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GEOCHEMISTRY

Paramagnetic *N*1 Center in Plastically Deformed and Differently Colored Crystals of Natural Diamond

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Among more than 100 paramagnetic centers discovered to date in diamond [1, 2], only approximately one dozen centers are sufficiently widespread in natural crystals [3]. In other words, the concentrations of such centers appear to be relatively high and responsible for certain physical properties of crystals in some cases. In other cases, although the centers lack direct relationships with physical characteristics of the crystals, their presence and mode of occurrence reflect certain structural and physical features of the crystals [4, 5].

The present paper reports results of the electron paramagnetic resonance (EPR) investigation of the well-known *N*1 center [6–10], which includes two nonequivalent nitrogen atoms. We also scrutinized associations of this center with other paramagnetic centers and specific features of the distribution of various types of centers in the crystal volume. These characteristics are essential for the reconstruction of epigenetic alterations of diamond and the elucidation of the genesis of some color types associated with the epigenetic impact.

EPR spectra reported in the present paper were recorded with a Varian E-115 spectrometer operating in the X range with a frequency modulation of 100 and 25 kHz at room temperature. The magnetic field was measured with an E-500 NMR gaussmeter. The angular dependence was analyzed with a two-circle goniometer providing the rotation of a sample around two mutually perpendicular axes and its orientation in any direction relative to the applied magnetic field with a maximal precision of 0.5°. Sample DFPG containing $4 \cdot 10^{16}$ paramagnetic centers was used as the standard. Concentrations of paramagnetic centers in the samples were measured by the method of comparison of integral intensities of spectral lines of these centers and the DFPG standard.

At the first stage of investigation, we performed the EPR examination of several hundreds of differently colored diamond crystals using the standard diagnostic device with the magnetic field $H \parallel [001]$. The diamond crystals were taken from the Yakutian kimberlite pipes (Internatsional'naya, Dachnaya, Yubileinaya, Udachnaya, Aikhal, Komsomol'skaya, and Nyurbinskaya). We studied 80 diamond crystals ranging in mass from 0.5 to 1.8 ct. Paramagnetic *N*1 centers were only observed in 20 brown, dark brown, gray, and gray-lilac crystals from the Internatsional'naya and Dachnaya pipes of the Mirnyi kimberlite field. The relatively rare dark brown crystals with a unique distribution of *N*1 centers were investigated in more detail.

Paramagnetic *N*1 centers formed on two nonequivalent nitrogen atoms in the diamond structure are relatively well studied to date. Shcherbakova et al. [6] discovered *N*1 centers as early as 1969 and assumed that this center represents the $C–N_1–N_2^+$ chains. In the later model [7], Shcherbakova assumed that the vacancy is captured by the N–N pair. In 1985, Loubser and Wyk [8] concluded that the *N*1 center represents a noncomplanar structure $N_1–C_1–C_2–N_2^+$. Its model was proposed previously in [7] for the *W*7 center. Based on the ENDOR investigation of the *N*1 center [9] and the comparative analysis of all known centers containing two nitrogen atoms [10], Newton and Baker concluded that nitrogen atoms in the *N*1 center model represent the second neighbors; i.e., the center can be presented as $N_1–C–N_2^+$. Hence, the center can possess 12 geometrically nonequivalent positions with similar occupancy. Since the main direction of the tensor of hyperfine interactions with the nearest (relative to the noncoupled electron) atom *N*1 nearly coincides with the ⟨111⟩ direction (deviation is only 0.4°), one can only discriminate four nonequivalent positions in the EPR spectrum. If the crystal axis [001] is oriented along the magnetic

