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Effect of thermobaric treatment on magnetic and superconductive properties of HPHT-grown nitrogen-doped diamond crystals

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ABSTRACT

The effect of thermobaric treatment (TBT) at P = 5.5 GPa T = 1900 °C for 4 h on the concentration of single substitutional atoms (P1 centers) in nitrogen-doped synthetic single crystal Ib type diamonds grown by the temperature gradient high-pressure high-temperature (TG-HPHT) method and on their magnetic properties in the temperature range of 2–300 K was investigated. The initial concentration of P1 centers in 2 crystals was 3.0 $\times 10^{19}$ cm⁻³ and 5.6 $\times 10^{19}$ cm⁻³, respectively, which decreased by ~96–98 % after TBT. At T < 10 K, an anomalous hysteresis of the magnetic moment is observed in the range of magnetic fields up to $H_c = 70$ kOe, the amplitude of which is half the value of the paramagnetic saturation moment, corresponding to the number of spins of the P1 centers. The shape of the hysteresis loops after subtracting an intrinsic diamond diamagnetic component and the calculated paramagnetic component indicates a granular (local) superconducting state. The fact that the amplitude of the magnetic moment generated by superconducting currents is equal to half the total number of Bohr magnetons of P1 centers may indicate that elementary currents occur in pairs of adjacent P1 centers. As a result of a decrease in the number of P1 centers in diamonds after TBT, the saturation values of the paramagnetic moment of the induced superconducting currents decrease proportionally.

1. Introduction

The magnetic properties of nitrogen-doped natural and synthetic type Ib diamonds occur due to the paramagnetic properties of isolated substitutional nitrogen atoms (C-centers), their complexes with vacancies, and some more complex aggregates [1–9]. Paramagnetic and ferromagnetic impurities are also observed in synthetic diamonds grown by the high pressure-high temperature (HPHT) method from a growth medium that contains solvent/catalyst transition metals such as Fe, Ni, Co [10,11]. However, metal impurities in synthetic diamonds are usually considered undesirable because they impair mechanical properties of diamonds and reduce thermal conductivity. In this regard, modern technologies for the growth of high quality synthetic diamond single crystals make it possible to obtain crystals with very low concentrations of metal impurities. Isolated substitutional Ni atoms, nickel-related and cobalt-nitrogen paramagnetic defects in synthetic single-crystal

diamonds have been discussed in [12]. The effect of high-pressure-hightemperature annealing on these type defects in diamonds grown by TG-HPHT method at P = 6 GPa; T = 1450 °C using Ni–2 wt% Ti and Ni–20 wt% Fe solvents/catalysts was investigated in [13]. EPR spectrometry method was used for identification of paramagnetic defects and calculation of their concentrations. The concentrations of Ni-related paramagnetic centers were 3–15 ppm in as-grown crystals, but after TBT they reduced to 1 ppm and less. Isolated substitutional Fe atoms or ironrelated paramagnetic centers were not identified. The concentration of paramagnetic nitrogen C-centers (P1 centers) was by an order of magnitude higher than that of Ni-related centers in the case of crystal grown without Ti nitrogen getter. In the last 10 years, due to the rapid development of quantum magnetometry based on nitrogen vacancy centers (NV-centers) [14,15], studies of the spin properties of the nitrogen defects in diamond have received much attention. At the same time, recent low-temperature studies of HPHT-grown single crystals of

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type Ib diamond and the effect of high-energy electron irradiation of them [16,17] revealed the presence of an unconventional hysteresis of magnetization in the temperature range below 25 K, not associated with ferromagnetism, but peculiar to the granular superconducting state, similarly to heavily boron-doped diamonds, which exhibit both local and global superconductivity [18,19]. The superconductivity of nitrogen-doped diamonds has also been considered theoretically [20–22].

In addition to irradiation with a beam of high-energy electrons, other ways of influencing C-centers in nitrogen-doped diamonds are possible, in particular, by the aforesaid thermobaric treatment (TBT) [13,23–27]. As a result of TBT, a part of paramagnetic C-centers can be transformed into non-magnetic A-centers, i.e. complexes of two nitrogen atoms in a diamond unit cell, with mutually compensated spins of additional valence electrons [8,9]. A correlation between the concentration of C-centers and the magnitude of magnetization was revealed in [16], but the role of A-centers and other nitrogen complexes remained unclear. Therefore, the study of the effect of the transformation of C-centers into A-centers as a result of thermobaric processing of type Ib diamonds on their low-temperature magnetic properties is of considerable interest for a better understanding of the mechanism of the observed low-temperature diamagnetic superconductor-like contribution to the total magnetic moment.

In this regard, we have experimentally investigated the effect of a decrease in the concentration of C-centers after TBT of diamond single crystals with an initial concentration of nitrogen C-centers up to 320 ppm on their magnetic properties in the temperature range of 2–300 K and magnetic fields up to 7 T, analyzed the experimental data obtained and proposed a new physical model to explain the unpredicted phenomena.

2. Experimental samples and methods

Two nitrogen-doped diamond single crystals, designated as samples A and B, approximately 2 and 1.5 carats in weight, were grown by TG-HPHT method [10] at P = 5.5 GPa; $T = 1500-1550^{\circ}$ C in the Fe-Co-C-N system without nitrogen getters [10,11]. The solvent metal alloy was smelted from a powder mixture of 99.99 % pure iron and 99.98 % pure cobalt in a 1:1 weight ratio in an induction furnace in a nitrogen atmosphere. Graphite of 99.9995 % purity was used as the carbon source. Using laser cutting followed by mechanical polishing, 4 plates with maximum dimensions of approximately $4.0 \times 8.0 \times 0.4$ mm³ with a crystallographic orientation of the large faces (100) and a total weight of 0.16 g were produced from sample A (Fig. 1(a)).

From sample B (Fig. 2(a)), a 0.5 mm thick bottom layer with a seed crystal in the center was laser cut off, and its final weight was 0.316 g. Using the floating on water test on a non-magnetic support with a strong permanent magnet, all samples were preliminarily checked for the

absence of ferromagnetic micro-inclusions of the solvent metal. Sample B was laser cut into 3 pieces, the largest of which, weighing 0.256 g, was designated B1. It is shown in Fig. 2 (b) after TBT. The other 2 parts are sample B2 (Fig. 2(c)). The B series samples were not mechanically processed. Prior to all magnetic measurements and EPR analysis, all samples were cleaned from any surface contamination by treatment in a boiling mixture of hydrochloric and nitric acids (3:1 volume ratio) for 2 h, washed in deionized water and annealed in air at a temperature of 680 °C for 20 min. Using the Skyrary EDX3600K energy dispersive X-ray fluorescence analyzer, we found about 1 ± 0.5 ppm Fe and 0.3 ± 0.2 ppm Co in sample B.

