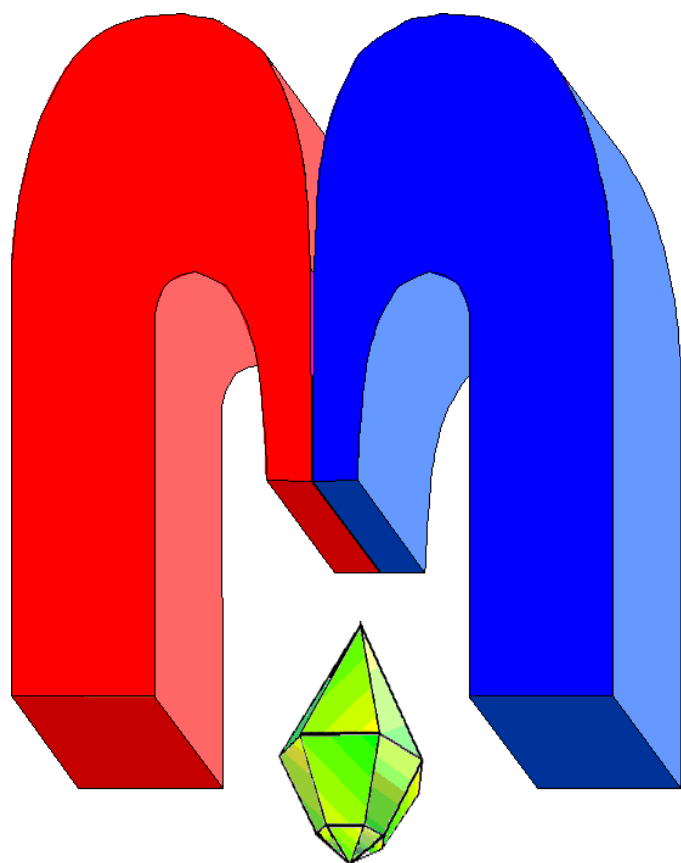


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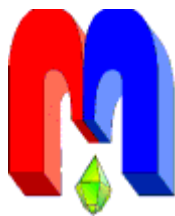
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† In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Paramagnetic complexes in beryllium-doped hexagonal boron nitride crystals

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This work is devoted to the investigation of paramagnetic centers in a single crystal of hexagonal boron nitride (h-BN) with beryllium introduced via high-temperature diffusion. Electron paramagnetic resonance (EPR) spectra and their dependence on the orientation of the magnetic field relative to the crystallographic axes and temperature were measured in hexagonal boron nitride crystals. The observed dependencies are explained by the presence of two types of paramagnetic centers. The first type consists of three exchange-interacting paramagnetic centers, each with spin $S = \frac{1}{2}$, with g -values of $g_{\parallel} = 2.0$ and $g_{\perp} = 2.7$, which allow for the observation of lines with effective g -values of $g_{\parallel} = 6.0 \pm 0.3$ and $g_{\perp} = 3.5 \pm 0.2$ at 16 K. The exchange coupling constant was estimated from the temperature dependence of the g -factor at 16–120 K range. The second type of centers is attributed to a defect with spin $S = \frac{1}{2}$, exhibiting g -values of $g_{\parallel} = 2.18 \pm 0.01$ and $g_{\perp} = 2.06 \pm 0.01$, with a distinct orientation in the ab plane of the crystal.

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1. Introduction

In recent years, two-dimensional materials have emerged at the forefront of fundamental research and applied nanotechnology, offering unique platforms for the development of next-generation electronic, optoelectronic, and mechanical devices. Among them, hexagonal boron nitride (h-BN) often referred to as “white graphene” holds a special place due to its structural similarity to graphene, yet it possesses fundamentally different electronic properties. Unlike graphene, which has a zero bandgap, monolayer h-BN is a wide-bandgap semiconductor with a bandgap of approximately 6 eV in the bulk and roughly 4.6–6.0 eV in the monolayer [1]. This characteristic makes h-BN an exceptionally promising material for high-voltage electronic components, transparent conductive contacts, substrates for heterostructures based on other two-dimensional materials (such as graphene or molybdenum disulfide), as well as for ultraviolet light-emitting diodes and photodetectors [2, 3].

Despite its outstanding physical properties, pure h-BN has a significant drawback: its 6 eV bandgap hinders its direct use as an active channel in transistors or in devices operating within the visible spectrum. To overcome this barrier and fine-tune the electronic properties of wide-bandgap semiconductors, the doping method of pure crystals has been actively investigated [4]. Doping enables modification of the band structure, reduction of the bandgap, introduction of charge carriers (electrons or holes), and induction of magnetic moments, thereby transforming an insulator into a semiconductor or even a metal. Among various dopant elements, beryllium (Be) doping has received particular attention due to its unique ability to induce p-type conductivity in such nitrides [5–7].

