Eur. J. Mineral.
2006, **18**, 71–81

Infrared spectroscopy study of nitrogen centers in microdiamonds from Ukrainian Neogene placers

MICHAIL N. TARAN[1]*, VICTOR M. KVASNYTSYA[1], KLAUS LANGER[2] and KATERINA O. ILCHENKO[1]

[1]Institute of Geochemistry, Mineralogy and Ore Formation, National Academy of Sciences of Ukraine, Palladin Ave. 34,
03680 Kyiv-142, Ukraine
* Corresponding author, e-mail: taran@mineral.freenet.kiev.ua
[2]Institute of Applied Geosciences, Technical University of Berlin, D-10623 Berlin, Germany

Abstract: Microdiamonds from two different Ukrainian Neogenic placer deposits, Samotkan and Zeleny Yar, and from kimberlite pipe Udachnaya, Yakutia, Russia, were studied by FTIR absorption spectroscopy. The spectra were normalized to sample thickness of 1 mm, background corrected and analyzed by curve fitting with Peakfit 4.0 software. For this purpose, four user-defined functions which simulate the absorption of the nitrogen-bearing centers A, B, C and D were synthesized using each seven to nine Gaussians or Lorentzians out of the list of spectroscopic functions of the Peakfit 4.0 program.

One result was that with respect to the IR active forms of nitrogen, most diamonds from Ukrainian Neogenic deposits are nitrogen-free. The rare nitrogen-bearing crystals from Samotkan (~25% of total amount studied) contain nitrogen mainly in the A-form (pairs of adjacent nitrogen ions in regular sites of the structure) and, partly, in the C-form (single atoms randomly dispersed over regular sites of the diamond structure). This indicates either a relatively low temperature or a relatively short residence time of such crystals under Mantle conditions. The rare (~10% of total) nitrogen-bearing crystals from Zeleny Yar contain nitrogen mainly in the A- and B-forms (four nitrogen atoms arranged around a carbon vacancy) with predominance of B. According to existing theory this indicates higher temperatures or longer Mantle residence times of such diamonds compared with those from Samotkan.

Most of the Yakutian diamonds studied (~95%) contain nitrogen-bearing defects. The curve fitting analysis shows a wide range of N_B/N_{total} ratios which suggests a wide range of Mantle residence temperatures. With respect to the temperatures, the Yakutian diamonds may be regarded as intermediate between those from Samotkan and Zeleny Yar.

Key-words: diamond, nitrogen impurities, infrared spectroscopy, curve fitting analysis.

Introduction

One of the most effective and widely used methods of investigation of very small diamonds is nowadays Fourier transformation infrared spectroscopy (FTIR). When equipped with an infrared microscope accessory, FTIR spectrometers allow for measuring spectra on objects down to about 100 µm or even less which is typical of the natural diamonds to be studied here.

Microdiamonds of dimensions less than *ca.* 500 µm are widely dispersed in various sedimentary rocks of the Ukrainian shield and its rims. Since their discovery in the sixties of the last century (Kashkarov & Polkanov, 1964) and, especially, during the last ten years, Ukrainian diamonds were an object of numerous investigations. However, despite growing scientific interest and rather intense geological explorations no primary sources and no host rocks of such diamonds have been found as yet.

A major result of recent FTIR spectroscopic studies of Ukrainian diamonds is that the various impurity centers, active in infrared (IR) spectra, as well as their concentrations differ significantly from, for instance, kimberlitic diamonds from Yakutia (Ilchenko *et al.*, 2003). The most distinct differences are usually seen in the spectral range ~2800 to 4000 cm^{-1}, which is commonly regarded as a range of hydrogen-bearing structural impurities (*e.g.* Mendelssohn & Milledge, 1995). In addition, absorption features, some of which are obviously related to the bands of the hydrogen-bearing defects, frequently appear in the range ~700–1800 cm^{-1} (Ilchenko *et al.*, 2003; Taran *et al.*, 2003), *i.e.* in the range where the characteristic bands caused by various nitrogen centers are usually observed in diamonds from other deposits.

Nitrogen is the main substitutional impurity in natural diamonds. It is established that it enters the diamond structure in many different forms combining with other defects as impurities, vacancies, interstitial atoms *etc.* There are only four nitrogen-bearing substitutional defects, A, B, C and D, which are active in IR spectra. The A- and B-forms of nitrogen are interpreted as pairs of nitrogen atoms jointly substituting a single carbon atom in the structure (*e.g.* Davies, 1976) and four nitrogen atoms tetrahedrally arranged

DOI: 10.1127/0935-1221/2006/0018-0071

0935-1221/06/0018-0071 $ 4.95

around a vacancy of a carbon site (Sutherland *et al.*, 1954), respectively. The D-defect is probably also a sort of aggregated nitrogen atoms, but of unclear structure, whereas C is caused by isolated nitrogen atoms. Historically, the diamonds which contain A- or B-forms of nitrogen are classified as diamonds of IaA- or IaB-types, respectively, forming the Ia-group of diamonds. Diamonds the IR spectra of which show only the presence of C-type defects are classified as Ib, whereas diamonds whose spectra lack nitrogen bands in the range 900 to 1400 cm^{-1} are called IIa-type. It should be noted that diamonds of Ib-type are very rare among natural crystals, presumably, not more than one crystal of Ib-type in a thousand. However, as found by Cartigny *et al.* (2004), most of microdiamonds from Akluilâk minette dykes (Nunanunt, Canada) are of Ib-type, *i.e.* contain nitrogen mostly in C-form.

Besides the IR active centers A, B, C and D, nitrogen seems also to be related to thin planar precipitates, usually called platelets. These platelets cause a sharp IR absorption peak of variable position (from *ca.* 1358 to 1378 cm^{-1}) and variable asymmetry (Woods, 1986). The energy of the band is found to be the higher the higher the total nitrogen content is (Mendelssohn & Milledge, 1995). By thermal behavior of the platelet peak and its relation to the concentration of the B-form of nitrogen, diamonds of Ia-type may be distinguished into two categories, "regular" and "irregular" (Woods, 1986).

Among Ukrainian diamonds, the crystals with typical nitrogen center bands are rare (Ilchenko *et al.*, 2003), *i.e.* the great majority can be regarded as nitrogen-free. Nevertheless, the IR spectroscopic study of the rare nitrogen-bearing Ukrainian diamonds is insofar important as it provides information on their thermal history. Therefore, the present paper presents results of IR-spectroscopic studies of such rare nitrogen-bearing Ukrainian diamonds from Zeleny Yar and Samotkan titanium-zirconium Neogenic placer deposits. The results are compared with those on small (*ca.* 0.5–1.0 mm in diameter) diamonds from the Udachnaya kimberlite pipe (Yakutia, Russia). It is worth mentioning that the two Ukrainian placers, Zeleny Yar and Samotkan, are rather distant from each other (~500 km) and located in different megablocks of the Ukrainian shield (Kvasnytsya *et al.*, 2004). Thus, it is unlikely that they originated from the same source.

Experimental details

Diamond specimens to be studied spectroscopically with size of 0.2–0.3 mm, were selected from a set of microcrystals and their fragments under a binocular microscope. Each sample was oriented to be most convenient for spectroscopic measurements, *i.e.* maximal light transmission through the sample, and molded into a perforated lead plate of 0.3 mm thickness. This allows for reliable operation of small objects in the spectroscopic measurements. No additional treatment of the samples like polishing has been undertaken.

Infrared spectra were measured in the range 700–4000 cm^{-1} at a resolution of 2 cm^{-1} by means of a FTIR-spectrometer (Bruker IFS 66) with KBr beam-splitter and attached IR-microscope equipped with mirror optics. An LN$_2$-cooled MCT (Mercury-Cadmium-Telluride) semiconductor was used as detector and a globar as light source.

200 scans were averaged for every measurement. Due to small dimensions and frequently complicated irregular shapes, spectra of most of the samples were measured only in one point.