Thermobaric treatment was carried out at P = 5.5 GPa; $T = 1900^{\circ}$ C for 4 h using the method described in [13,23–27], by which the majority of C-centers were transformed into A-centers. Photos of the samples after TBT, designated as A1_{TBT} – A4_{TBT} and B1_{TBT}, are shown in Fig. 1(b) and Fig. 2(b). Before TBT, the nearly colorless diagonal areas with prevailing A-centers in {100} growth sectors are clearly visible in samples A1-A4 (Fig. 1(a)). Concentrations of C-centers in these areas are 3–10 times lower than in the yellow areas. The plates are yellow due to optical absorption of C-centers. After TBT, samples A1 – A4 became just slightly vellow (Fig. 1(b)). This indicates a decrease in the number of C-centers. The color of sample B1_{TBT} became much brighter yellow comparing to the initial crystal (Fig. 2(a)) and the unannealed parts (Fig. 2(c)), also due to the reduction in the concentration of C-centers. TBT makes it possible to modify the structure of the nitrogen impurity centers without changing the chemical composition of the samples, and, thus, to investigate the effect of the transformation of C-centers into A-centers on the magnetic properties of nitrogen-doped diamonds.

Local concentrations of C-centers and A-centers in samples before and after TBT were measured using the IR absorption spectrometry method [8,9]. Details are described in the Appendix. We did not observe any spectra associated with vacancies, B-centres or other nitrogen vacancy centres in the as-grown samples or after TBT.

The integral numbers of P1 centers in each sample were measured by EPR spectrometry [1–6]; spectra and measurement procedure conditions are also presented in the Appendix. In addition, the integral numbers of paramagnetic centers such as P1-centers were calculated based on the Curie constant data obtained via the magnetic moment as a function of reverse temperature, and the magnetic moment saturation values at T = 2 K, H = 70 kOe. The values obtained were in good agreement with each other and also with EPR and IR spectrometry data for samples A and B, but there were deviations by factors 1.5–2 for the post-TBT samples. We suggest that such deviations might occur due to some systematic error in the spectroscopic data in cases of low concentrations of C-centers (P1 centers) and unclear role of small fractions of Fe and Co impurities.



The DC magnetic moment m of the samples studied was measured

Fig. 1. Samples A1 – A4 of nitrogen-doped diamond plates cut from type Ib synthetic single crystal grown by HPHT method. (a) – initial, (b) – after thermobaric treatment at P = 5.5 GPa, T = 1900 °C for 4 h.



Fig. 2. Sample B of a nitrogen-doped synthetic single crystal diamond grown by the HPHT method (a), and its parts B1 (b), B2 (c). Part B1 is shown after thermobaric treatment.

using a Quantum Design MPMS XL SQUID magnetometer in a constant field in the range (-70 kOe) - (+70 kOe) in the temperature range 2–400 K. The sensitivity of the magnetic moment measurements was of the order of 1 µemu. A series of m(H) dependencies were measured at fixed temperatures of 300 K, 15 K, 10 K, 5 K, and 2 K (Fig. 3). The field change rates were 1 kOe/min in the range (-10 kOe) – (+10 kOe) and 5 kOe/min outside this range. We also measured the m(T) dependencies during cooling from 400 K to 2 K (Fig. 4(a)); as well as from 50 K to 2 K and subsequent heating to 50 K at fixed magnetic field values of 0.1, 0.2, 5, 10, 15, 20, 40, 70 kOe (Fig. 4(b)). Cooling and heating were performed at the rate of 0.5 K/min in the range of 2–50 K, and 1 K/min in the range of 2–400 K. The samples were positioned in the applied field so that their [100] crystallographic direction was perpendicular to the field vector.

The total mass of samples A1–A4 (designated as A_{Σ}), the mass of sample B1, the results of IR and EPR spectroscopy analysis, and the numbers of paramagnetic P1 centers evaluated from the analysis of magnetic measurement data before and after TBT are presented in Table 1. More detailed information on all the samples investigated is given in Tables A1, A2 in the Appendix.

3. Magnetic measurements results

Fig. 3 shows the dependence of the longitudinal magnetic moment of the samples on the magnitude and direction of the magnetic field vector m(H) before TBT (a,b,e) and after TBT (c,d) at fixed temperature values in the range from 2 K to 300 K. At T = 300 K the paramagnetic contribution is insignificant and all samples have negative magnetic susceptibility $\chi = (-3.9; -4.0; -4.1; -4.3; -4.4) \times 10^{-7}$ emu×g⁻¹ × Oe⁻¹, for samples B1, B2, A, A_{TBT} and B1_{TBT}, respectively. These values are close to the known data for undoped diamonds $(-4.5 \pm 0.2) \times 10^{-7}$ emu×g⁻¹ × Oe⁻¹ [16,28,30]. As the temperature decreases below T = 200 K, the paramagnetic contribution to the magnetic moment becomes noticeable; it dominates at T < 25 K in samples B1 and B2, and at T < 20 K in sample A (Fig. 4).

After TBT, the diamagnetic nature of the m(H) dependence dominates in both A_{TBT} and $B1_{\text{TBT}}$ samples over an entire temperature range (Fig. 3(b,d)). At T < 7 K, H > (10-20) kOe a saturation of m(H) occurred in samples A, B1, B2, as can be seen in Fig. 3 (a,c,e). The saturation can be seen most clearly at T = 2 K in all of the samples after subtraction of the intrinsic diamagnetic component of diamond, Fig. 6. We thus observe the well-known paramagnetic behavior of type Ib diamond with magnetic moment saturation at high magnetic fields as in [16,17]. In addition, very characteristic hysteresis loops in the m(H) dependencies at T < 10 K, first observed and analyzed in [16,17], are very evident. We also observed the temperature hysteresis of the magnetic susceptibility at T < 15 K (Fig. 5 (c-d)) in sample B2, for which such measurements were performed.

Fig. 5 (d,e) shows the temperature dependencies of the $(\chi - \chi_{dia}) * T$

function for this particular sample at different magnetic field values, and the χ dia * *T* component in Fig. 5 (e) for comparison. The dashed lines in Fig. 5 (d,e) indicate the Curie constant $C = 1.16 \times 10^{-5}$ emu \times g⁻¹ \times Oe⁻¹ for the paramagnetic susceptibility at T > 15 K.

Besides a clear paramagnetic component, an additional diamagneticlike hysteresis loop is present at T < 15 K even at the lowest magnetic field strength H = 200 Oe, although the signal is relatively weak and noisy at this field strength (Fig. 5 (d)). When the magnetic field was above 5 kOe the amplitude of the diamagnetic-like deviation from the paramagnetic behavior increased, but the span of the hysteresis loop decreased considerably at H = 70 kOe, as can also be seen in Fig. 5 (c). The saturation of the magnetic moment at T < 7 K, H > 10 kOe, is the main reason for the diamagnetic-like behavior at high fields and low temperatures, while at low fields and temperatures in the range of ~ (2–15) K the diamagnetic-like component of the magnetic moment and the temperature hysteresis has another reason.

Thus, the low-temperature magnetic measurements of nitrogendoped synthetic diamond single crystals carried out in this work confirm the anomalous behavior of their magnetic moment at low temperatures, discovered in [16,17]. At the same time, the main novelty of the present work is the study of the effect of thermobaric treatment on the magnetic properties of nitrogen-doped diamonds and a new physical model describing the results obtained.

4. Analysis of experimental results

Fig. 6 shows the magnetization vs field dependencies of the studied samples after the subtraction of the intrinsic diamagnetic component.

It is clearly seen that the type of the magnetization curves $\Delta M(H) = M_{2K}(H) - M_{300K}(H)$ after TBT (Fig. 6 (b,c)) is quite different from similar dependencies obtained on the same samples before TBT (Fig. 6 (a)). While the dependencies for samples A and B1 before TBT, and after TBT look similar. We used the saturation value of the magnetization at T = 2 K, H = 70 kOe to estimate the number of P1-centers in each sample using the Brillouin function [31].