Beryllium, being an element in Group II of the periodic table, possesses two valence electrons,

whereas a nitrogen atom in the h-BN lattice provides five. When a nitrogen atom in the h-BN lattice is substituted by a beryllium atom, a deficit of electrons (hole doping) arises, leading to the formation of acceptor levels within the bandgap. This shifts the Fermi level downward toward the valence band, promoting hole conductivity. Previous experimental studies have indicated the feasibility of achieving p-type conductivity in h-BN films through beryllium implantation [3].

2. The experimental part

h-BN crystals were grown by HQ Graphene. As shown in Figure 1, the sample takes the form of a platelet with dimensions of approximately 2×1 mm and a thickness of about $100 \mu\text{m}$. For the first time, we employed the high-temperature diffusion method to introduce beryllium doping. Diffusion was carried out within a closed container made of tantalum carbide. The samples were positioned on high-purity boron nitride plates. Doping was performed via the vapor phase, using metallic beryllium placed inside the container as the dopant source.

The heating system was evacuated to a high vacuum and heated to 1700°C to remove oxygen traces, after which it was filled with high-purity nitrogen gas (nitrogen pressure: 1 bar). Diffusion was conducted at a temperature of 2100°C for one hour. It was anticipated that the high diffusion rate would ensure uniform beryllium doping of the sample at a level of no lower than 10^{19} cm^{-3} . After diffusion, a change in the sample's color was observed, as clearly seen when comparing Figures 1 A and 1 B.

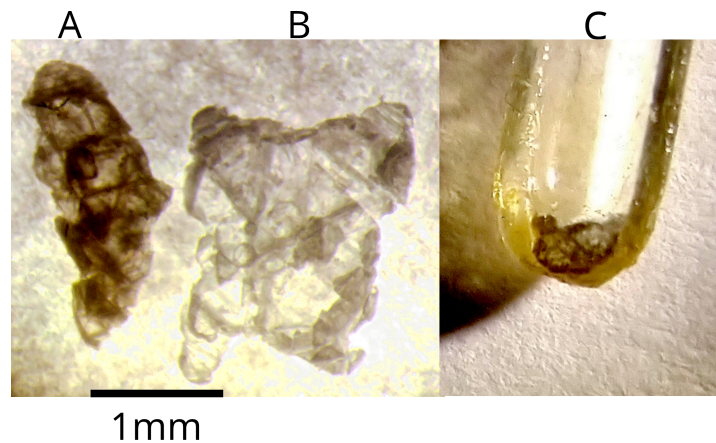


Figure 1. Effect of ion implantation on the transparency and color of the sample: A) h-BN crystal sample after beryllium ion implantation, one month later. B) h-BN crystal sample without further processing. C) Sample mounted on a 3 mm quartz tube holder. An optical fiber is positioned inside the tube, 15 mm above the sample.

Measurements were performed four days after the beryllium diffusion on three series of samples. A h-BN crystal, mounted on a quartz holder, was placed in a dielectric (sapphire) resonator of the Elexsys-580 spectrometer, with an optical fiber guiding light along the layers of the crystal (Figure 1 C). To measure the orientational dependence of the electron paramagnetic resonance (EPR) signal relative to the magnetic field in the ab plane of the crystal, the crystal was mounted on the end face of the quartz rod, and illumination was not used. The sample temperature was regulated using an Oxford flowing helium cryostat in the range of 296 K down to 16 K, while the resonator frequency was varied from 9.73 to 9.78 GHz. EPR spectra were recorded in continuous wave (CW) mode with a second harmonic modulation amplitude of 1 mT. The microwave power was set to approximately 0.63 mW to avoid saturation of the EPR lines.

3. Results and Discussion

CW EPR spectra were recorded at temperatures ranging from 16 to 120 K in the X-band of the spectrometer. Electron spin echo signals were not observed, which is presumably related to the crystal properties described below. In the EPR spectrum of the unirradiated sample at 120 K, no significant EPR lines were detected (Figure 2 A). After beryllium doping, a series of EPR spectral lines with g -factors greater than 2 appeared. For the orientation of the magnetic field parallel to the crystal c -axis, three lines with g -factors of 2.09 ± 0.02 , 2.91 ± 0.03 , and 5.74 ± 0.05 can be observed (Figure 2 C). For the magnetic field orientation in ab crystal plane (Figure 2 B), two lines with g -factors of 2.12 ± 0.02 and 4.42 ± 0.05 were observed. Following the decreasing g -factor, the observed lines for the orientation parallel to the crystal c -axis were labeled as 1, 2, and 3, respectively.