Mathematical treatment of the spectra

Normalization and background correction

The digital spectroscopic data were stored as ASCII files converted from the OPUS-format used in the Bruker FTIR spectrometers. Origin 5.0 software was applied for plotting and preliminary treatment of the spectral curves.

As the thickness of many samples studied very frequently of rather irregular shapes could not be measured in a conventional way (*e.g.* with a micrometer screw), an alternative method of determining optical path length was applied: the effective thickness was evaluated from the absorption coefficient of two-phonon diamond lattice bands at 1992 cm^{-1} (Mendelssohn & Milledge, 1995). Note that in this spectral range no other bands appear, except those caused by vibrations of the diamond lattice itself. Even a doublet absorption peak of atmospheric CO$_2$ at ~2338 and 2363 cm^{-1}, not completely compensated due to the single-beam technique, does not hamper the thickness determination.

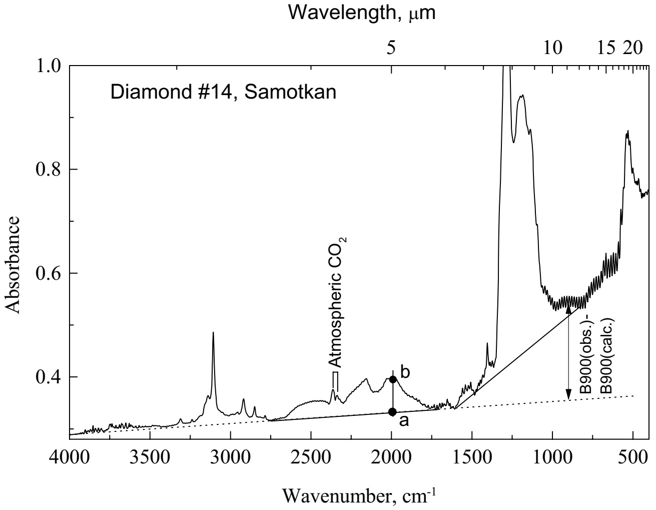

Fig. 1. FTIR spectrum of Samotkan diamond #14 ~0.25 mm of size in the spectral range 400–4000 cm^{-1}. Absorption background in the range ~1700 to ~2700 cm^{-1} is approximated by a straight line shown by solid line. The straight dotted line designates the background suggested by Mendelssohn & Milledge (1995). Absorption coefficient at ν = 1992 cm^{-1}, α_{1992}, used for thickness normalization, is taken as a difference between ordinates of a and b points. The absorption background in the range of nitrogen-bearing center bands and platelet peak, *ca.* 800–1500 cm^{-1}, is also taken as a straight line. For the sake of simplicity it is shown on the original spectrum. In fact, the absorption background is chosen after normalization of the spectrum to a diamond thickness of 1 mm. B900(obs.)–B900(calc.) is a quantity used by Mendelssohn & Milledge (1995) for estimation of goodness of nitrogen aggregation state determination.

In this procedure the absorption background is approximated by a straight line tangent to the local minima of the spectral curve at around 1750 and 2700 cm^{-1} (Fig. 1). In many samples studied such background nearly coincides with the background suggested by Mendelssohn & Milledge (1995) for the whole spectral range from 4000 to 650 cm^{-1}, *i.e.* the linear baseline drawn between the absorption measured at 4000 cm^{-1} and at the local minimum in the region 1600–1400 cm^{-1} (Fig. 1). The absorption coefficient a_{1992} was taken as a difference between ordinates of a and b points (Fig. 1). Each spectrum was normalized to a thickness of 1 mm so that absorption coefficient a_{1992} becomes 1.23 mm^{-1} (*cf.* Mendelssohn & Milledge, 1995). As was shown by Taylor *et al.* (1990), such thickness normalization is correct enough for diamonds thinner than *ca.* 1.5 mm. Therefore, it is quite acceptable for both the Ukrainian samples, with thickness below ~0.3 mm, and Yakutian diamonds, not thicker than 1 mm.

The background absorption in the range of nitrogen center bands is taken as a straight line tangent to local minima of the spectral curve at 800–850 cm^{-1} and ~1500 cm^{-1} scaled to a diamond thickness of 1 mm. This is demonstrated in Figure 1 for an original, non-normalized spectrum. It should be noted that such baseline significantly differs from that suggested by Mendelssohn & Milledge (1995), *i.e.* a straight line drawn through absorbance at 4000 cm^{-1} and the spectral minimum at 1600–1400 cm^{-1} and then extended to 650 cm^{-1}. Perhaps, the latter is good enough for other diamonds. In our case, for instance, it seems quite acceptable for many Yakutian samples. However, it is obviously bad for Ukrainian microdiamonds frequently showing a strong slope of the spectral curve in the spectral range in question (*cf. e.g.* Fig. 1). Particularly, in such cases the value B900(obs.) – B900(calc.) = B900(est.) (Fig. 1) used for checking of goodness of nitrogen aggregation state determination by Mendelssohn & Milledge's (1995) method becomes inapplicably large.

Curve fitting

After the background correction, the spectral curves in the range from 900 to 1400 cm^{-1} were subjected to curve fitting.

The Peakfit 4.0 software (Jandel Scientific) was used for decomposing the spectral curves into four "component curves", A, B, C and D, caused by vibrational transitions of differently aggregated nitrogen atoms (see Introduction). The tabulated spectral curves, intrinsic to A-, B-, C- and D-form of nitrogen impurities, were taken from literature (*e.g.* Davie, 1981; Taylor *et al.*, 1990). They were scanned, digitized with the Graph Digitizer 1.3 software and then fitted by sums of seven to nine Gaussians and Lorentzians available from the list of spectroscopic functions of the Peakfit 4.0 program. The results were used to synthesize "theoretical" A, B, C and D User-Defined Functions (UDF) for Peakfit 4.0 software (Fig. 2).

The modeled curves A, B and D are normalized such that at a wavenumber of 1282 cm^{-1} their intensities are 1.0, whereas the intensity of the C function is taken as 1.0 at 1134 cm^{-1} (Fig. 2). Our normalization ($\alpha_{1282} = 1$ mm^{-1}) of the A-, B- and D-functions corresponds to nitrogen concentrations of 150, 650 (Mendelssohn & Milledge, 1995) and 50 at. ppm (Taylor *et al.*, 1990), respectively. For the C-form a_{1134}=1.0 mm^{-1} corresponds to 250 at. ppm of nitrogen content as defined by Kiflawi *et al.*, (1984). It should be pointed out here that these values are rather different in different publications (*cf. e.g.* Taylor *et al.*, 1990; Mendelssohn & Milledge, 1995; Kaminsky & Khachatryan, 2001).