To describe the experimentally obtained dependencies of the magnetic moment on the magnitude and direction of the magnetic field m(H) at low temperatures, we used the three-component superposition model (1), as done in [16].

$$m(H) = m_{dia}(H) + m_{SPM}(H) + m_{SC}(H),$$
(1)

The first component, $m_{dia}(H)$, is the diamagnetic contribution due to the intrinsic diamagnetism of pure diamond. The second one, is the paramagnetic contribution of nitrogen P1-centers known for nitrogendoped diamonds [1–4], which saturates at $T_c < 7$ K, and in the case of exchange interaction can be ferromagnetic or superparamagnetic $m_{SPM}(H)$. And the third contribution is responsible for the observed diamagnetic-type hysteresis, which we presumably call the superconducting contribution $m_{sc}(H)$, in analogy to [16,17]:



Fig. 3. The magnetic moment of samples A, B1 and B2 (a,c,e), and A_{TBT}, B1_{TBT} (b,d), as a function of the magnitude and direction of the magnetic field at fixed values of *T* as indicated in the plots. The arrows mark the path of the magnetic field change.



Fig. 4. (a) Temperature dependencies of the magnetization of samples A, and B1 before and after TBT in a magnetic field of 70 kOe. (b) Temperature dependencies of the magnetization of sample B2 at H = 0.1, 5, 15, 40 kOe during cooling and heating. The inset shows data at H = 0.1 kOe with higher magnification on the vertical axes.

Table 1

Masses of the samples, mean concentrations of C-centers and A-centers in them according to IR spectroscopy, mean concentrations N_{P1} of P1 centers and their absolute numbers according to EPR spectroscopy, and the numbers of paramagnetic nitrogen centers n_p found from Curie constant measurements and Brillouin function approximation. The values in brackets are $N_C^* = 0.9N_C$, as explained in the Appendix.

$N^{\underline{\circ}}$ sample	m, g	Initial				After TBT			
		$N_{ m C}, \ { m cm}^{-3} \pm 20\%$	$egin{array}{l} N_{ m A},\ cm^{-3}\ \pm 20\% \end{array}$	$egin{array}{l} N_{ m P1},\ { m cm}^{-3}\ \pm 10\% \end{array}$	$\begin{array}{c} n_p \\ \pm \ 10 \ \% \end{array}$	$N_{ m C},\ { m cm}^{-3}$ $\pm 20\%$	$egin{array}{c} N_{ m A},\ cm^{-3}\ \pm 20\% \end{array}$	$N_{ m P1},\ { m cm}^{-3}\ { m \pm}20\%$	n _p ±20%
A_{Σ}	0.16	$\begin{array}{c} 5.2\times 10^{19} \\ (4.7\times 10^{19}) \end{array}$	1.3×10^{19}	3.3×10^{19}	2.1×10^{18} (IR) 1.5×10^{18} (EPR) 1.4×10^{18} (Curie) 1.4×10^{18} (Brill)	5.6×10^{17}	7.0×10^{19}	$\begin{array}{c} 5.9\times 10^{17} \\ 1.1\times 10^{18} \\ 1.1\times 10^{18} \end{array}$	2.6×10^{16} (IR) 2.7×10^{16} (EPR) 5×10^{16} (Curie) 4.9×10^{16} (Brill)
B1.	0.256	$\begin{array}{c} 6.6\times 10^{19} \\ (5.9\times 10^{19}) \end{array}$	2.3×10^{18}	$5.6 imes 10^{19}$	$\begin{array}{l} 4.3 \times 10^{18} \mbox{ (IR)} \\ 4.1 \times 10^{18} \mbox{ (EPR)} \\ 4.2 \times 10^{18} \mbox{ (Curie)} \\ 4.2 \times 10^{18} \mbox{ (Brill)} \end{array}$	2.3×10^{18}	$5.3 imes 10^{19}$	$\begin{array}{c} 2.5\times 10^{18}\\ 1.5\times 10^{18}\\ 1.4\times 10^{18}\end{array}$	$\begin{array}{c} 1.7 \times 10^{17} \ \text{(IR)} \\ 1.8 \times 10^{17} \ \text{(EPR)} \\ 1.1 \times 10^{17} \ \text{(Curie)} \\ 1.0 \times 10^{17} \ \text{(Brill)} \end{array}$

A conventional linear on-field relationship was used to describe the intrinsic diamagnetic contribution:

$$m_{dia}(H) = -\chi_d(T) \cdot H,\tag{2}$$

where $-\chi_d(T)$ is the diamagnetic susceptibility which is characteristic for each sample and weakly depends on temperature.

To calculate the m_{SPM} , contribution we used the phenomenological model of an isotropic material in which the magnetization has no preferred direction. At low temperatures and strong fields, the magnetization is described by the Brillouin function, which takes into account the spatial quantization of the magnetic moment of the atoms:

$$B_J(H) = \frac{2J+1}{2J} coth \left[\frac{2J+1}{2J} \cdot \beta H\right] - \frac{1}{2J} coth \left[\frac{1}{2J} \cdot \beta H\right], \tag{3}$$

where $\beta = \frac{g\mu_B J}{kT}$, $g \cong 2$ – is the Lande factor, μ_B – the Bohr magneton, J is the total quantum number of the total momentum. Then the (super) paramagnetic component of the magnetic moment is equal to:

$$m_{SPM}(H) = N\mu_z^m B_J(H),\tag{4}$$

where $\mu_z^m = g\mu_B J$ is the maximum value of the projection of the magnetic moment along the z-axis (direction of the magnetic field vector), *N* is the number of paramagnetic atoms. In the limit of strong magnetic fields or

low temperatures, $B_J(H) = 1$ and $m_{SPM}(H) = N\mu_z^m = Ng\mu_B J$. For a single nitrogen atom in the substitutional position (C-center) J = 1/2. Accordingly, $\mu_z^m = \mu_B$, and we determined *N* from the experimental data for each sample using this relationship (Table 1).

As a result, using expression (1), the $m_{sc}(H)$ component at T = 2 K can be represented as follows:

$$m_{SC}(H) = m(H) - m_{dia}(H) - m_{SPM}(H),$$
 (5)

We found the m(H) - $m_{dia}(H)$ part of this expression as the difference between the experimental data m(H) at T = 2 K and the intrinsic diamagnetic contribution $m_{dia}(H)$ measured at T = 300 K considering $m_{dia}(H)$ as temperature-independent. So, this part of the expression (5) is shown by black symbols and lines in Fig. 7 (a-e) as in Fig. 6, but expressed in terms of Bohr magnetons and normalized to the number $n_{\rm P1}$ of P1-centers in each sample, calculated via the Curie constants C. The numbers of n_P based on the Curie constants $C = p^2 n_p / (3k_B)$ were calculated from the *M*-*M*_{dia} dependencies (Fig. 5(a)) at T > 10 K, H = 70kOe, using the Curie law for paramagnetic susceptibility: $\chi_p = C/(T-\Theta)$. The Curie temperature Θ was found to be equal to zero within the accuracy of ± 0.3 K of the linear fit of $1/\chi_p$ as a function of temperature at T > 15 K, as shown in Fig. 5(b) for the case of sample B2. The absence of ferromagnetism is also demonstrated by this fact. In the expression for C, $k_{\rm B}$ is the Boltzmann constant; p is the magnetic moment of paramagnetic atoms: as a first approximation we consider only single nitrogen atoms