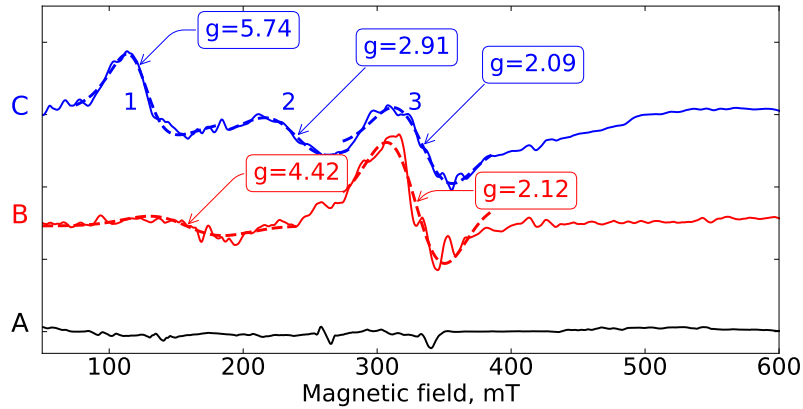


Figure 2. CW EPR spectra of the h-BN crystal. A) EPR spectrum of the unirradiated crystal. B) EPR spectrum of the beryllium-doped crystal with the magnetic field in the ab plane. C) EPR spectrum of the beryllium-doped crystal with the magnetic field parallel to the c -axis. Dashed lines indicate the approximation of individual lines. Spectrometer frequency: 9.75 GHz; temperature: 120 K.

Studying the magnetic field orientation dependence (Figure 3 A) allows us to understand the relationship between these lines. The linewidth increases significantly as the magnetic field direction deviates from the main crystallographic axes; therefore, individual lines were approximated to more accurately determine their g -factor, whose orientation dependence is shown in Figure 3 B. The standard orientation dependence of the g -factor can be described as the dependence of the anisotropic g -factor for a spin $S = \frac{1}{2}$ system.

$$g(\vartheta) = \sqrt{g_{\parallel}^2 \cos^2 \vartheta + g_{\perp}^2 \sin^2 \vartheta}, \quad (1)$$

where $g_{\parallel}$ and $g_{\perp}$ are the g -factors for the magnetic field oriented parallel and perpendicular to the c -axis of the crystal, respectively.

It should be noted that, unlike the g -factor, the linewidths of lines 1 and 2 in the EPR spectrum change upon a 180° rotation of the magnetic field, whereas line 3 exhibits a much weaker change. Additionally, the orientation dependence of the magnetic field rotated within the ab -plane of the crystal was measured, as shown in Figures 4 A and 4 B. As evident from the figures, lines 1, 2, and 3 show practically no shift in position, while the group of lines 4 substantially alters the EPR spectrum shape. This indicates that lines 1, 2, and 3 are described by a Hamiltonian of axial symmetry, whose symmetry axis coincides with the crystallographic c -axis. For the paramagnetic center responsible for lines 4, the axial symmetry is broken; that

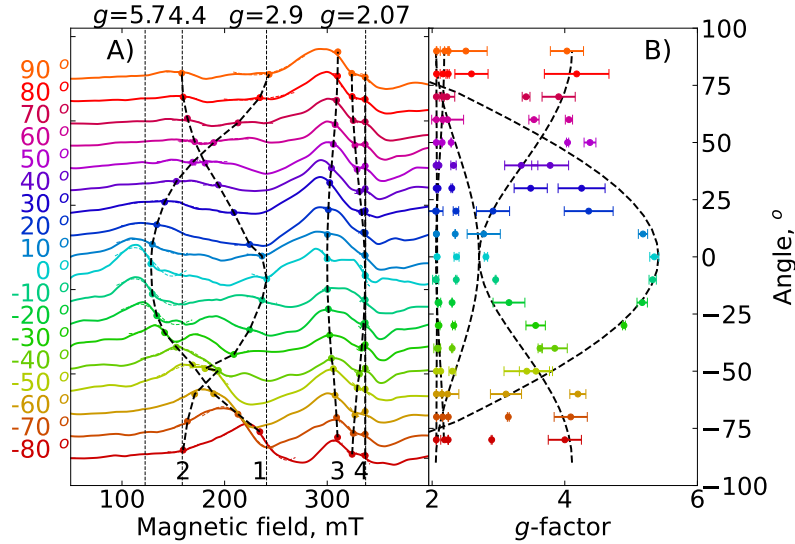


Figure 3. Dependence of CW EPR spectra on the magnetic field orientation relative to the crystal c -axis. A) Orientation dependence of the EPR spectra. B) g -factor dependence for paramagnetic complex. Spectrometer frequency: 9.75 GHz; temperature: 120 K. The dashed line indicates the g -factor corresponding to the spin Hamiltonian (2).