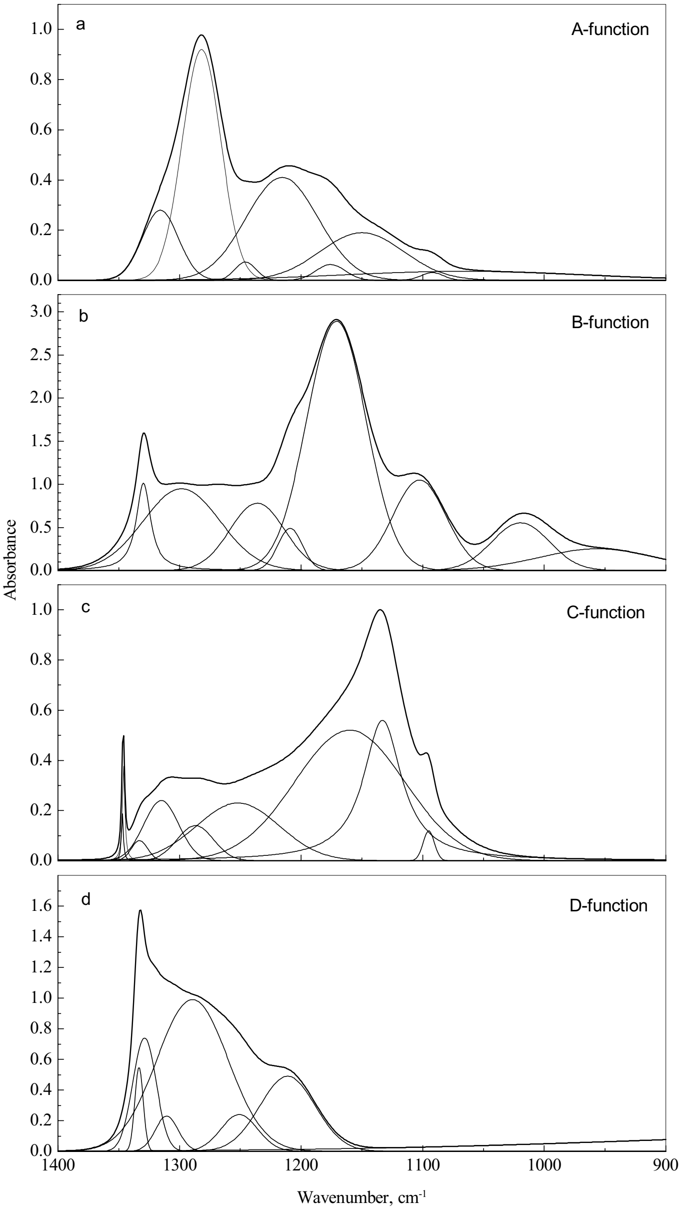

Fig. 2. Synthesized spectral curves of four nitrogen-bearing centers, A, B, C and D. From seven to nine component Gaussians and Lorentzians are used for building up the curves. A-, B- and D-curves are normalized so that at 1282 cm^{-1} their intensities are 1.0. Intensity of the C-function is taken to be 1.0 at 1134 cm^{-1}.

Some investigators suggest that a part of nitrogen concentration in diamonds may be related to platelet content (see *e.g.* Taylor *et al.*, 1990). However, as far as we know, no relationship is found between intensity of the platelet peak at 1358–1378 cm^{-1} and concentration of nitrogen related to these defects. Usually, this quantity is conventionally represented by the band intensity [α, mm^{-1}] of the platelet peak.

Results and discussion

The nitrogen-bearing microdiamond specimens studied here are listed in Tabs. 1 and 2 together with the results of their spectral evaluations. Concentrations [at. ppm] of nitrogen in different forms, A to D, for diamonds from Samotkan and Zeleny Yar, derived in this work from their FTIR spectra, are compiled in Tab. 1, those from the Udachnaya kimberlite in Tab. 2. The contents of platelets are represented as linear absorption coefficient, $\log_{10}(I_0/I)/t$ [mm^{-1}], of the absorption peak at ~1370 cm^{-1}, and percentage of IaB aggregation of B-form of nitrogen, $N_B/N_{total}\cdot 100\%$, – as $N_B\%$.

Three characteristic spectra of Ukrainian microdiamonds and their curve fitting are shown in Fig. 3. As seen from the figure, the ratios of intensities of the four functions, A to D, are rather different in the three diamonds: Whereas in the diamonds from Samotkan, #25 and 14, all four functions contribute to the resulting synthesized curve with a significant predominance of C and A, respectively (Fig. 3 a, b), in the diamond from Zeleny Yar, 5ZYA, the B-curve is stronger than A and D, and the contribution of the C-function is practically zero (see also Tab. 1). On the other hand, in the latter sample a large concentration of platelets is displayed as a strong peak with maximum at around 1370 cm^{-1}. Such a peak is practically absent in the spectra of diamonds #25, 14 (Fig. 3 a, b).

The deviations of the experimental curves from the synthesized ones are evidently due, at least partly, to somewhat incorrect shapes of the basic UDFs A to D, caused by the uncertainties of their shapes taken from literature and the restricted number of modeling functions (max. 9 in Peakfit

Table 1. Concentrations [at. ppm] of different nitrogen-bearing centers, total nitrogen concentration and content of platelets, $\log_{10}(I_0/I)/t$ [mm^{-1}], in Ukrainian diamonds obtained by curve deconvolution of their spectra. r^2 is coefficient of determination.

Sample	A, ppm	B, ppm	C, ppm	D, ppm	$N_B\%$	Total, ppm	Platelet, $\log_{10}(I_0/I)/t$	r^2
Samotkan								
C12-2A	88	0	0	0	0	88	0	0.76
10	310	0	0	2	0	312	0	0.97
12	316	0	0	0	0	316	0	0.98
012	321	0	0	5	0	326	0	0.98
C22-IR	375	0	0	0	0	375	0	0.8
015	323	63	0	23	15	409	0	0.78
C12-4	570	0	0	0	0	570	0	0.7
C12-2B	610	0	0	0	0	610	0	0.83
02	788	0	0	17	0	805	0	0.98
013	826	0	30	24	0	880	0	0.93
25	234	19	858	17	2	1128	0	0.96
12-409	1044	9	11	21	1	1085	0	0.99
21	1312	20	0	23	1	1355	0	0.99
C30-IR	1346	0	213	15	0	1574	0	0.99
9	1577	0	0	25	0	1602	0	0.99
31	1367	0	780	16	0	2163	0	0.99
10	2083	0	61	21	0	2165	0	0.99
04	2298	0	33	33	0	2364	0	1
11	1648	157	785	34	6	2624	0.61	0.99
14	1632	162	918	46	6	2758	0	0.99
43	1958	67	914	27	2	2966	0	0.99
36	2448	123	427	34	4	3032	0	1
15	2970	0	183	0	0	3153	0	0.99
3	780	186	2262	83	6	3311	0	0.92
UK-24	2700	720	90	54	20	3564	0	0.99
5	3360	0	188	33	0	3581	0	1
30	2957	612	960	75	13	4604	0	0.99
Zeleny Yar								
Z35–5	198	0	0	0	0	198	0	0.68
26ZYA	816	61	46	17	6	940	0	0.96
8ZYA	158	933	0	39	83	1130	5.84	0.97
5ZYA	166	1244	0	51	85	1461	7.33	0.98

Table 2. Concentrations [at. ppm] of different nitrogen-bearing centers, total nitrogen concentration and content of platelets, $\log_{10}(I_0/I)/t$ [mm^{-1}], in small diamonds (< 1 mm) from the Udachnaya kimberlite pipe (Yakutia, Russia). r^2 is coefficient of determination.

Sample	A, ppm	B, ppm	C, ppm	D, ppm	$N_B\%$	Total, ppm	Platelet, $\log_{10}(I_0/I)/t$	r^2
50AUV	121	33	0	2	21	156	0.34	0.98
42AUV	101	47	0	4	31	152	0.95	0.95
43AUV	129	80	6	5	36	220	1.02	0.89
53AUV	416	88	0	8	17	512	0.93	0.99
54AUV	1192	0	17	9	0	1218	0	1.00
47AUV	1201	0	32	10	0	1243	0	1.00
39AUV	1182	161	0	16	12	1359	0	0.99
46AUV	1358	16	0	9	1	1383	0	0.99
37AUV	1456	114	4	14	7	1588	0	1
40AUV	1720	0	0	18	0	1738	0	1
48AUV	1784	0	32	15	0	1831	0	1
44AUV	1850	0	31	23	0	1904	0	0.99
38AUV	2202	0	7	16	0	2225	0	1
36AUV	2597	156	0	34	6	2787	0.85	1
AUZ20	143	123	2	6	45	274	1.19	0.97
10AUZ	273	55	0	7	16	335	0.63	0.99
11UAZ	274	45	0	5	14	324	1.14	0.98
9AUZ	624	28	0	4	4	565	0	1
AUZ34	662	48	0	1	7	711	0	0.98
6AUZ	537	389	0	30	41	956	1.47	0.98
AUZ27	620	453	11	24	41	1108	1.56	0.99
8AUZ	605	675	52	14	50	1346	1.92	0.94
7AUZ	1394	0	84	25	0	1503	0	0.98
AUZ23	970	788	0	39	44	1797	2.59	0.98
AUZ13	2042	0	0	12	0	2054	0	1
6Ud	135	26	23	5	14	189	0	0.95
7Ud	353	85	0	6	19	444	0.53	0.99
12Ud	518	57	9	7	10	591	0.33	1
17Ud	755	0	10	5	0	770	0	1
18Ud	630	64	14	21	9	729	0	0.97
2Ud	665	65	95	2	8	827	0	0.98
13Ud	791	161	2	12	17	966	1.10	0.99
1Ud	850	134	0	11	13	995	0.6	1
16Ud	943	165	0	14	15	1122	0.67	1
4Ud	1104	5	0	11	0	1120	0	1
20Ud	818	221	4	32	21	1075	1.8	0.98
11Ud	1174	0	0	8	0	1182	0	1
19Ud	858	0	326	14	0	1198	0	0.98
15Ud	725	3	500	6	0	1234	0	0.99
5Ud	1051	223	0	15	17	1289	1.1	1
10Ud	1730	0	0	10	0	1740	0	1