Fig. 5. (a) Paramagnetic contribution to the magnetization of the original samples A, B1, B2 and A_{TBT}, B1_{TBT}, for which *M* values are multiplied by a factor of 10; (b) Temperature dependence of the inverse of the paramagnetic susceptibility $1/(\chi \cdot \chi_{dia})$ of the sample B2 at fixed values of the magnetic field for the estimation of the Curie temperature Θ . (c) The dependencies of the magnetic susceptibility of sample B2 on the reverse temperature 1/T, in the temperature range of 50 K – 2 K at the values *H* indicated in the plot. (d) Temperature dependencies of the $(\chi \cdot \chi_{dia})T$ function of sample B2 during cooling and heating at H = 0.2, 5 and 10 kOe. (e) Temperature dependencies of the $(\chi \cdot \chi_{dia})T$ function of sample B2 during at H = 20, 40 and 70 kOe. The green line shows the $\chi_{dia}T$ function for comparison. The dashed lines in (d,e) show the value of the Curie constant.



Fig. 6. Magnetization as a function of magnetic field for samples A and B1 at T = 2 K before TBT (a) and after TBT (b,c), after subtraction of the intrinsic diamagnetic component of the diamond measured at T = 300 K. The arrows indicate the path of the magnetic field change.

in the substitutional position in the diamond lattice, i.e. P1-centers, $p = g\mu_B[J(J+1)]^{1/2}$; $g \approx 2$ – the Lande factor; μ_B – Bohr magneton; J – total quantum number, J = 1/2.

The red symbols and lines in Fig. 7 (a–e) show the $m_{SPM}(H)$ contribution at T = 2 K calculated using the relation (4) and also normalized to the number n_{P1} of P1-centers in each sample. Finally, the blue symbols and lines in Fig. 7 (a–e). show the $m_{SC}(H)$ contribution at T = 2 K, calculated using the relation (5), also normalized to the number n_{P1} of P1-centers in each sample.

Fig. 7(f) shows the dependencies of the total magnetization amplitude of the samples at T = 2 K, H = 70 K and the maximum amplitude of the superconducting contribution m_{sc} at T = 2 K on the concentration of P1-centers before and after TBT. For comparison, data from Ref. 16 are presented for 2 samples with the highest and lowest concentrations of Ccenters examined therein.

5. Discussion

We have grown two nitrogen-doped (Ib-type) diamond crystals by the TG-HPHT method in the Fe-Co-C-N system with different concentrations of C-centers (P1-centers) and prepared a set of experimental samples from them, designated as A and B series. Using IR and EPR spectrometry, we determined the concentrations of optical and paramagnetic centers in the samples. Their magnetic properties were then measured, after which TBT was carried out at P = 5.5 GPa; T =1900 °C for 4 h, and the spectral analyses and magnetic measurements were repeated again. Under the same TBT conditions, 98 % of the Ccenters were converted to A centers in the series of A samples with an initial concentration of C-centers of 3.0×10^{19} cm⁻³, and about 96 % in sample B1 with an initial concentration of 5.6 \times 10¹⁹ cm⁻³. The EPR spectra of the initial A and B series samples are strongly broadened and have additional weak lines due to dipole-dipole [4], quadrupole and exchange interactions [5]. After TBT, the EPR spectrum lines of the ATBT series samples became narrow, indicating a significant weakening of such spin interactions. At the same time, the type of EPR spectrum of the B1_{TBT} sample retained all the features of the original crystal before TBT, only the intensity of the resonance lines decreased. The concentrations of P1 centers (C-centers) in the initial samples A and B1 determined by spectral methods correspond within the measurement error (<10 %) to the quantities of paramagnetic centers calculated on the basis of the Curie constants C and the amplitude of the paramagnetic moment at saturation m_s . After TBT, the numbers of P1 centers in A_{TBT} and B1_{TBT} samples determined from the EPR spectra (n_{P1}), differ by 1.5–2 times with the ones obtained from magnetic measurements data via the Curie constants C and magnetic moment saturation values m_s . To some extent, this may be due to lower measurement accuracy and systematic errors at



Fig. 7. Dependencies of the difference in the magnetic moment of samples A (a) and B1 (c) at T = 2 K and 300 K, expressed in Bohr magnetons and normalized by the number n_p of P1-centers according to EPR spectroscopy data before and after TBT (b,d); and of sample B2 (e), on the magnitude and direction of the magnetic field. Black symbols and lines represent experimental data; red – the calculated paramagnetic contribution according to the Brillouin model for the number of paramagnetic n_p atoms at T = 2 K, using relation (4); blue symbols and lines – the difference between the experimental data and the calculated paramagnetic contribution according to relation (5). (f) The dependencies of the amplitude of the total magnetization M_{tot} and the superconducting contribution of M_{SC} at T = 2 K on the concentration of P1-centers for the studied samples (solid lines and symbols) and data [16] for comparison (dashed lines and open symbols). Squares and stars show data obtained by magnetic measurements; rectangles depict the concentrations of P1 centers calculated from EPR spectra of A_{TBT} and $B1_{TBT}$ samples. At high concentrations, the EPR data agree with those obtained from magnetic measurements.

low concentrations of C-centers. In addition, at low contents of C-centers, small but comparable amounts of iron and cobalt impurities can also increase the total paramagnetic moment. This may be the reason why the number of paramagnetic centers derived from magnetic measurements of the A_{TBT} sample is higher, than that obtained from spectroscopic data related to nitrogen P1-centers only. However, the situation is opposite for the $B1_{TBT}$ sample. Thus, more detailed and precise studies should be carried out in the case of low concentrations of nitrogen C centres.

We observe an increase of about 10 % in the magnitude of the negative susceptibility of the samples after TBT (A_{TBT} , $B1_{TBT}$ with respect to A, B1)) up to the value proper to an undoped diamond value of $(-4.5 \pm 0.2) \times 10^{-7} \text{ emu} \times \text{g}^{-1} \times \text{Oe}^{-1}$ [16,28,30], and this is mainly due to the reduction of the content of paramagnetic P1-centers by 96–98 %. Indeed, at T = 300 K the paramagnetic susceptibility of sample B1 can be calculated using the experimentally determined Curie constant of $C = 1.16 \times 10^{-5} \text{ emu} \times \text{g}^{-1} \times \text{Oe}^{-1} \times \text{K}$ (Fig. 5a,d). Then χ_{PM} (300K) = C/300 $\approx 0.4 \times 10^{-7} \text{ emu} \times \text{g}^{-1} \times \text{Oe}^{-1}$. This value actually gives a 10 % increase in the magnitude of the negative susceptibility after thermobaric treatment of sample B1, with 96 % of the C- centers being converted to A-centers.

The number of nitrogen atoms in the form of diamagnetic A-centers increased after TBT by only about 0.01 % relative to the total number of diamagnetic carbon atoms in the crystals, i.e. much less than the 10 % difference registered. This is why we don't distinguish a separate role for diamagnetic A-centers from the diamagnetic contribution of an undoped diamond in the three-component model. The 0.01 % addition is beyond the accuracy of our measurements.