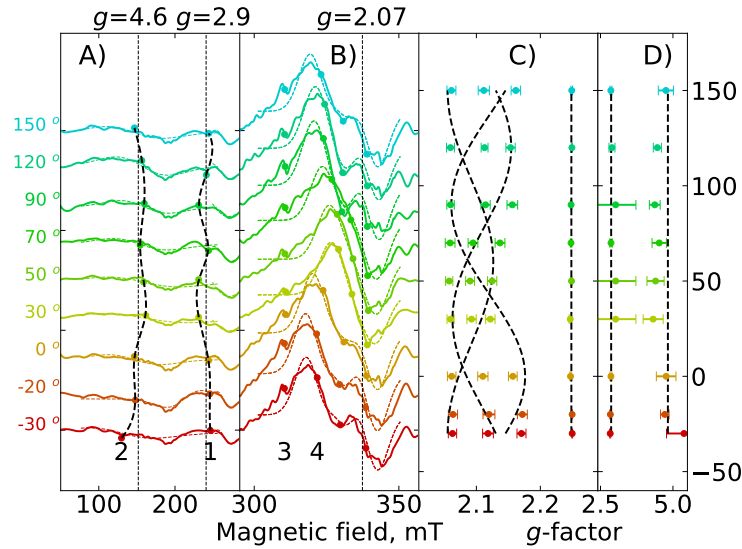


Figure 4. Dependence of the CW EPR spectra on the orientation of the magnetic field within the ab -plane of the crystal. Panels A and B show the orientation dependence of the EPR spectra. Panels C and D display the g -factor dependence for the paramagnetic center. The spectrometer frequency was 9.75 GHz, and the temperature was 120 K. The dashed line indicates the g -factor dependence corresponding to the eq. (1).

is, the principal axes of the g -tensor for this center are deviated from the c -axis. Such a situation can arise, for example, upon local charge compensation, where the direction of the paramagnetic center – compensator pair does not align with the c -axis. Given the hexagonal symmetry of the h-BN crystal, there must be three structurally equivalent centers whose g -factors are identical but whose orientation dependences differ by 120° . As can be seen from Figures 3 A and 4 B, the spectrum of this paramagnetic center can be well approximated by three EPR lines. The positions of the fitted lines (marked as round dots in Figures 3 and 4) were converted into

g -factors, whose dependencies are plotted in Figure 4 C. As evident from the figure, these dependencies are also well described by Equation (1) when the z -axis of the paramagnetic center's coordinate system is rotated within the ab -plane of the crystal. Unfortunately, the low accuracy of the approximation, associated with the relatively large EPR linewidth, does not allow us to determine a possible difference between g_{xx} and g_{yy} for this center.

Next, the dependence of the EPR spectra on temperature was measured for the magnetic field direction at -50° relative to the crystal's c -axis. As can be seen in Figure 5 A, the EPR spectral lines shift monotonically toward lower magnetic fields, while the g -factor increases by approximately 1.5 times. The calculated g -factors are presented in Table 1.

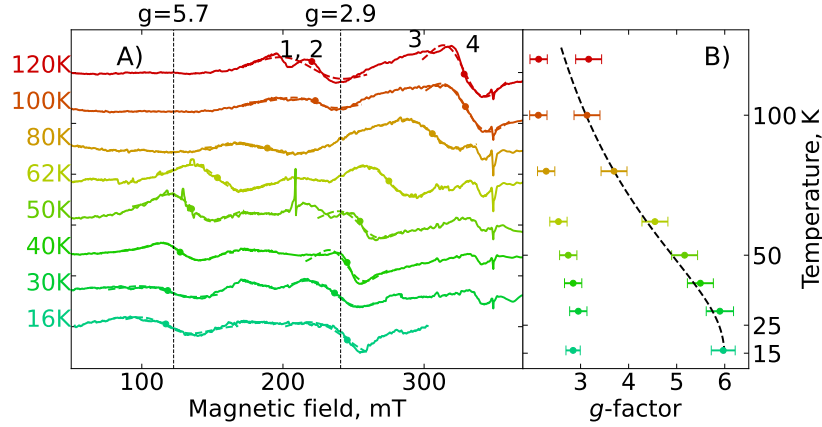


Figure 5. Temperature dependence of the CW EPR spectra for the magnetic field orientation at -50° relative to the crystal's c -axis. Spectrometer frequency: 9.75 GHz. Excitation by a laser with a wavelength of 532 nm and a power of 200 mW.

