion, the addition of a wide range of PL spectra should suffice to eliminate beyond any reasonable doubt that the diamonds share a common progenitor.

As explained above, the intensity variations of defects in PL are more common than in absorption spectroscopy; the two samples shown here nicely demonstrate that such intensity variations are not actual reliable indications of some real spectral differences as the H3 center was shown to be slightly more intense in sample a) at 402 nm while it was shown to

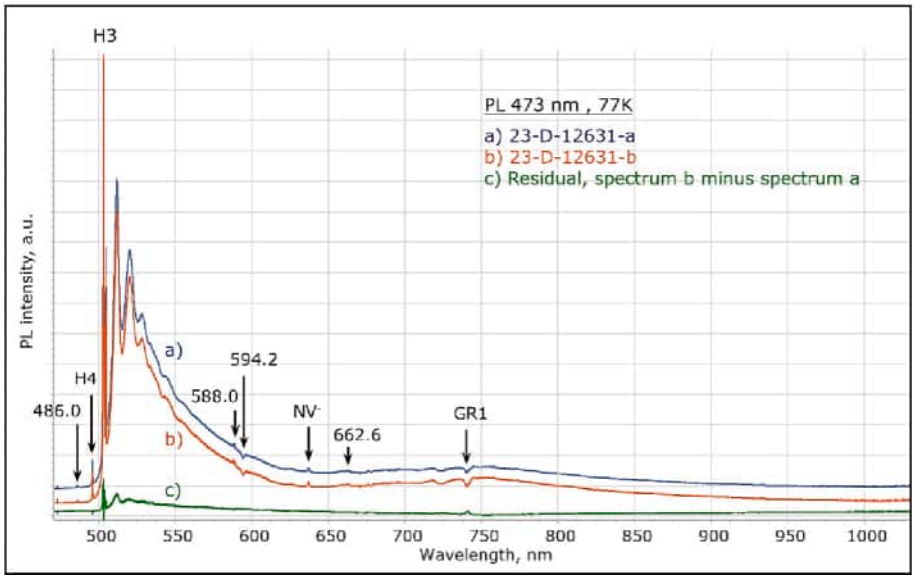

Fig. 14. The 473 nm laser PL spectra of the diamonds cooled to 77 K and their residual trace show that the spectral features are all present in the two diamonds, not a single PL peak found in sample a) is absent in sample b) and vice-versa. The only apparent slight difference of the spectra of the two diamonds is the intensity of some of the spectral features, which is of no contradiction of the suggested common origin as discussed above. Spectra shifted vertically for enhanced clarity.

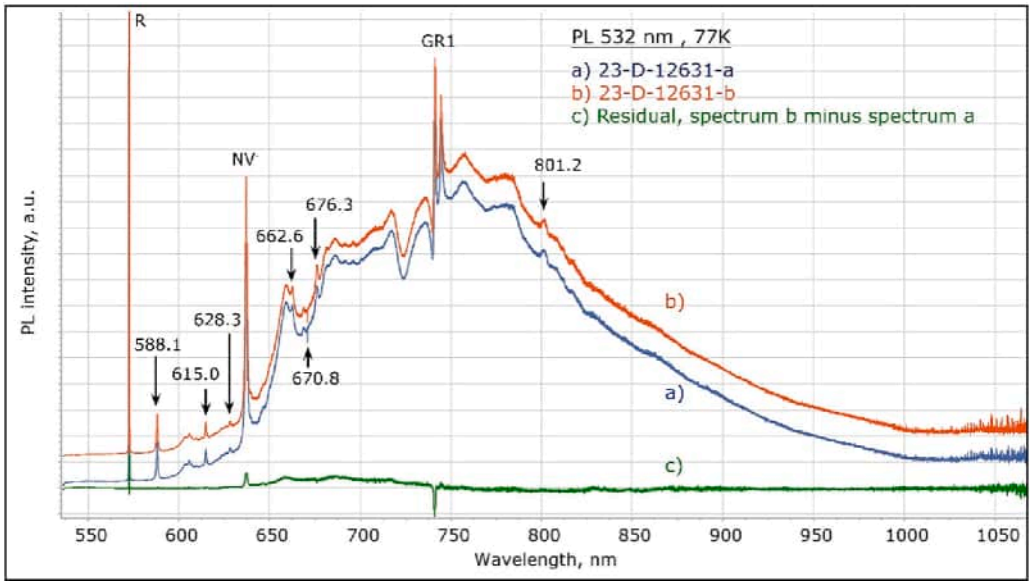

Fig. 15. The 532 nm laser PL spectra of the diamonds cooled to 77 K and their residual trace show that the spectral features of the two diamonds are all identical, only slight intensity differences can be seen. Spectra shifted vertically for enhanced clarity.

be slightly weaker under 473 nm. This difference shows clearly that such a variation is related to the factors discussed above for the PL spectroscopy of pair 1.

4. Conclusions

Detailed microscopic analysis, fluorescence imaging, absorption spectroscopy and photoluminescence spectroscopy were used to characterize two pairs of polished diamonds colored by radiation-related defects and to confirm that each pair originated from the same rough diamond. The data acquired convincingly demonstrates that the two pairs of diamonds indeed share a common progenitor each.