Since the regular diamagnetic susceptibility is known to be temperature independent, and an additional strong (up to $-3 \times 10^{-7} \text{ emu} \times \text{g}^{-1} \times \text{Oe}^{-1}$ in sample B2) *low-T* diamagnetic component has an apparent superconductor-like dependence on the magnetic field at T = 2 K, we conclude that such strong temperature-dependent diamagnetism observed at T < 15 K, with a magnetic moment amplitude up to half that of the paramagnetic contribution, may originate from local superconductivity associated with paramagnetic P1 centres, but not diamagnetic A centres.

The obtained experimental dependences m(H) of all samples measured in the range H = (-70) - (70) kOe at fixed temperatures in the range 2–300 K (Figs. 3,6) independently confirmed an anomalous hysteresis of the magnetic moment at temperatures below about ~7 K first observed in [16,17].

The calculation of the dependence of the paramagnetic (superparamagnetic) moment on the magnitude of the magnetic field according to the Brillouin model, which takes into account the quantization of spin vectors at low temperatures (Fig. 7), describes well the experimentally observed dependences in samples A, B1, B2 at low and high fields, but does not explain the observed hysteresis loops with increasing and decreasing magnitude of the magnetic field and change of its vector to the opposite. The type of hysteresis loops observed does not correspond to the ferromagnetic type, but has a diamagnetic-like origin.

As a result of subtracting the intrinsic diamagnetic contribution $m_{dia}(H)$ of an undoped diamond and the paramagnetic contribution $m_{spm}(H)$ according to the Brillouin model from the experimentally measured values of m(H), we obtained the $m_{sc}(H)$ dependencies, which have a diamagnetic character proper to the superconductivity (Fig. 7). The curves are rotationally symmetric (2nd order) with respect to the H = 0 point, like the initial m(H) dependencies. The obtained $m_{sc}(H)$ dependencies for samples B1 and B2, cut from the same initial sample B,

are almost the same, while significant differences are noticeable compared to sample A with a lower concentration of C-centers. Common features in the $m_{sc}(H)$ dependencies are also observed for the A_{TBT} and B1_{TBT} samples. All obtained $m_{sc}(H)$ dependencies can be characterized as inherent to granular superconductors in a non-superconducting matrix. The $m_{sc}(H)$ dependencies for the A_{TBT} and B1_{TBT} samples with low concentrations of P1 centers: $N_{\rm P1} = 5.9 \times 10^{17}$ and 2.5×10^{18} cm⁻³ are the most typical for superconductors (Fig. 7 (b, d)). The difference between the $m_{sc}(H)$ hysteresis loops and those typical of superconductors, such as boron-doped diamond [18,19] or EuRbFe₄As4 [32], is a sharp decrease in the magnetic moment as the field decreases below 3 kOe for the A_{TBT} sample and below 5 kOe for the $B1_{TBT}$ sample. When the field value was increased from H = 0 to the specified values, a similar course of the curves was observed, but with a negative sign of $m_{sc}(H)$ (Fig. 7 (ae)). This behavior is peculiar to any superconductor when the field is turned on and turned off. When the external field is turned off, the induced currents persist for a long time in superconductors with low dissipative losses. In our case, the reduction time of the external field from H = 3-5 kOe to H = 0 was 14 and 18 min, respectively. These values correspond to the characteristic relaxation time $t_0 \sim 12$ min for the time dependence of the magnetic moment $m(t) = m(0) - m_1 \exp[1 - (t/t)]$ $t_0)^{\beta}$, determined in the previous study [16] also at T = 2 K. In this expression, β is a fitting parameter in the range of 0.8–1.0, whose real value depends on the degree of homogeneity of the system [16].

As Figs. 7(a,c,e) show, in initial samples A and B1, B2 with higher concentrations of P1-centers, the external field magnitudes below which $m_{sc}(H)$ starts to decrease are ~10 kOe and ~ 20 kOe respectively. After TBT, Fig. 7 (b,d), this value is <3–5 kOe. In addition, in the initial samples A, B1 and B2 with a high concentration of P1-centres, the maximum amplitude of $m_{sc}(H)$ reaches only ~30 % of the magnetic moment saturation value m_s in sample A and ~ 15 % in samples B1, B2 with the highest concentration, while this value reaches 50 % for samples A_{TBT} and B1_{TBT}. Therefore, as the concentration of P1-centres (C centres) increases, a relative decrease in the value of $m_{sc}(H)$ is observed in the region of small fields, which may be related to the competing process of collinear ordering of spins in the PM state. The emergence and strengthening of the exchange interaction between the spins of the P1-centres as their concentration increases hinders the formation of Cooper pairs and the transition to a superconducting state.

Fig. 7(f) clearly shows that despite the \sim 2-fold proportional increase of the M_{tot} magnetization amplitude with increasing concentration N_{P1} of P1-centers in samples B1 and B2 compared to sample A, the amplitude of the M_{sc} did not increase, mainly because at H < 20 kOe the m_{sc} value decreases in samples B1, B2, while it still increases with decreasing H from 20 to 10 kOe in sample A. The data of the previous work [16], presented in Fig. 7(f) show that a maximum of the $M_{sc}(N_p)$ amplitude can occur in the range of concentrations $N_{p1} \sim 1 \times 10^{19} \text{ cm}^{-3}$. Note that the amplitude of the magnetic moment caused by the superconductivity effect does not exceed 1/2 of the saturation value of the paramagnetic moment at H > 60 kOe, since the elementary magnetic moment of the induced superconducting currents in an external magnetic field is generated by Cooper pairs of electrons of two nitrogen atoms (P1 centers), but not by single paramagnetic P1 centers. We assume that if nitrogen is initially present in the growth medium during diamond synthesis mainly in molecular form, the dissociation of N2 molecules leads to only a short distance of the atoms from each other and accordingly to a relatively small average distance between C-centers forming local pairs. In such a case, conditions of high concentration of nitrogen atoms of the order of \sim 5 %, i.e. 2 nitrogen atoms in the cluster of 40 carbon atoms, can be fulfilled locally, at which, according to

theoretical calculations [22], superconductivity with a critical temperature of about $T_c \sim 7$ K can occur. Moreover, according to [22], the value of T_c should increase sharply with increasing concentration of Ccenters. So far, additional theoretical calculations are needed for small nanodiamonds, consisting of ~40 carbon atoms and 2 nitrogen atoms in the form of C-centers. It is also possible that the choice of starting materials and the thermodynamic conditions of crystal growth affect the structure of such carbon-nitrogen nanoclusters, and the critical temperature T_c . This may explain the difference between $T_c \sim 7-15$ K in this study and $T_c \sim 25$ K in [16], since diamond samples produced by SUMITOMO Company were investigated in the previous work.

Considering the model of elementary superconducting circuits of the two adjacent diamond unit cells with C-centers, and taking into account their concentration and sample sizes, we have estimated the induced current densities in such circuits at given external field values, B = 1 T and 7 T. The procedure for estimating the current in a circular electric circuit induced by an external magnetic field using conventional relationships and the calculated values are described in the *Supplementary Material*.

