

of boron into the diamond structure. The lattice vibrations appear from 4000 to 1200  $\text{cm}^{-1}$ , and consist of the transverse optic (TO) mode, the Raman-active mode, and bands in the second- and third-phonon regions (King et al., 1998). The broad absorbance that results from substitution of small amounts of boron for carbon in the diamond structure starts roughly at 3000  $\text{cm}^{-1}$  and extends into the near-infrared and red region in the visible spectrum; it is the cause of the blue color (see S.D. Smith and W. Taylor, "Optical phonon effects in the infra-red spectrum of acceptor centres in semiconducting diamond," *Proceedings of the Physical Society, London*, Vol. 79, 1962, pp. 1142–1153; I. G. Austin and R. Wolfe, "Electrical and optical properties of a semiconducting diamond," *Proceedings of the Physical Society*, Vol. 69B, No. 3, 2003, pp. 329–338). As reported by Smith and Taylor (1962), the other absorption features seen in figure 4 are due to boron-related electronic transitions (2928, 2799, and 2460  $\text{cm}^{-1}$ ) and the combination modes of the boron transitions and lattice vibrations (5404, 5041, 4097, and 3726  $\text{cm}^{-1}$ ). The spectra of all three blue diamonds lacked any detectable nitrogen bands in the 1400–1000  $\text{cm}^{-1}$  region, consistent with the definition of type II diamonds.

To our knowledge, this is the first mid-infrared spectrum obtained on the Hope diamond; it shows features consistent with the presence of boron as the cause of the blue coloration and its categorization as a type IIb diamond.

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**A natural yellow diamond with nickel-related optical centers.** A Fancy Light yellow 2.95 ct round brilliant diamond was recently submitted to the SSEF Swiss Gemmological Institute for color authenticity determination (figure 5). In the course of standard testing, we noticed the presence in its UV-visible spectrum of clear nickel-related optical centers, which are usually encountered in flux-grown synthetic diamond. Further spectroscopic analysis, as described below, in combination with the growth patterns, proved that this Ni-containing diamond was natural and not a synthetic. Although the presence of nickel in natural diamonds has been previously documented (C. J. Noble et al., "Electron paramagnetic resonance investigations of nickel defects in natural diamonds," *Journal of Physics: Condensed Matter*, Vol. 10, 1998, pp. 11781–11793), we are not aware of any previous mention of this in the gemological literature.

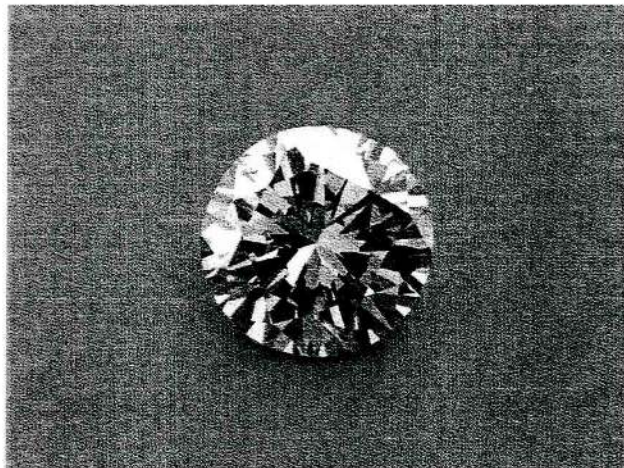
Microscopic observation of this diamond revealed several small black-to-brown inclusions of unknown origin. Numerous swirl-like patterns were visible with darkfield illumination, and were more distinct when

crossed polarizers were used. With long-wave UV radiation, the stone showed a strong "lemon" yellow reaction, which was mostly even except for a few weaker zones close to the culet. The short-wave UV reaction was similar in color though weaker in intensity. No magnetic test was performed.

The infrared spectrum showed a strong platelet-related peak (higher than the two-phonon zone) and a large and saturated absorption band between 1300 and 1050  $\text{cm}^{-1}$ . These features are typical for type Ia diamonds that contain significant concentrations of nitrogen. Several characteristic peaks in both the one- and three-phonon zones indicated that the diamond also contained a moderate concentration of hydrogen. This is consistent with its yellow UV fluorescence. If we consider both the presence of a well-defined 1010  $\text{cm}^{-1}$  peak and the absence of the 484  $\text{cm}^{-1}$  peak, it is reasonable to assume that the majority of nitrogen was present as B aggregates.

The UV-Vis absorption spectrum, recorded at approximately  $-120^\circ\text{C}$ , showed a strong N3 center, with an absorption coefficient of 2.0  $\text{cm}^{-1}$  at 415.2 nm. A series of weak peaks (343.6, 347.3, 360.3, 363.5, and 366.9 nm) were recorded that so far have been described only in synthetic diamonds (J. E. Field, *The Properties of Natural and Synthetic Diamond*, Academic Press, London, 1992). Also present was another series of weak peaks (467.9, 473.0, 477.5, and 546.7 nm) that have been previously attributed to nickel- and nitrogen-related absorptions in annealed type Ib synthetic diamonds (J. E. Shigley et al., "The gemological properties of Russian gem-quality synthetic yellow diamonds," *Winter 1993 Gems & Gemology*, pp. 228–248). In addition, a weak peak was recorded at 793.3

Figure 5. This 2.95 ct Fancy Light yellow natural diamond was found to contain Ni-related absorption features in the UV-visible region that have previously been associated only with synthetic diamonds. Photo by M. Krzemnicki, © SSEF.