For the diamond pair 1 the luminescence imaging alone unambiguously demonstrated their origin from the same rough by analysis and superposition of the fine growth structure visualized by luminescence. For the other pair of diamonds this proof was elaborated via the spectral analysis since besides nearly identical luminescence color and intensity, no fine structure could be visualized by luminescence imaging. This study demonstrates that carefully performed detailed analysis with as many methods as possible creates a type of data fingerprint. Such a fingerprint can be used to either characterize a diamond in a way that it can be identified at any time - even if recut - or to determine whether two diamonds originate from the same rough diamond, as shown in this work. The identification at any time, even after recutting, is limited to "reasonable" weight loss during the recut; obviously, if a 10 carat diamonds would be cut down to a 0.05 ct diamond, such a procedure would likely fail, especially if heterogeneous defect sectoring is prominent. Therefore, the procedure is limited to recutting as is typically done for such valuable goods, i.e. changing the dimensions and weight by up to 10–20 %, or in the extreme case making two stones out of one stone.

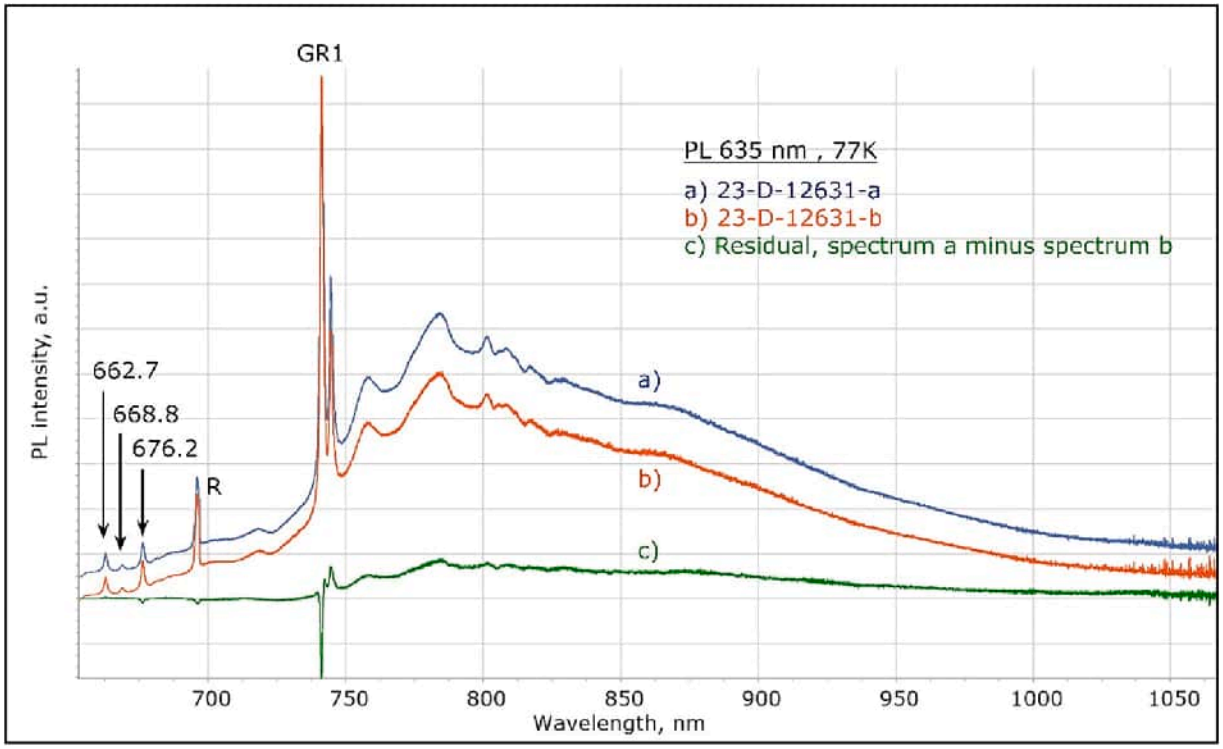

Fig. 16. The 635 nm laser PL spectra of the diamonds cooled to 77 K and their residual trace show that the spectral features of the two diamonds are all identical, only slight intensity differences can be seen, mainly of the GR1 PL. This difference of the GR1 PL is obviously only caused by the variations of PL intensities related to the technique of PL spectroscopy discussed in the text, as the GR1 absorption of the two diamonds was shown in Fig. 12 to be precisely the same. Spectra shifted vertically for enhanced clarity.

For the cases presented in this work, the creation of this fingerprint has another positive side-effect, which is the unambiguous conclusion that both diamonds had the same color origin. The determination of color origin for diamonds with radiation-related coloration is challenging [15], and conclusions made by *gem* testing labs are unfortunately often questionable or even contradictory. The reason for this is that the distinction of color caused in diamond by artificial irradiation from color caused by natural irradiation is a very complex and difficult procedure; the properties of naturally and artificially irradiated diamonds are extremely similar. But once a diamond is determined to be of natural color origin, that same color determination should continue to hold through subsequent polishing steps if there is no detected significant change in that diamonds' spectrum.

When two stones that originate from the same rough diamond obtain contradicting conclusions concerning their color origin - such as occurred in both cases for the two pairs presented here - the elaboration of such a complex fingerprint can help to prove beyond any doubt that the color origin of two diamonds must be identical. For the four diamonds of the present study the color origin was determined to be natural by the authors' extensive testing.

We suggest that a similar methodology will be useful to link diamonds sawn apart decades or centuries ago to hide their provenance.

Prime novelty statement

This paper demonstrates a new approach to create a unique data-based “fingerprint” for a diamond which can be used to either identify such a stone at any time after analysis, even after “commercially reasonable” recutting or to prove that two or more cut diamonds originate from the same rough diamond. Further, the method can be used to prove that two diamonds have an identical color origin, which is particularly useful when differing conclusions for several stones from the same rough that were determined by a *gem* testing lab need to be disputed.

CRediT authorship contribution statement

Thomas Hainschwang: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Franck Notari:** Writing – review & editing, Investigation. **Gianna Hainschwang:** Writing – review & editing, Data curation. **Michael Shara:** Writing – review & editing, Writing – original draft, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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