The maximum current density values were found in the range up to 2×10^6 A/cm², which is about two orders of magnitude smaller than the critical current in conventional superconductors. Values of the order of 10^{5} – 10^{6} A/cm² are consistent with the critical current of weak superconductivity in Josephson junction structures. At a current density $j = 2 \times 10^{6}$ A/cm², the current value in the elementary circuit $I = \pi R^2 j$ is equal to 8×10^{-9} A. If we calculate the current in units of the electron charge per second, then this value is equivalent to 5×10^{10} e/s. Since the Cooper pair consists of 2 electrons, the transfer of Cooper pairs per second in the elementary circuit, this value corresponds to the circulation frequency of 25 GHz. Superconducting circuits are known to operate in the THz frequency range. Therefore, such an estimate of the Cooper pair circulation frequency in an elementary circuit is consistent with the properties of superconductors.

In sample A1, we observed the low temperature admittance peak with the maximum at 12 K (at 100 kHz) and the permittivity step with the midpoint at the same temperature. Their frequency shift indicates a free carrier activation energy of \sim 0.5 meV [33]. These results are in good agreement with the magnetic measurements.

It should also be noted that the value of the critical field at which the magnetization hysteresis disappears at T = 2 K is about $H_c = 70$ kOe for all samples. This value is close to the data for the above mentioned compound EuRbFe₄As₄ also at T = 2 K [32], and about 2 times higher than H_c^{onset} for superconducting boron-doped diamonds [18,19].

So far, comparing the paramagnetic and superconducting components of the magnetic moment at T < 15 K of the samples before and after TBT, and taking into account the theoretical analysis of the superconductivity effect in diamond doped with nitrogen in a single atom substitutional position (C-centers) [20–22], we can assume that very small superconducting nanoclusters containing 2 C-centers in adjacent diamond unit cells form molecular-like elementary superconducting circuits in the intrinsically insulating diamagnetic diamond matrix. Such a composite possesses not global but granular superconducting properties.

6. Conclusion

The experimental data obtained confirm the existence of an anomalous hysteresis of the magnetic moment at T < 15 K in nitrogen-doped type Ib diamonds with different concentrations of P1 centres (single substitutional nitrogen atoms). No ferromagnetic-like hysteresis was observed. The values of magnetic susceptibility and magnetic moment saturation at T = 2 K, H = 70 kOe correspond with an accuracy of ± 5 % to the number of paramagnetic P1-centres in the initial samples with their concentrations of 3.0×10^{19} cm⁻³ and 5.6×10^{19} cm⁻³, and differ by 1.5-2 times in the samples after TBT with the concentrations of P1-centres 5.9×10^{17} cm⁻³ and 2.5×10^{18} cm⁻³, which may be due to the lower accuracy of the determination of the number of P1 centres by spectroscopic methods in the latter cases, and also to the additional paramagnetic moment of iron and cobalt impurities in the case of the A_{TBT} sample with the lowest content of nitrogen P1 centres. By thermobaric treatment at P = 5.5 GPa; $T = 1900^{\circ}$ C for 4 h we converted 96–98 % of C-centers into A-centers and accordingly reduced the concentration of C-centers).

The dependence of the paramagnetic moment on the magnetic field strength obeys the Brillouin model, which takes into account the quantization of the spin vector at low temperatures. The Brillouin function describes the experimentally observed dependencies in the field ranges H < 10 kOe and H > 60 kOe, but does not explain the observed hysteresis in the range H = 10-60 kOe with increasing and decreasing magnetic field and changing its vector in the opposite direction. Subtracting the intrinsic diamagnetic contribution of pure diamond $m_{dia}(H)$ and the paramagnetic contribution described by the Brillouin model $m_{pm}(H)$ from the experimentally measured values m(H)yields the superconductor-like dependencies $m_{sc}(H)$, which have a diamagnetic character and explain the observed hysteresis loops. Similar to the initial dependencies m(H), the curves obtained show 2ndorder rotational symmetry around the H = 0 point. The temperature dependencies of the susceptibility also show hysteresis proper to an additional diamagnetic contribution below 15 K. The obtained $m_{sc}(H)$ dependencies can be characterized as inherent to granular superconductors in an insulating matrix.

In the initial samples with a high concentration of paramagnetic nitrogen centres, the EPR spectra indicate the exchange interaction and therefore the evaluated relative maximum amplitude $m_{sc}(H)$ reaches only 15-30 % of the total magnetic moment, while after TBT and a significant reduction in the concentration of P1 centers this value reaches 50 %. The appearance of an exchange interaction between the spins of the P1 centers as their concentration increases favors the spontaneous collinear orientation of the spins, which prevents the formation of Cooper pairs at low temperatures. However, quantization of the spin orientation under the additional influence of an external magnetic field at low temperatures increases the probability of anticollinear spin states and thus promotes the formation of Cooper pairs and the transition to the superconducting state. It is natural that the amplitude of the magnetic moment due to superconducting currents induced by an external magnetic field does not exceed 1/2 of the paramagnetic moment saturation value $m_{\rm s}$, since the elementary moment $m_{\rm sc}$ is generated by the electrons of two adjacent C-centers, and not by each of them, as in the case of paramagnetism. The fact that the amplitude m_{sc} is equal to half of the total number of Bohr magnetons of P1 centers may indicate that elementary superconducting currents are generated in pairs of adjacent P1 centers, which are formed during the dissociation of sorbed N2 nitrogen molecules in the diamond growth process. It is important to note that the superconducting component of the magnetization is present regardless of the concentration of nitrogen P1 centres in diamond. Such a phenomenon was not predicted theoretically. During TBT treatment, nitrogen atoms in adjacent P1 centers can "rejoin" to form diamagnetic molecular-like A centers.

As a result of a decrease in the number of P1 centers in diamond after

TBT, the amplitudes of $m_{\rm pm}$ and $m_{\rm sc}$ decrease proportionally. The magnitude of the critical field at which the magnetization hysteresis disappears is about $H_{\rm c} = 70$ kOe at T = 2 K for all samples. This value is about 2 times higher than $H_{\rm c}^{\rm onset}$ for boron-doped superconducting diamonds [18,19].

Diamonds with a higher concentration of C-centers should be investigated to obtain a higher fraction of the superconducting component. The influence of transition metal impurities, such as Fe, Co and Ni, on the superconducting properties of diamonds with low concentrations of C-centers is of fundamental scientific interest. Research in this area should also be continued.

The results obtained may be helpful in the development of lowtemperature quantum optoelectronic devices and magnetic sensors based on nitrogen vacancy (NV) centers in diamond.

CRediT authorship contribution statement

S.G. Buga: Funding acquisition, Project administration, Supervision, Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing, Validation. V.A. **Kulbachinskiy:** Methodology, Investigation, Formal analysis, Writing – review & editing. G.M. Kvashnin: Formal analysis, Validation. M.S. **Kuznetsov:** Resources. S.A. Nosukhin: Resources. E.A.

Appendix A. Appendix

A.1. Analysis of C-centers and A-centers concentrations using IR absorption

Konstantinova: Investigation. V.V. Belov: Investigation, Writing – review & editing. D.D. Prikhodko: Formal analysis, Writing – review & editing, Validation.

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

Data will be made available on request.