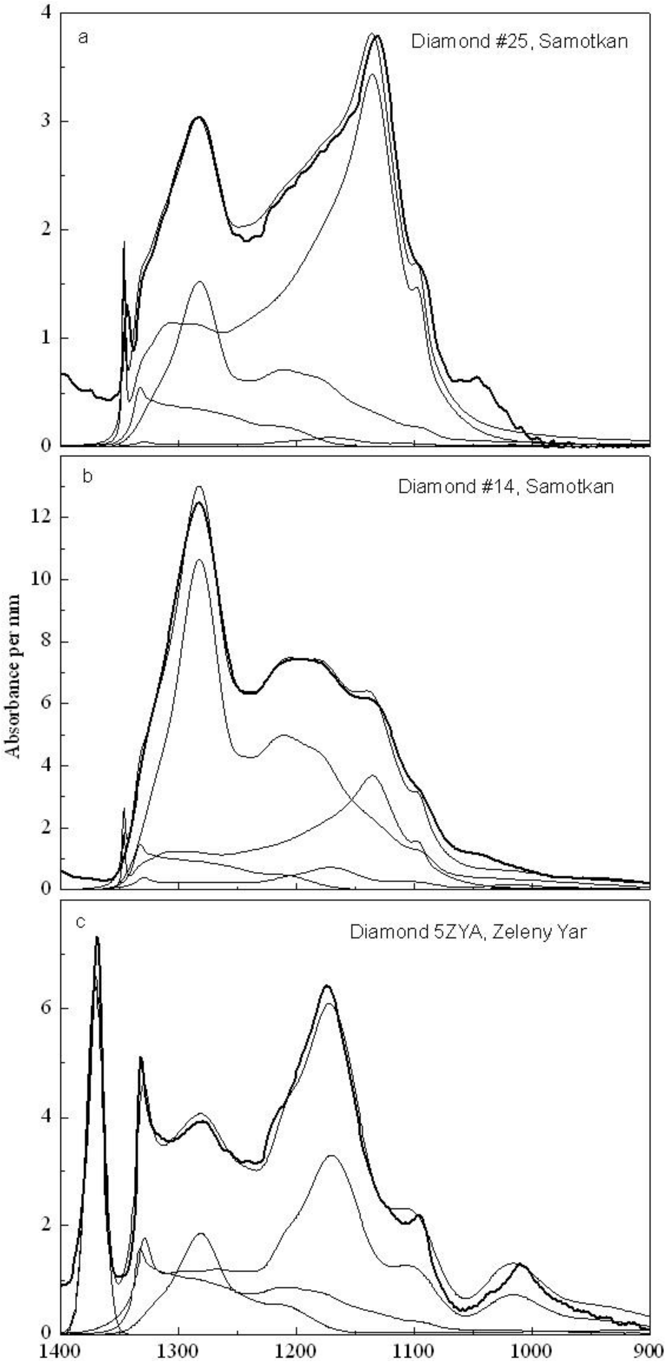

Fig. 3. The results of curve fitting analyses of spectra of three Ukrainian diamonds, #25 (a), #14 (b) from Samotkan and 5ZYA from Zeleny Yar (c), showing different contribution of the A-, B-, C- and D-form of nitrogen impurities. In the spectrum of 5ZYA diamond a significant content of platelets is displayed by the narrow absorption line at 1370 cm^{-1} (c), which is absent in the spectrum of diamonds #25 (a) and 14 (b). The experimental curves are shown by the thick line; the component functions are shown by the thin lines.

4.0). Nevertheless, the coefficient of determination, r^2, which indicate the reliability of the fits ($r^2 = 1.00$ is a perfect fit and $r^2 = 0.00$ is a complete lack of fit) are rather high, 0.99 and 0.97 for #14 and 5ZYA, respectively. For diamond #25 (Fig. 3a) r^2 is a little lower, 0.96 (compare also r^2 values in Tabs. 1 and 2). In the latter case, as well as in the case of specimen 5ZYA (Fig. 3c), some discrepancy obviously originates from the low and high energy parts of the spectrum, where an unaccounted contribution of defects, other than A-, B-, C- and D-centers or platelets, is relatively large: an appreciable contributions of D-function in these two cases, not expected for this diamond type, may just be due to this.

Among the four UDFs only the A-function seems very closely simulating the true spectral envelope of A-center. This follows from the fact that for many samples studied the A-function alone perfectly fits the experimental curves. Obviously, such diamonds (*e.g.* C12-2B, 02 (Tab. 1) or AUZ13, 10UD, 11UD (Tab. 2)) are to be regarded as of pure IaA-type. In many N_A-rich samples weak contents of other forms of nitrogen, only a few percents of the total N-contents (Tabs. 1, 2), may be regarded as artifact of the curve fitting procedure[1]. Especially, this concerns the D-form, which, as mentioned above, is not expected for this diamond type.

When A- and C-functions are highly predominant in spectra (*e.g.* #C30-IR, 15 (Tab. 1)) the fitting is frequently rather good (*cf.* r^2-values) thus indicating that, very likely, the C-function is also well constructed and closely simulates a real spectral curve of the N_C-center. On the other hand, the presence of nitrogen in the C-form may look somewhat questionable because, as believed (*e.g.* Kurdumov *et al.*, 1994), the C-center is discernible in the spectra, first of all, as a sharp absorption line with maximum at 1345 cm^{-1} (Fig. 2c). However, from our experience, this band is not always seen although many spectra show appreciable concentrations of N_C as revealed by the fitting. On the other hand, in such cases the fitting without C-component yields unsatisfactory results. In addition, the distinct absorption features, seen in experimental spectra as a shoulder at around 1135 cm^{-1} (Fig. 3, a and b), is consistent with the interpretation as one of the N_C-bands. Indeed, as seen from Fig. 2c, at these wavenumbers the C-function has a rather sharp maximum different from the curves modeling the other N-bearing defects, A, B or D (*cf.* Fig. 2, a to d). It is worth noting that such reasoning was also offered by Finne *et al.* (1994) to prove the presence of N_C-form of nitrogen in metamorphic diamonds from Kokchetav massif in Kazakhstan. Note that in the spectrum of Samotkan diamond #25 (Fig. 3a) where, by the fitting, the C-forms of nitrogen is predominant and of relatively high contents (Tab. 1) the harp line at 1345 cm^{-1} is quite distinct, although weaker and broader than in the modeling C-function. On the other hand, in Samotkan diamond #3 of the highest N_C-content among all samples studied (Tab. 1) this line is relatively weak. Thus, we assume that although the narrow line at 1345 cm^{-1} is not always discernable in the FTIR spectra of our samples, in some of them appreciable amounts of nitrogen enter the structure in the C-form. It should also be added for proof that in a number of crystals from Samotkan a very weak but distinct absorption, characteristic of the C-form including the narrow line at

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[1] For many samples (*e.g.* #02, 013, 9, AUZ13, 7AUZ *etc.* in Tabs. 1, 2) we could confidently have omitted these negligible quantities as insignificant artifacts. However, for the sake of clearness we keep all the data exactly as obtained by the curve fitting procedure.