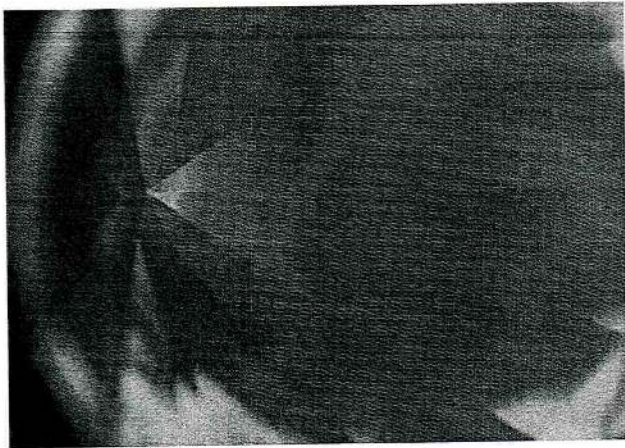


Figure 6. This De Beers DiamondView image of the Fancy Light yellow diamond with Ni-N-related optical centers shows irregular patterns of blue fluorescence, indicative of natural origin. Photo by J.-P. Chalain, © SSEF.

nm (with an absorption coefficient of  $0.1 \text{ cm}^{-1}$ ), which is commonly observed in both natural and synthetic nickel-containing diamonds and is almost certainly due to a nickel-nitrogen complex (D. Fisher, pers. comm., 2003).

The Raman photoluminescence spectrum of this diamond, recorded at approximately  $-120^\circ\text{C}$  with a 514.5 nm (green) laser, showed two peaks of moderate intensity at 640.5 and 693.9 nm, and a very strong peak at 700.5 nm. This last peak is usually seen in natural type Ia diamonds. None of the Raman photoluminescence peaks could be ascribed to Ni-related optical centers.

Notwithstanding the features seen in the UV-Vis spectrum, the natural origin of this diamond was supported by many properties, the first of which was the presence of irregular growth patterns. A DiamondView image (figure 6) revealed blue fluorescence with irregular patterns close to the culet and no phosphorescence (a synthetic diamond would have displayed regular cubo-octahedral growth patterns, as shown in C. M. Welbourn et al., "De Beers natural versus synthetic diamond verification instruments," Fall 1996 *Gems & Gemology*, pp. 156–169). The high concentration of nitrogen, especially in the form of B aggregates, the presence of a high platelet peak, and a strong N3 center are also valuable indications for natural diamond.

In conclusion, examination of this interesting diamond allowed us to observe, for the first time, Ni-related defects in a natural diamond by means of UV-visible absorption spectroscopy. The natural origin of the diamond's color was proven by the absence of any coating, as well as the lack of any spectroscopic features indicative of HPHT treatment or irradiation and annealing.

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## COLORED STONES AND ORGANIC MATERIALS

**Gem-quality afghanite.** While on a gem-buying expedition in Peshawar, Pakistan, Dudley Blauwet, a gem dealer from Louisville, Colorado, obtained five cabochons and an excellent crystal specimen of afghanite. The stones were said to have come from Kiran, Kokcha Valley, Badakhshan Province, Afghanistan. Although in the past these contributors have seen a few afghanite crystals at various gem and mineral shows, we had never seen gems fashioned from this rare mineral, so for us this was a first opportunity to examine polished samples of afghanite. A member of the cancrinite group, the chemical formula of afghanite is  $(\text{Na,Ca,K})_8(\text{Si,Al})_{12}\text{O}_{24}(\text{SO}_4,\text{Cl},\text{CO}_3) \cdot \text{H}_2\text{O}$ . It has a hardness of  $5\frac{1}{2}$ –6 on the Mohs scale.

The crystal measured  $23.0 \times 14.5$  mm and was partially embedded in white calcite matrix (figure 7). Although we could not find it reported in the literature, an interesting feature of afghanite that should prove useful in its identification is its strong, bright orange fluorescence to long-wave UV radiation (see, e.g., figure 8), which we also observed in all five cabochons. All of the samples were inert to short-wave UV radiation, and no phosphorescence was observed in either case.

The five cabochons (ranging from 2.87 to 7.25 ct) yielded refractive index readings of 1.52, which, given that these are spot readings, is consistent with published R.I. values for afghanite ( $n_o = 1.522$ – $1.528$ ,  $n_e = 1.528$ – $1.533$ ; R. V. Gaines et al., *Dana's New Mineralogy*, John Wiley & Sons, New York, 1997, p. 1634). The hydrostatic specific gravity ranged from 2.52 to 2.56, with one cabochon giving a 2.60 value. The S.G. value reported in the literature is 2.55–2.65 (Gaines et al., 1997), and the slightly low reading of some of the samples is probably due to variable amounts of lazurite inclusions, which were present in all of our samples. In addition, inclusions of calcite and pyrite were identified with Raman analysis in some of the samples. In the previously published descriptions of afghanite, no mention was made of any inclusions.

To the unaided eye, the samples appeared translucent light blue; the mineral is described in the literature as "bluish" to colorless (Gaines et al., 1997). All the polished cabochons we examined contained numerous intense blue inclusions of lazurite that certainly added color to their host. As shown in figure 9, the lazurite inclusions also gave the polished cabochons a speckled appearance. With magnification, the irregularly shaped lazurite inclusions stood out in high relief due to their color (figure 10), while the (essentially colorless) calcite inclusions were much harder to see. It is not clear how much of the blue color in these afghanites is derived from the deep blue inclusions, and how much is actually intrinsic to the mineral.

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