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Prior to the magnetic and EPR measurements, IR absorption spectra were measured to determine the local content of optically active nitrogen impurity centers [8,9] and to estimate their mean values. We used a Bruker Vertex 80v Fourier transform spectrometer equipped with a HYPERION 2000 optical microscope. The focal spot diameter of the optical system was $\sim 20 \,\mu$ m. The measurement results are therefore local. In each sample, the spectra were collected at several points and the final mean concentrations of nitrogen optical centers were obtained by averaging over several points. For example, in the initial samples A1–A4 (Fig. 1a), the spectra were collected at 3 points in yellow areas (growth sectors {111}) and at 3 points in colorless areas (growth sectors {100}). After TBT (Fig. 1b), the spectra were taken at approximately the same points on each sample. Examples of IR spectra measured in the center of sample A3 (yellow area) before and after TBT are shown in Fig. A1. Fig. A2 shows the change in spectra of highly N-doped diamonds after TBT, normalized to the intrinsic 2-phonon absorption band of diamond in the range of 1600–2400 cm⁻¹. The images illustrate models of 2 substitutional nitrogen atoms (C-centers) in 2 adjacent diamond unit cells in as-grown crystals, and 2 nitrogen atoms in the model of A-center in the diamond unit cells appearing during TBT.

The concentrations of C-, A- and B-centers in diamond have been estimated from the intensity of the corresponding optical absorption bands in the range of 700–1400 cm⁻¹ [8]. The bands of all these centers are in the same spectral region. We have mathematically deconvoluted the IR absorption spectrum in a given energy range into the sum of the diamond model spectra containing only A-, B-, and C-centers. Model spectra were obtained from selected diamond samples containing only one type of nitrogen center. All IR absorption spectra were first calibrated using the intrinsic two-phonon absorption band in the range 1500–2700 cm⁻¹ to ensure correct comparison of the intensities of the nitrogen-related bands. The calibration technique was similar to that previously described by us [34] for the absorption spectra of boron-doped diamonds. We did not observe any spectra associated with vacancies, B-centres or other nitrogen vacancy centres in the as-grown samples or after TBT.

Concentrations of A- and C-centers were obtained from decomposed spectra using empirical formulae from [8]:

$$N_A[ppm] = 16.3\mu_{1282}[cm^{-1}], \tag{1}$$

$$N_{C}[ppm] = 25\mu_{1135}[cm^{-1}],$$
⁽²⁾

where μ_x is the intensity of the spectra at wavenumber x[cm⁻¹].

The accuracy of the mathematical deconvolution of each spectrum is up to ± 1 ppm, but deviations between local values along the faces of samples A1–A4 were up to 10–15 %.



Fig. A1. Typical IR absorption spectra of series A samples in yellow areas before TBT (a), and after TBT (b) in the frequency range of absorption by nitrogen impurity centers (dashed curves) with deconvolution into components of the spectra corresponding to C-centers (brown lines), and A-centers (blue lines). The red lines are the total spectra of the components of the C- and A-centers. Spectral components of B-centers are absent.



Fig. A2. Transformation of the IR-spectrum of C-centers (black line) into the spectrum of A-centers (red line) after thermobaric treatment.

The results of N_C concentration measurements for each of the A1–A4 samples in growth sectors {111} and the total data for sample A are presented in Table A1. The concentration of C-centers in growth sectors {100} before TBT is about 3–10 times lower than in sectors {111}, but the concentration of A-centers in sectors {100}, on the contrary, is higher than in {111}. At the same time, the area and volume of sectors {100} is about 20 % of the total area and volume of the samples. Accordingly, the average concentration of C-centers, N_C^* , is less than the mean values in yellow {111} sectors: about $0.9N_C$, and the average concentration of A-centers is higher, than in colorless {100} sectors, N_A^* , is $\sim 1.1N_A$. The values of N_C^* are given in brackets in italics in Tables 1, A1, A2. After TBT, the concentration of C-centers was approximately the same in all sectors.

Table A1

Masses of A-series samples, concentrations of C-centers, A-centers in them according to IR spectroscopy, mean concentrations of N_{P1} -centers and their absolute numbers according to EPR spectroscopy, and the numbers of paramagnetic nitrogen centers n_p found from Curie constants measurements and Brillouin function approximations. The values in brackets are $N_{C^*} = 0.9N_{C_2}$ as discussed in the text.

$N^{\underline{\circ}}$ sample	m, g	Initial				After TBT				
		Nc, cm ⁻³ ±20 %	$egin{array}{c} N_{ m A},\ cm^{-3}\ \pm 20~\% \end{array}$	$N_{ m P1},\ { m cm}^{-3}\pm 10~\%$	n_p ±10 %	Nc, cm ⁻³ ±20 %	$egin{array}{c} N_{A,}\ cm^{-3}\ \pm\ 20\ \% \end{array}$	$N_{ m P1},\ { m cm}^{-3}\pm 10~\%$	n_p $\pm 20~\%$	
A1. A2. A3 A4 A _Σ	0.044 0.049 0.038 0.028 0.16	$\begin{array}{l} 5.2\times10^{19}\\ 5.0\times10^{19}\\ 5.5\times10^{19}\\ 5.2\times10^{19}\\ 5.2\times10^{19}\\ (4.7\times10^{19})\end{array}$	$\begin{array}{c} 1.7 \times 10^{19} \\ 1.4 \times 10^{19} \\ 0.5 \times 10^{19} \\ 1.5 \times 10^{19} \\ 1.3 \times 10^{19} \end{array}$	$\begin{array}{c} 3.5 \times 10^{19} \\ 3 \times 10^{19} \\ 3.9 \times 10^{19} \\ 2.8 \times 10^{19} \\ 3.3 \times 10^{19} \end{array}$	$\begin{array}{l} 4,4 \times 10^{17} \ (5.9) \\ 4.2 \times 10^{17} \ (6.3) \\ 4.2 \times 10^{17} \ (5.3) \\ 2.3 \times 10^{17} \ (3.7) \\ 2.1 \times 10^{18} \ (IR) \\ 1.5 \times 10^{18} \ (EPR) \\ 1.4 \times 10^{18} \ (Curie) \\ 1.4 \times 10^{18} \ (Brill) \end{array}$	$\begin{array}{l} 7.1 \times 10^{17} \\ 5.5 \times 10^{17} \\ 6.9 \times 10^{17} \\ 1.7 \times 10^{17} \\ 5.6 \times 10^{17} \end{array}$	$\begin{array}{l} 7.3 \times 10^{19} \\ 7.0 \times 10^{19} \\ 6.6 \times 10^{19} \\ 7.2 \times 10^{19} \\ 7.0 \times 10^{19} \end{array}$	$\begin{array}{l} 6.4\times 10^{17}\\ 5.3\times 10^{17}\\ 6\times 10^{17}\\ 5.9\times 10^{17}\\ 5.9\times 10^{17}\\ 1.1\times 10^{18} \end{array}$	$\begin{array}{l} 8.1 \times 10^{15} \\ 7.4 \times 10^{15} \\ 6.5 \times 10^{15} \\ 4.7 \times 10^{15} \\ 2.6 \times 10^{16} \ (IR) \\ 2.7 \times 10^{16} \ (EPR) \\ 5 \times 10^{16} \ (Curie) \\ 4.9 \times 10^{16} \ (Brill) \end{array}$	

In sample B and its parts B1, B2, IR spectra were taken only in sectors {111}, and the relative fraction of sectors {100} is unknown. The results of the average N_C concentration measurements in sectors {111}, sample B and its parts B1, B2 are presented in Tables 1, A2. We assume that the average concentration of C-centers in the B-series samples before TBT was $0.9N_C$, as well as in the A-series samples.