~1345 cm^{-1}, is revealed in nearly "pure" form. Such crystals represent very rare Ib-type diamonds. All above reasoning proves the abundance of N_C substitutional impurity in diamonds from Samotkan deposit.

Simultaneous presence of considerable amounts of B- and C-form of nitrogen in some Ukrainian diamonds, as revealed by the curve fitting (*e.g.* #11, 14 or UK-24 (Tab. 1)), is not consistent with general opinion that C-form (single nitrogen atoms) can not maintain in diamonds with high N_B-contents (*e.g.* Clark & Davey, 1984; Mendelssohn & Milledge, 1995). Note, however, that the presence of appreciable amounts of both B- and C-forms of nitrogen is confidently revealed only in some Ukrainian crystals. In Yakutian samples such situation encounters mostly in low nitrogen diamonds as 8AUZ, 6Ud, 2Ud, 18Ud (Tab. 2) wherein the precision of the curve fitting (*cf.* r^2-values) is relatively low and, therefore, N_C-content can quite be an artifact of the fitting procedure.

As a matter of fact, the results of curve fitting depend on the choice of the absorption background in the range 800–1400 cm^{-1}. Sometimes such choice is not an easy task, especially in cases of low-nitrogen samples from Ukrainian deposits, when the presence of numerous intense bands of other than nitrogen-bearing centers influences the shape of the spectral curves and makes determination of the absorption background in this spectral range rather difficult: in such cases the spectral envelopes in 800–1400 cm^{-1} range obviously can not be satisfactorily fitted by the four functions A to D alone yielding low values of r^2 and suggesting an appreciable contribution of other than nitrogen-bearing centers. Besides, spectra of some samples studied are influenced by interferences on the sample faces which are very difficult to avoid for diamonds. A great disadvantage is that we had to measure spectra of naturally shaped, not ground and polished samples. This causes frequently significant losses of light intensity and results in an intense pseudo-absorption background. Note that it is very difficult to polish such objects because of their tiny dimensions and extremely high hardness.

Depending on all above factors we estimate the precision of N_A- to N_D-content determinations by our method from ~25% in low-nitrogen imperfect samples to a few percents in high-nitrogen diamonds having perfect parallel, most frequently the octahedral (111) faces, suitable for spectroscopic measurements. Probably, the precision of our method is commensurable with that of Taylor *et al.* (1990) based on consequent subtraction of A-, B- and D-curves from experimental spectra.

We may also compare the results of the nitrogen content determinations in A-, B-, C- and D-forms, obtained by the methods described here, with those obtained by the graphical method developed by Mendelssohn & Milledge (1995). For such comparison we chose well-shaped Yakutian diamonds of octahedral habit with perfectly transparent {111} faces. In these samples the background induced by Mendelssohn & Milledge (1995) practically coincides with that used by us. As an example, a raw spectrum of a low-nitrogen Yakutian diamond in the whole spectra range measured, 4000–500 cm^{-1}, normalized to the thickness 1 mm and derived from it the background corrected spectrum in the range 1400–900 cm^{-1} together with the result of its decomposing to A, B, C and D UDF are shown in Fig. 4, a and b, respectively. As one can see in Fig. 4a there is really no problem in choice of the baseline in this case.

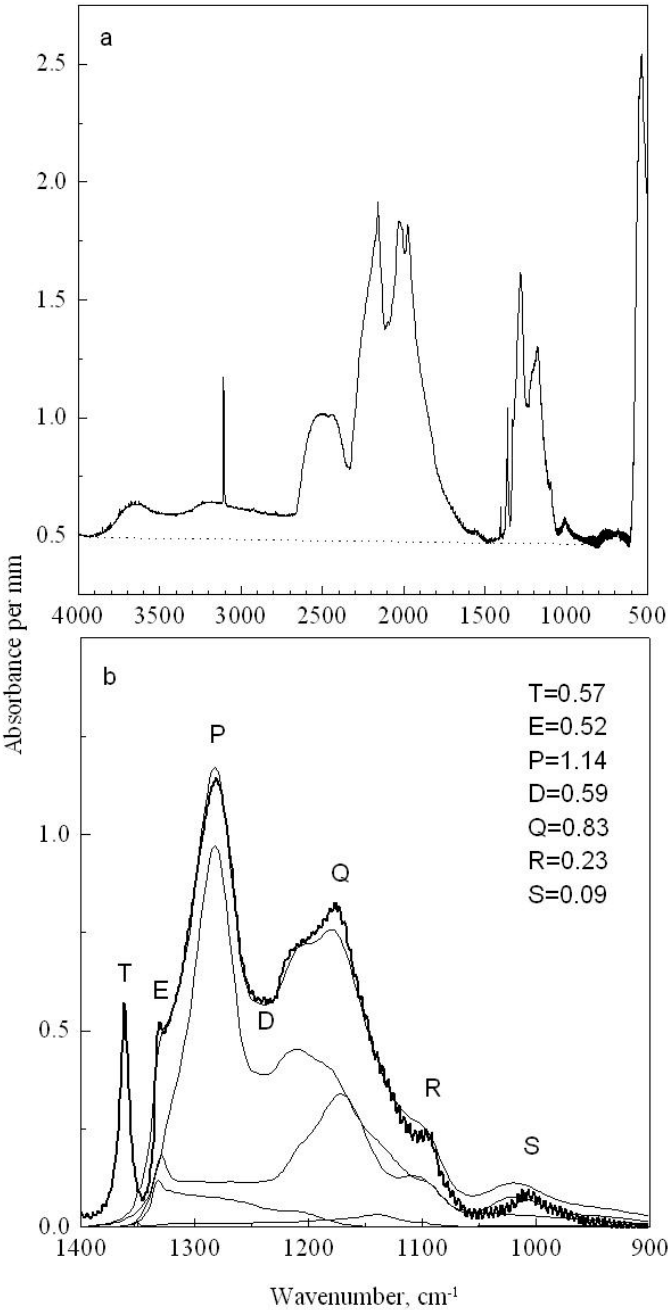

Fig. 4. (a) Spectrum of a low-nitrogen Yakutian diamond in the range 4000–500 cm^{-1} normalized to thickness 1 mm. The background chosen is shown by the dotted line. (b) the same spectrum in the range 1400–900 cm^{-1} after the background correction together with the results of its curve fitting. The experimental curve is shown by the thick line; the component functions are shown by the thin lines. The characteristic points, T, E, P *etc.*, used for graphical evaluation of the percentage of IaB aggregation in the method developed by Mendelssohn & Milledge (1995) and the values of absorption in these points are also shown.

The characteristic absorbance values T, E, P *etc.*, defined by Mendelssohn & Milledge (1995), are also shown in Fig. 4b. From the ratios obtained, E/P = 0.455, D/P = 0.512 and Q/P = 0.721, the percentage of the IaB aggregation, derived from the diagram in Fig. 6 of Mendelssohn & Milledge (1995), varies from *ca.* 12 to 22%. The value, obtained by our method, is appreciably higher, ~32%. Remember that in the latter case the total nitrogen content was summarized over A-, B-, C- and D-forms of nitrogen. If the summation was taken over A- and B-forms only, as is the usual procedure (*e.g.* Kaminsky & Khachatryan, 2001), the percentage of IaB aggregation, obtained by our methods, would have been even higher.