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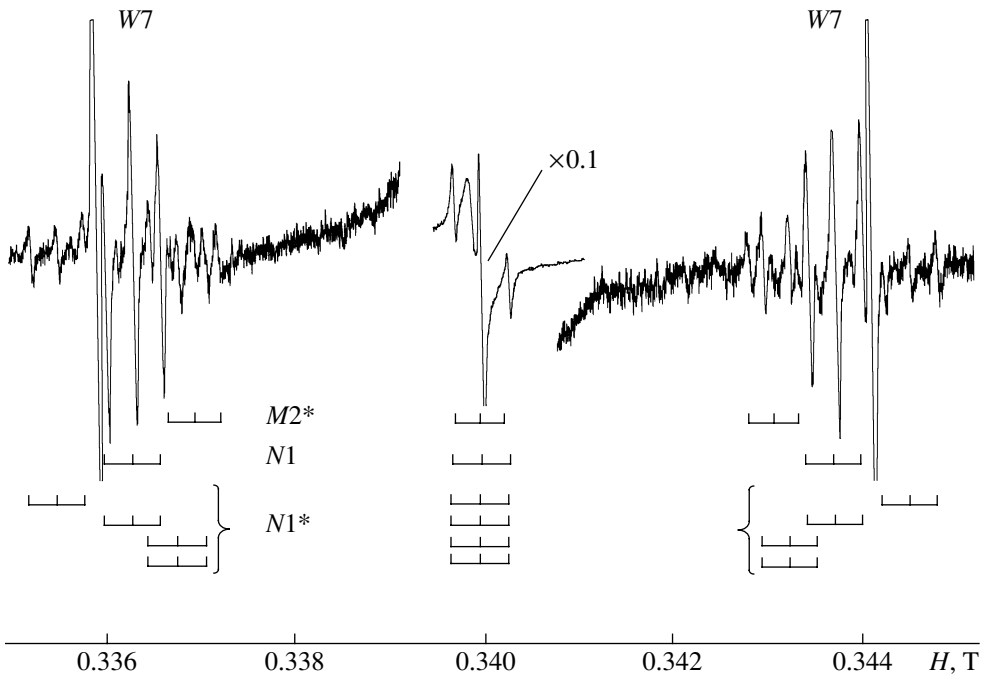

Fig. 1. X-band EPR spectra of the dark brown diamond with *M*2 and *N*1 centers recorded at room temperature with the magnetic field $H \parallel [001]$. Asterisks show centers confined to twinned sectors relative to the major part of crystal.

field, the spectra of these four positions should coincide under our experimental conditions. Figure 1 shows the EPR spectrum of diamond sample In-5 when $H \parallel [001]$. In addition to the well known *N*1 and *W*7 centers (structure with noncomplanar chains N_1–C_1–C_2–N_2^+) [11] that are typical of the brown plastically deformed diamond crystals, *M*2 centers (spherical structures with noncomplanar chains N_1–C_1–C_2–C_3–N_2^+) [5] were detected in twinned lamellas. Moreover, we detected previously unknown lines related to centers with two nonequivalent nitrogen atoms. Since the crystal included deformation microtwins, we had to check first whether or not the additional lines belong to *N*1 centers located in microtwins similarly as *M*2 centers.

It is known that plastic deformation can occur in the diamond structure by mechanisms of both slip and mechanical twinning. In the case of deformation with crystal twinning, crystallographic axes of the deformed and undeformed parts of the crystal turn out to be differently oriented. Figure 2 shows the stereographic projection of a diamond crystal with mechanical twins. It is evident that all ⟨111⟩ axes are oriented at similar angles relative to [001] in the case of the major undeformed part of the crystal. In the case of twinned lamellas that represent deformed parts of the crystal, only one axis (among four ⟨111⟩ axes) shows such orientation. The second and third axes are oriented at 78.9° to the chosen [001] axis, while the fourth ⟨111⟩ axis is oriented at 15.8° to [001]. Consequently, if the [001] crystal axis is oriented along the magnetic field direction, we should observe three geometrically nonequivalent positions of centers with trigonal symmetry confined to lamellas.

If the parameters of the center are known, we can predict lines in the EPR spectrum of the center for any direction of crystal twinning. In order to be convinced that the *N*1 center is present in both parts of the twin, we calculated the position of lines of the *N*1 center spectrum for cases when various ⟨111⟩ axes coincide with the magnetic field direction. EPR spectrums should be similar in both parts of the crystal only for one axis common for two twinned individuals. This pattern should also be typical of the undeformed part of the crystal if it is oriented along any other ⟨111⟩ axes. At the same time, spectra of twinned lamellas in these cases should include lines of three different geometrically nonequivalent positions. Spectra thus calculated coincided well with the experimental ones. A similar modeling accomplished for ⟨110⟩ axes also demonstrated the coincidence of both calculated and experimental EPR spectrums.