Taking into account local variations and the assumptions discussed above, the possible error in the measurement of the concentrations of C- and Acenters and their absolute numbers by IR spectroscopy in our samples was about ± 20 %. Since the determination of the concentrations of optical centers in diamond is an indirect method based on calibration procedures, namely on EPR spectrometry data for P1 centers, we consider the IR spectrometry results in this study to be approximate, less accurate than the data obtained by EPR spectrometry.

Thus, according to IR spectrometry, the total number of paramagnetic centers n_p in A, B1, and B2 samples was $(2.1 \pm 0.5) \times 10^{18}$; $(4.3 \pm 1.0) \times 10^{18}$; and $(1.0 \pm 0.2) \times 10^{18}$, respectively. For A_{TBT} and B1_{TBT}, the values became $(2.6 \pm 0.5) \times 10^{16}$ and $(1.7 \pm 0.4) \times 10^{17}$, respectively. Within the error ranges these numbers correspond to those obtained by EPR spectroscopy and found via Curie constants and Brillouin function approximations, except in the case of the A_{TBT} sample for which both IR and EPR spectroscopy data gave values about twice lower than those found from Curie constants at different values of *H* and Brillouin function approximation at T = 2 K; H = 70 kOe (Tables A1, A2).

Table A2

Masses of B and B2 samples, concentrations of C-centers, A-centers in them according to IR spectroscopy, mean concentrations of P1-centers and their absolute numbers according to EPR spectroscopy, and the number of paramagnetic nitrogen centers n_p found from Curie constant measurements and Brillouin function approximations. The values in brackets are $N_C^* = 0.9N_C$, as discussed in the text.

N° sample	<i>m</i> , g	Initial	Initial				After TBT			
		Nc, cm ⁻³ ±20 %	$egin{array}{c} N_{ m A},\ cm^{-3}\ \pm 20~\% \end{array}$	P1, cm $^{-3}$ ± 10 %	n _p ±10 %	Nc, cm ⁻³ ±20 %	$\begin{array}{c} \text{N}_{\text{A}\text{,}}\\ \text{cm}^{-3}\\ \pm 20~\% \end{array}$	P1, cm ⁻³ ±10 %	$n_p \pm 10 \%$	
В	0.33	6.6×10^{19} (5.9 × 10 ¹⁹)	$\textbf{2.3}\times \textbf{10}^{\textbf{18}}$	5.6×10^{19}	5.6×10^{18} (IR) 5.3 $\times 10^{18}$ (FPR)	No data				
B2. 2 parts	0.061	$6.6 \times 10^{19} (5.9 \times 10^{19})$	2.3×10^{18}	$\textbf{5.6}\times \textbf{10}^{\textbf{19}}$	$\begin{array}{l} 1.03\times 10^{18} \ ({\rm IR}) \\ 0.98\times 10^{18} \ ({\rm EPR}) \\ 1.08\times 10^{18} ({\rm Curie}) \\ 1.1\times 10^{18} ({\rm Brill}) \end{array}$	No data				

A.2. EPR spectroscopy analysis

We studied the EPR spectra of the samples before and after TBT to measure the total number of C-centers in each of them and to compare them with the data obtained by IR spectrometry and with the results of the magnetic measurements (Fig. A3).

The EPR spectra were recorded using a Bruker Elexsys E500 EPR spectrometer (operating frequency 9.4–9.8 GHz) in continuous wave mode (CW-EPR). The diamond sample was placed in a standard 10 mm diameter quartz ampoule (Wilmad-labglass) and then fixed in the center of the resonator of the EPR spectrometer using a special holder. The orientations of the magnetic field were parallel to the axes of the crystallographic directions [100], and [110]. Spectra were recorded at room temperature with the following parameters: microwave power 0.6 µW, modulation amplitude 0.2 G, modulation frequency 100 kHz, time constant 20.48 ms.



Fig. A3. EPR spectra of the initial samples A2 and B (a), and A2_{TBT}, B1_{TBT} (b). The values of *I* for samples B and B1_{TBT} are multiplied by coefficients of 0.25 and 10 respectively for better comparison of the line shapes.

To determine the number of paramagnetic centers in the samples, the crystalline $CuCl_2 \bullet H_2O$ reference sample sealed in a glass ampoule with a known number of spins $n_{ref} = (6.0 \pm 0.2) \times 10^{18}$ was used. The EPR spectrum of the reference sample was recorded with the same experimental parameters as the diamonds under investigation. The number of paramagnetic centers is directly proportional to the area *S* under the EPR absorption curve. Since the recorded EPR spectra are the first derivative of the absorption, the *S* values were obtained by double integration of the spectra. The numbers of paramagnetic centers in the samples n_x were determined using the calibration ratio:

$$n_x = \frac{S_x}{S_{ref}} n_{ref},\tag{4}$$

where S_{ref} and S_x are the areas for the reference and diamond samples, respectively.

Fig. A3 shows the EPR spectra of samples A2 and B before TBT and A2_{TBT}, B1_{TBT} after TBT. The observed EPR spectra are typical of nitrogen doped diamonds [1–5].

The unpaired electron is localized along the N-C bond (P1 center, [3]) and interacts with paramagnetic nitrogen and carbon nuclei (hyperfine interaction - HFI). The contribution of HFI with carbon nuclei is negligible, since the content of paramagnetic carbon nuclei is only 1.1 % and can therefore be neglected. From the analysis of the EPR spectra we found $g = 2.0018 \pm 0.0004$, the HFI constants $a1 = a2 = a3 = 33.5 \pm 0.3$ G (*H* parallel to the [100] axis), $a1 = 32.9 \pm 0.3$ G; $a2 = a3 = 34.3 \pm 0.3$ G (*H* parallel to the [110] axis), which are in good agreement with literature data [1,3]. At a high concentration of P1 centers in the starting samples, the EPR spectral lines are broadened and, in addition to the main lines, weak additional

spectral lines are observed, which have been explained as a signature of quadrupole and exchange interactions [5], or as a negligible contribution of HFI with paramagnetic carbon ¹³C nuclei [2–4]. The broadening and amplitude of the additional lines relative to the main resonance lines is much greater for sample B with the highest concentration of P1 centres than for the A series samples with lower concentrations. The EPR spectra of the initial samples A1, A2, A3, A4 and B differ only in intensity, Fig. A3(a) shows the spectra of samples B and A2 for comparison. After TBT, the intensity of the EPR resonance lines decreased by more than an order of magnitude, the lines in the spectra of all A-series samples became very narrow and sharp, while the spectrum of B1_{TBT} changed only in intensity with respect to the spectrum of initial sample B (Fig. A3(b)). The line width of A1_{TBT} - A4_{TBT} samples is $\Delta H = 0.25$ G, indicating almost complete absence of dipole-dipole and/or exchange interactions. The threshold value of the concentration of C-centres in HPHT-grown Ib-type diamonds, at which magnetic interactions between their pairs appear, is in the range of (1.0–2.5) × 10¹⁸ cm⁻³, which is in agreement with earlier data [2].

The numbers of uncompensated spins n_p and the concentrations of P1 centers according to the EPR spectra of the A-series and B-series samples are given in Tables 1, A1 and A2. The numbers of uncompensated spins n_p in all samples before TBT and in the B1_{TBT} sample have been calculated with correction for the dipole-dipole interaction.

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.diamond.2023.110759.

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