For a couple of other samples, the methods of Mendelssohn & Milledge (1995) also gave rather divergent results, different from ours. Thus, in one sample, #5UD, the percentage of IaB aggregation determined from Q/P-ratio (*cf.* Fig. 4b) is only ~2%, that derived from E/P is ~6% and from D/P – 7%. The value obtained by our method is 17% (Tab. 2). For diamond #16UD Q/P-, E/P- and D/P-ratio yielded, respectively, ~1, 5 and 6%.[2] Our method gives 15% (Tab. 2). All these discrepancies indicate that the graphical method, developed by Mendelssohn & Milledge (1995) and broadly used nowadays for analysis of nitrogen content in diamonds (*e.g.* Meyer *et al.*, 1997; Kaminsky & Khachatryan, 2001; Khachatryan, 2003 a, b), gives results rather inconsistent with ours. Therefore, we have to analyze this circumstance a little more closely.

One of the important deductions of Mendelssohn & Milledge's method is that the ratios E/P, D/P, Q/P *etc.* are linear functions of percentage of IaB aggregation (*cf.* Fig. 6 in the cited paper). To verify this important statement upon our model curves we built up simulated envelopes as linear combinations of A and B UDFs computed at 10% intervals for the diamond thickness 1 mm and for the total nitrogen content 1000 ppm (Fig. 5). From this set of curves the E/P-, D/P-, Q/P- *etc.* ratios were calculated for each N_B% and plotted in Fig. 6 as E/P, D/P, Q/P *etc. vs.* N_B%. As seen from the figure, these dependencies remind in a way the dependences constructed by Mendelssohn & Milledge (1995, Fig. 6), but in contrast to the latter, which are all straight lines, ours are noticeably curved and, when applied to the same samples, give significantly different results. Also, all of them, except Q/P, weakly depend on N_B% in the range up to 60–70% N_B. From this we conclude that only Q/P-ratio is applicable for more or less reliable determination of N_B%. Naturally, our N_B%-values, derived from the diagram in Fig. 6, are in better agreement with the results obtained by the curve fitting than the values obtained by Mendelssohn & Milledge's method. For instance, for the E/P-, D/P-, Q/P-ratios in Fig. 4b the respective values of N_B% are ~48, 49 and 38% (those obtained from Mendelssohn & Milledge's (1995) diagram are ~22, 15 and 12%). The N_B%-value obtained by the curve fitting (see above) is 32%. This is rather close to 38% derived from the Q/P-ratio in Fig. 6 but significantly differ from the values derived from E/P- and D/P-ratios. This and several other attempts on a number of diamonds of predominantly IaAB-type show that, as stated before, in case of the modified diagram in Fig. 6 only Q/P *vs.* N_B% dependence, which is most sensitive among all others, gives results close to those obtained by the curve fitting procedure.

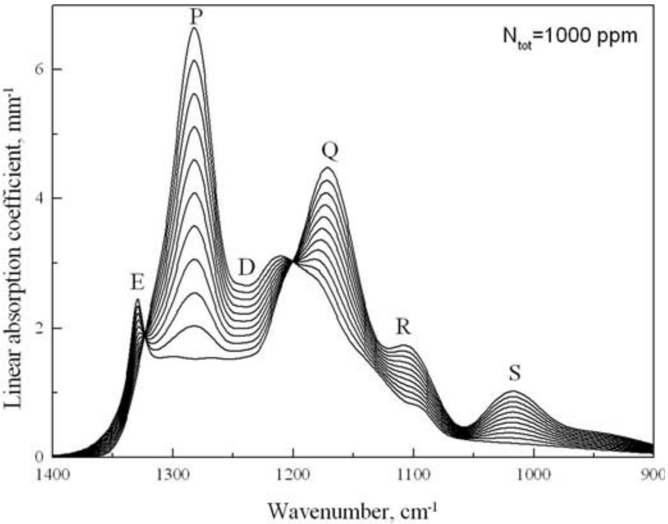

Fig. 5. Simulated spectra, computed for diamond thickness 1 mm at 10% intervals using A and B UDFs in the IaA/IaB aggregation series. The total nitrogen content, N_{tot}, is taken 1000 ppm. The characteristic points, E, P, D *etc.*, used in the method developed by Mendelssohn & Milledge (1995), are shown.

Taking all above argumentations into account, we should notify that the results obtained by our curve fitting method are hardly comparable with those obtained by the older graphical method of Mendelssohn & Milledge (1995). Since our method is based on a certain mathematical model we consider it as more grounded and providing more realistic results. Perhaps, the Mendelssohn & Milledge's method, which as a first approximation is undoubtedly of a great importance, needs some corrections. Probably, it has to be verified and corrected with a curve fitting procedure like that used here. This, however, is not an item of this study.

It should be emphasized that the total number of diamond crystals from the three deposits, Samotkan, Zeleny Yar and Udachnaya, studied here, are much larger, namely 112, 48 and 57, respectively, than compiled in Tabs. 1 and 2. But, as mentioned above, in most of the Ukrainian diamonds the concentrations of IR-active nitrogen are too low to be discerned in all the crystals. The Yakutian diamonds studied are in this respect much more "nitrogeneous". Thus, the average nitrogen content in diamonds from Samotkan, Zeleny Yar and Udachnaya, as evaluated from infrared spectra of all samples studied, *i.e.* taking into calculation also nominally anitrogenous ones, not sited in Tabs. 1 and 2, is 426, 78 and 785 at. ppm, respectively. Note that the latter value is nearly two times larger than that obtained for Udachnaya by Kaminsky & Khachatryan (2001), 428 at. ppm.

As seen from Tab. 1, there is a distinct difference between contents of different nitrogen-bearing centers, A, B, C and D, in diamonds from Samotkan and Zeleny Yar deposits. First of all, in all Samotkan diamonds the predominant form

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[2] Meyer *et al.* (1997) suggest that in such cases the mean N_B%-value is probably more reliable than a single determination. However, we doubt that that is so since the values obtained, say, ~1, 5 and 6% for #16UD, differ from each other several times.

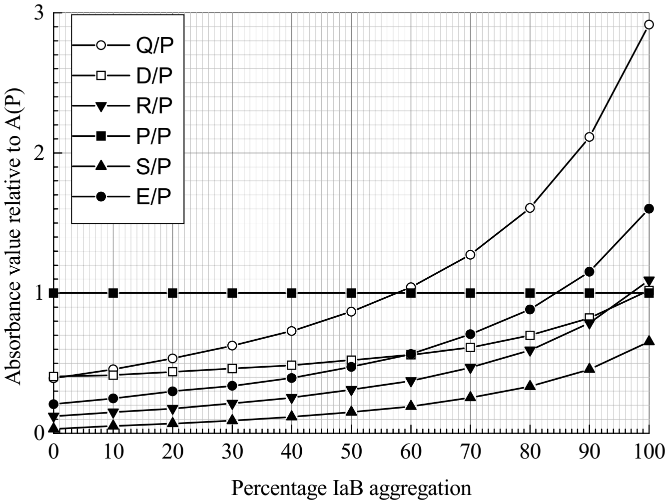

Fig. 6. Calculated from the simulating envelopes in Fig. 5 the variations in the absorbance features at the selected points E, P, D *etc.* normalized to a value of unity for the absorbance at P, 1282 cm^{-1}.

of nitrogen is the A-center. Some contributions of B-defects (up to 20% in UK-24, Tab. 1) are revealed only in a few samples. The presence of D-center is rather an artifact (see above) except, perhaps, a few samples with appreciable amounts of N_B, #11, 14 and UK-24 (Tab. 1). On the other hand, as was already emphasized, some crystals from this deposit contain high concentrations of C-defects (in two Samotkan samples, #3 and 25, the C-form of nitrogen is even highly predominant over A, B and D) in contrast to diamonds from Zeleny Yar, among which only one sample from four (26ZYA) seems containing some nitrogen as C-defects. The other three nitrogen-bearing samples from Zeleny Yar are enriched with N_B and platelets. In this respect they again differ from Samotkan diamonds, in whose spectra, except for one sample, #11, the platelet peak is not detected at all. This observation is consistent with the more general one that diamonds with low N_B-content are usually depleted with platelets (Clark & Davey, 1984; Woods, 1986).