Thus, analysis of the orientation dependence of spectrums showed that the studied dark brown diamond crystal incorporates *N*1 centers both in the major volume of the crystal and in the twinned sectors. The twins are probably related to deformation. Unfortunately, we could not observe lamella microtwins, because the crystals were opaque and we could not prepare their polished sections. However, the absence of signs of growth twinning on the crystal surface suggests that the

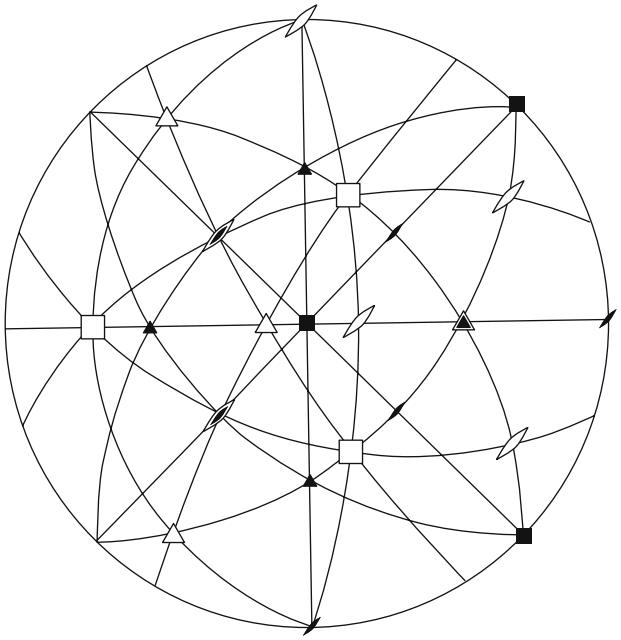

Fig. 2. Stereographic projection of three-bold axes for the major part of the crystal (small triangles) and its part twinned under the spinel law (large triangles).

crystal certainly includes deformation microtwins similar to those in the purple diamond.

Associations of paramagnetic centers have not been analyzed in the available publications. Classification of diamond crystals into groups based on the concentration of paramagnetic centers in them is reported in our previous work [12], in which we only considered the most widespread centers. Accumulation of new data on the already known and newly detected centers made it possible to recognize groups with specific properties. In the present work, our attention was focused on the set of paramagnetic centers with the color characteristics of the diamond. The table presents data on the plastically deformed diamond crystals from the Dachnaya and Internatsional'naya kimberlite pipes.

Our previous investigations revealed that all purple diamond crystals include *M*2 centers confined to intense colored thin lamellas twinned under the spinel law [4]. We also noted that *N*1 centers are absent in all explored purple crystals. In the present work, we investigated diamond crystals containing *N*1 centers. Some of these crystals also included *M*2 centers in twins, but their color was gray or lilac-gray. At the same time, *N*1 centers were missing in purple crystals (e.g., in sample D-72).

The concentration of *N*1 centers is maximal in dark brown crystals. Therefore, we believe that the spectra observed in these cases are related to the major and twinned parts of the crystal. The concentrations of *N*1 centers in both parts turned out to be virtually equal. We assume that the volumetric proportions of these parts are also similar. One can easily see that twinned sectors account for only *n* vol % of the purple crystals. If the twinned sectors are also subordinate in the gray-lilac diamond crystals, *N*1 centers cannot be detected in such sectors because of insufficient sensitivity of the spectrometer.

Analysis of data on concentrations of paramagnetic centers in diamond crystals from the Internatsional'naya and Dachnaya pipes (table) shows that the brown and smoky brown crystals typically contain *N*2 centers [13] associated with disrupted C–C bonds in the dislocation core. This conclusion is consistent with

Contents of paramagnetic centers in diamond crystals from the Dachnaya and Internatsional'naya pipes (10^{14} at/g)