The strongly different ratios of A and B nitrogen center concentrations in diamonds from Samotkan and Zeleny Yar (Tab. 1) indicate that the temperature or time (or both) of their residence under Mantle conditions were distinctly different. Indeed, B-defects appear, as experimentally established by Allen & Evans (1981) or Evans & Qi (1982), at the expense of thermally induced aggregating of A-centers. The activation energy of this process is evaluated to be ~7 eV (*e.g.* Mendelssohn & Milledge, 1995). With such activation energy at temperatures expected in the Mantle, the A→B aggregation reaction needs times of several billion years to reach N_B/N_{total} ratios, observed in natural diamonds. Therefore, absence or low contents of B-centers in N_A-rich diamonds from Samotkan suggests that they are either related to relatively cool interior of the lithosphere, or that the time of their residence at Mantle conditions was relatively short. Noticeable concentrations of C-form of nitrogen in many samples from the Samotkan deposit (Tab. 1) also support such suggestion because, according to the concept of overall aggregation sequence of nitrogen defects in diamond (Dyer *et al.*, 1965; Chrenko *et al.*, 1977), it begins with the incorporation of single N atoms into the structure during crystallization in the Mantle. Afterwards the primary defects transform in the sequence C→A→B (*e.g.* Mendelssohn & Milledge, 1995). Therefore, in accordance with this model significant contents of residual C-form of nitrogen impurity is in favor of the above suggestion on low temperature conditions or relatively short Mantle residence times of Samotkan diamonds. The circumstance that in some Ukrainian microdiamonds (*e.g.* #11, 14, UK-24 (Tab. 1)) there are considerable concentrations of both B and C forms of nitrogen may evidence a significant difference of their origin when compared with kimberlitic Yakutian microdiamonds where the presence of nitrogen in both forms C and B in some samples (Tab. 2) can be regarded rather as artifact of the fitting procedure (see above). As coexistence of B and C forms of nitrogen in Ukrainian diamonds conflicts with a commonly accepted concept of nitrogen defects transformation sequence C→A→B, we assume that two differently generated layers may constitute such samples, say, the inner one, enriched with N_B, and the outer rim overgrown latter, enriched with N_C. Note that such coated diamonds with different forms of nitrogen impurity in inner and outer parts of crystals were already described in literature (*e.g.* Amthauer *et al.* 1995). Of course, for Ukrainian microdiamonds such assumption should be confirmed (or disproved) by additional investigations although this is not an easy task considering tiny dimensions, extreme hardness and imperfectness of these objects.

In Fig. 7 (a and b) a series of isotherms depicting the extent of A→B conversion as a function of total nitrogen content are plotted. They are calculated from a second-order rate law, expressed by the equation $[A]_t = [A]_0/(1+k_2\cdot t\cdot[A]_0)$, where $[A]_t$ is A-defect concentration at time t and $[A]_0$ is initial A-defect concentration, $k_2 = A\cdot\exp(-E_a/RT)$, where A is Arrhenius constant and E_a is activation energy of A to B conversion (*e.g.* Taylor *et al.*, 1990). The values $\ln(A) = 12.59$ and $E_a/R = 81160$ K were taken from Leahy & Taylor (1997). As no information on age of diamonds from both Ukrainian placer deposits, Samotkan and Zeleny Yar, is available, the Mantle residence time, t, is assumed to be 3 Ga and 2 Ga.

In Fig. 7a the data on N_B% and N_{total} derived from FTIR spectra of diamonds from Samotkan (open squares) and Zeleny Yar (filled squares) are plotted over the calculated isotherms. It is seen that in the case of the Mantle residence time of 3 Ga the diamonds from Zeleny Yar exhibit a very broad range of temperatures showing for two samples, 5ZYA and 8ZYA, the highest temperature obtained, ~1150 °C. On the other hand, one sample from this deposit, Z35-5, contains nitrogen only in A-form, like most crystals from Samotkan (*cf.* Tab. 1). This again shows relatively low Mantle residence temperatures of such samples. As was established by Kiflawi *et al.* (1997) for {111} growth sectors of synthetic diamonds, C→A transformation obeys a second-order rate law with activation energy ~5.5±0.7 eV. However, the aggregation rate constant was found to be different even within the same {111} growth sector and strongly depends on pressure (see also Satoh *et al.*, 1990; Taylor *et al.*, 1990; Mendelssohn & Milledge, 1995). Therefore,

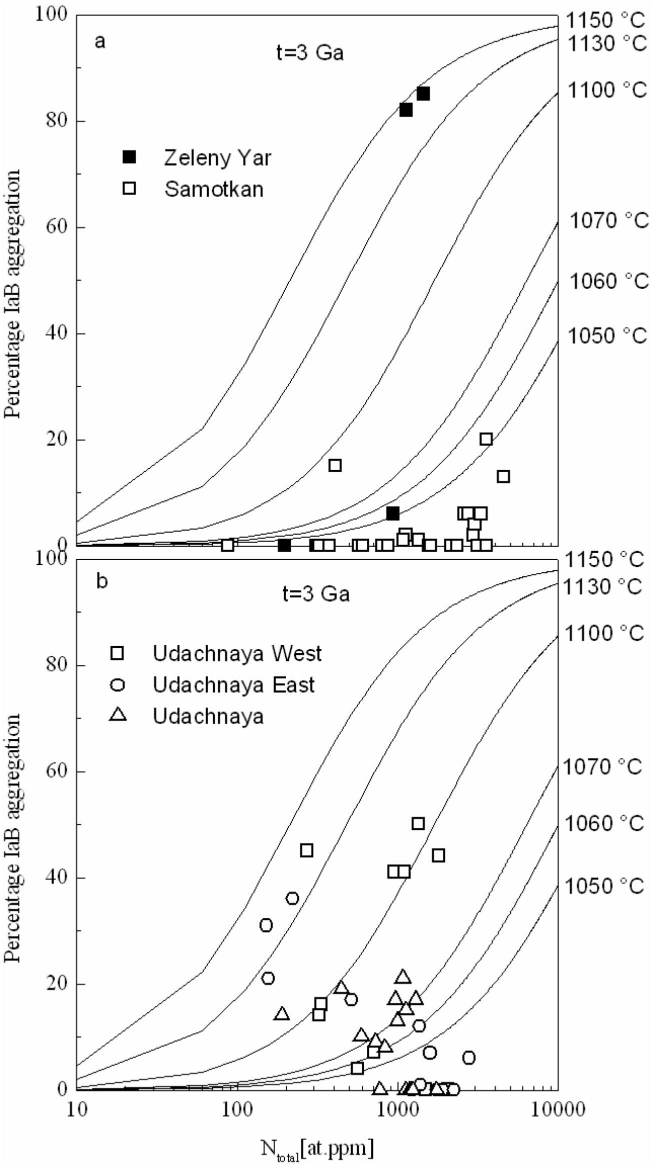

Fig. 7. Isotherms and loci of Ukrainian (a) and Yakutian diamonds (b) for a selected Mantle time residence of 3 Ga.