Sample no.	Centers					Color
	*P*1	*M*2	*N*1	*W*7	*N*2	
D-48	50		2	90	700	Smoky brown
D-54	70		1	10	125	The same
D-60	25		2	20	170	The same
D-71	60	1*	1	6	70	Gray-lilac
D-100	20		5	45	250	Smoky brown
D-131	70	2*	1	10	165	Gray
D-135	20	2*	2	8	60	Gray-lilac
D-138	55	1*	1	16	180	Gray
In-5	110	6*	8* and 7	140	800	Dark brown
In-28	80		2	40	200	Smoky brown
In-130	130		4	300	1200	Grayish brown
In-136	35		1	15	160	Brown
In-178	50	10*	5* and 5	170	700	Dark brown

Note: (*) Centers confined to twinned sectors relative to the major part of the crystal.

concepts of the correlation of intensity between the crystal center and its color [7]. The lilac (pale purple) tint appears in diamond only if the crystal includes *M*2 centers confined to lamellas twinned along (111). In purple crystals, these symmetry planes are nearly ideal, while the crystals are dichroic. The intensity of the 550-nm band, which governs the color, depends upon the observation direction [14]. Planes (110) are the characteristic ones for *N*1 centers. Atoms are shifted along these planes in the course of plastic deformation to produce the *N*1 centers. This process can disturb the ideal structure of (111) planes. Comparison of the *N*1-containing gray-lilac and gray crystals investigated in the present work with the *N*1-free purple crystals reported in [4] clearly shows that precisely the *N*1 center serves as an indicator of the degree of perfection of (111) planes. Hence, the *N*1 center governs the color of diamond crystals subjected to plastic deformation.

The *N*1 center can be generated in the course of plastic deformation (slip mechanism) or irradiation, whereas the *M*2 center is related to mechanical twinning provoked by the intricate displacement of atoms in the course of interaction between the twinning and emitted dislocations at the propagation front of lamella microtwins. Mechanical microtwinning in the highly symmetric crystals is mainly fostered by a relatively low temperature and short-term loading. The simultaneous presence of *N*1 and *M*2 centers in the diamond crystal studied indicates that the crystal underwent plastic deformations corresponding to at least two regimes in the course of its transportation from the upper mantle.

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REFERENCES

1. C. A. J. Ammerlaan, *Landolt–Bornstein Numerical Data and Functional Relationships in Science and Technology* (Springer, Berlin, 1990), New Ser. III, Vol. 22b, pp. 117–206.
2. J. H. N. Loubser and J. A. van Wyk, Repts. Progr. Phys. **41**, 1201 (1978).
3. L. V. Bershov, R. M. Mineyeva, A. V. Speranskiy, and S. V. Titkov, Geochem. Int. **32** (12), 91 (1995).
4. R. M. Mineeva, A. V. Speransky, S. V. Titkov, and N. G. Zudin, Phys. Chem. Minerals **34** (2), 53 (2007).
5. R. M. Mineeva and A. V. Speransky, Appl. Magn. Reson. **28**, 355 (2005).
6. M. Ya. Shcherbakova, E. V. Sobolev, N. D. Samsonenko, and V. K. Aksenov, Fiz. Tverd. Tela **11**, 1364 (1969).
7. M. Ya. Shcherbakova, E. V. Sobolev, V. A. Nadolinnyi, and V. K. Aksenov, Dokl. Akad. Nauk SSSR **225**, 566 (1975).
8. J. H. N. Loubser and J. A. van Wyk, *Mater. Res. Soc. Symp. Proc.* (1985), Vol. 46, p. 587.
9. A. Cox, M. E. Newton, and J. M. Baker, J. Phys.: Condens. Matter **4**, 8119 (1992).
10. M. E. Newton, and J. M. Baker, J. Phys.: Condens. Matter **3**, 3605 (1991).
11. J. H. N. Loubser and A. C. J. Wright, J. Phys. D: Appl. Phys. **6**, 1129 (1973).
12. R. M. Mineeva, S. V. Titkov, A. V. Speransky, and L. V. Bershov, Dokl. Earth Sci. **349**, 799 (1996) [Dokl. Akad. Nauk **348**, 668 (1996)].
13. M. E. Newton, and J. M. Baker, J. Phys.: Condens. Matter **1**, 9801 (1989).
14. A. F. Konstantinova, S. V. Titkov, K. B. Imangazieva, et al., Crystallogr. Rep. **51**, 465 (2006) [Kristallografiya **51**, 493 (2006)].