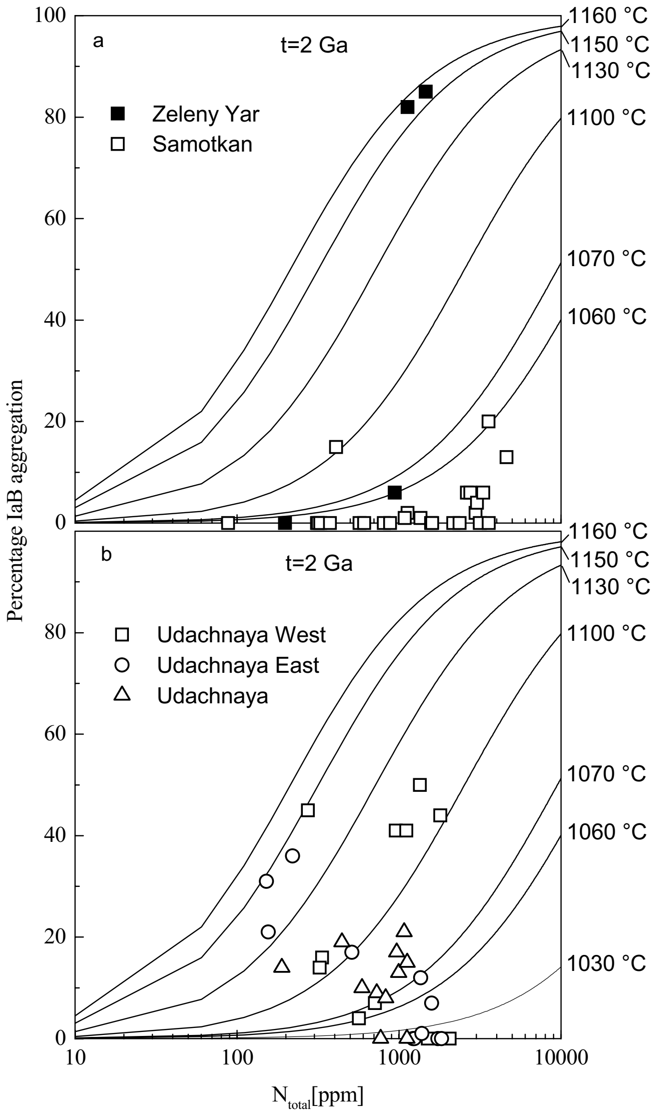

Fig. 8. As in Fig. 5, but for a Mantle time residence of 2 Ga.

Ib/IaA aggregation can hardly be applicable for consistent evaluation of temperature or time of residence of natural diamonds in Mantle conditions by calculations similar to those applied to IaA/IaB aggregation states.

One Samotkan crystal, #015, shows a rather high temperature, around 1100 °C, but this result seems doubtful taking into consideration a relatively low total nitrogen content in this sample (409 at. ppm, Tab. 1) and, thus, low precision of the curve fitting procedure (see above). The highest temperature, more reliably derived for Samotkan diamond #11 with total nitrogen ~2600 at. ppm is ~1050 °C (Fig. 7a). All other samples show lower temperatures. For many of them, having zero $N_B\%$ content, temperature can not be evaluated in this way at all (see above).

The samples from the Udachnaya kimberlite pipe designated as AUV and AUZ (Tab. 2) were collected in different times from, respectively, the Eastern and Western part of the deposit, whereas those labeled as Ud were independently collected over the whole deposit. As seen from Fig. 7b, the temperatures, obtained for these samples, vary in a rather broad range. The highest temperatures are evaluated to be ~1140 °C. Again, a part of samples contains negligible or no B-form of nitrogen that evidences much lower temperatures. In addition, as seen from Fig. 7b, there seems to be no noticeable difference between loci of the samples collected in the different parts of the deposit, Eastern and Western.

Under the assumption of Mantle residence times of 2 Ga for both Ukrainian and Yakutian diamonds (Fig. 8) the temperatures do not change much.[3] As seen from comparison of Fig. 7 and Fig. 8, the shortening of residence time from 3 to 2 Ga results in a temperature increase of only ~10 °C for all samples studied.

When one compares the results on Ukrainian and Yakutian diamonds, at least two conclusions can be drawn. First, Yakutian diamonds are in general more nitrogenous than

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[3] As established by Richardson & Harris (1997) from Sm-Nd isotope relationship in peridotitic garnet inclusions in Udachnaya diamonds the age is 2,010±60 Ma.

Ukrainian: up to 75% of the Yakutian crystals studied show IR bands of nitrogen intense enough for a reliable curve fitting procedure. About 20% of the Yakutian diamonds studied here show still discernable nitrogen-related IR bands. Therefore, up to ~95% of the Yakutian diamonds may be regarded as nitrogen-bearing. Note that a similar deduction was also made by Dyer *et al.* (1965) and Bilenko & Zhikhareva (1979), whereas Trautman *et al.* (1997) found up to 25% of Yakutian diamonds are of type II, *i.e.* nitrogen-free. Different from this, among the Ukrainian samples only ~25% and ~10% of Samotkan and Zeleny Yar samples, respectively, all compiled in Tab. 1, contain nitrogen in concentrations discernable in infrared spectra. On the other hand, among all samples studied, the highest total nitrogen concentration, *ca.* 4600 at. ppm, is incorporated in Ib-IaA-type diamond #30 from Samotkan (Tab. 1). In diamond #3 from this deposit up to ~2260 at. ppm of nitrogen is in C-form, the highest N_C-content among all samples studied. All this may suggest that Samotkan placer compiles diamonds from several different sources, or, if Samotkan diamonds grew in a single magmatic chamber, that there were highly inhomogeneous conditions of crystallization with respect of nitrogen contents and temperature of post-crystallization residence in the Mantle or, as mentioned above, they have grown in two or more stages.

Second, although in the Yakutian diamonds the predominant form of nitrogen is A-form, unlike most diamonds from Samotkan where A-form also predominates, the contents of B-form of nitrogen in the former is, on the whole, much higher than in the latter (*cf.* Tabs. 1, 2). The Yakutian diamonds should, therefore, be attributed to IaAB-type, while those from Samotkan – mostly to IaA- and, sometimes, to Ib-IaA-type. Correspondingly, the platelet contents in Yakutian samples are also high compared with Samotkan samples, which all show low, if any, platelet concentrations. Besides, in contrast to Samotkan diamonds, in Yakutian samples the concentrations of N_C are very low and can mainly be regarded as artifacts. By these three parameters, N_B%, platelet- and N_C-contents, Yakutian diamonds significantly differ from those from Samotkan. On this account a large part of Yakutian diamonds studied show temperatures of Mantle residence higher than Samotkan diamonds, but lower than the highest temperatures obtained for diamonds from Zeleny Yar (*cf.* Fig. 7, a and b, or 8, a and b).

In general, it should be emphasized that the method of evaluation of Mantle residence temperature from infrared spectra of diamonds evidences that in all three deposits studied, Samotkan, Zeleny Yar and Udachnaya, the temperatures derived vary in broad ranges. Probably, in case of the Samotkan and Zeleny Yar this may be due, at least partly, to different origins of diamonds concentrated in these placer deposits. In case of diamonds from Udachnaya, all of kimberlitic origin, the large difference in temperatures evidences either great temperature inhomogeneity during the residence in Mantle, or that temperature determination from infrared spectra of nitrogen-bearing centers in diamonds should be treated with caution. We should notice in this respect that the residence temperature, estimated by Kaminsky & Khachatryan (2001) for the whole Daldyn-Alakit diamond-bearing province to which the kimberlite pipe Udachnaya belongs, ranges only from *ca.* 1100 to 1140 °C (t = 3 Ga), whereas the temperature estimated for diamonds from the pipe itself varies even much less, hovering around ca. 1120 °C. These results differ significantly from those obtained here, which establish for diamonds from Udachnaya a much broader temperature range with maximum $T \approx 1140$ °C (Fig. 5b). Note that our data are more consistent with those of Richardson & Harris (1997), who found for diamonds from Udachnaya that temperatures vary in a broad range up to 1200 °C with the majority of diamond plot between 1125 and 1175 °C.

Acknowledgments: The authors are thankful to F.V. Kaminsky and P. Cartigny, the reviewers, who gave helpful comments which significantly improved the paper. We thank E. Libowitzky, the associated editor, who also gave very helpful comments and suggestions, kindly checked and improved the English style.

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Received 28 October 2004
Modified version received 10 June 2005
Accepted 19 September 2005