The effect of light on the EPR spectra was also assessed at a temperature of 16 K. As shown in Figure 6A, upon laser excitation with 532 nm light, the lines near $g = 5.7$ (lines 1 and 2) shift toward higher magnetic fields, while line 3 ($g = 2.9$) undergoes a stronger shift and simultaneously narrows in width. In contrast, radiation of the same power but at a longer wavelength (980 nm) has no effect on the EPR spectrum. Thus, this effect is not directly associated with simple sample heating by light. The dependencies of the g -factors and linewidths on laser power are shown in Figure 6 B,C,D. As evident from the figure, changes in the EPR spectrum occur upon exceeding a laser power of 160 mW; a laser with a shorter wavelength (405 nm) but lower power (100 mW) does not affect the EPR spectra.

Table 1. g -factors of various groups of lines in EPR spectra

N of line	120 K		16 K	
	$g_{ }$	$g_{\perp}$	$g_{ }$	$g_{\perp}$
1	5.55 ± 0.38	2.96 ± 0.09	6.0 ± 0.3	3.5 ± 0.2
2	2.98 ± 0.08	4.67 ± 0.28	4.2 ± 0.2	5.4 ± 0.3
3	2.36 ± 0.01	2.23 ± 0.01	3.48 ± 0.01	2.86 ± 0.01
4	2.18 ± 0.01	2.06 ± 0.01	—	—

Thus, the studied samples exhibit paramagnetic centers 1 and 2 whose EPR spectral behavior significantly deviates from that of conventional impurity or vacancy centers in boron nitride [8,9].

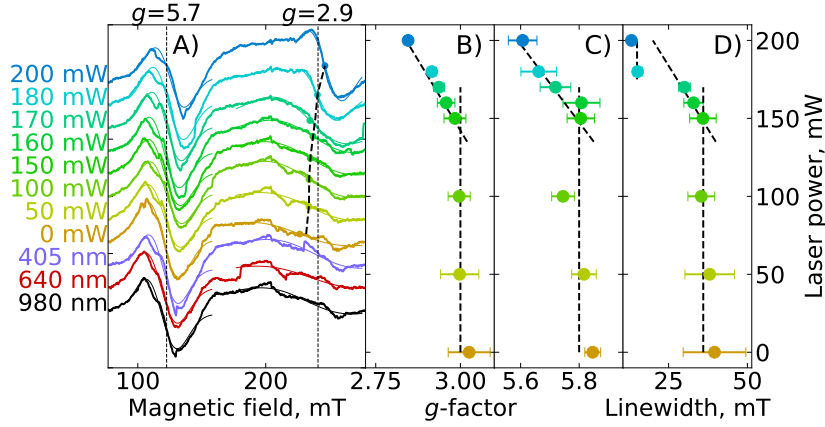


Figure 6. A) Effect of laser radiation on CW EPR spectra. Spectrometer frequency: 9.75 GHz, temperature: 16 K, magnetic field orientation: -50° relative to the crystal's c -axis. 405 and 640 nm lasers power were 100 mW, 980 nm – 200 mW. B and C) Changes in the effective g -factors of lines 1, 2, and 3. D) Linewidth of line 3 of the paramagnetic center as a function of laser radiation power. Spectrometer frequency: 9.75 GHz, temperature: 16 K, magnetic field orientation: -50° relative to the crystal's c -axis.

The absence of EPR lines with $g < 2$ precludes the use of a spin $S = 1$ center model with a large zero-field splitting D [10]. Additionally, we observed a 1.5-fold increase in the g -factor upon cooling the sample from 120 K to 16 K, as well as changes in both the linewidth and g -factor under the action of 532 nm laser radiation. Metallic beryllium or Be_3N_2 are diamagnetic and should not contribute to the EPR spectra of centers 1 and 2. However, paramagnetic properties may manifest when the crystal size is reduced or the system's dimensionality is decreased to that of a thin film [11–14]. To simplify the analysis, let us consider a minimal paramagnetic complex consisting of three paramagnetic centers with spin $\frac{1}{2}$, as dictated by the crystal symmetry, and linked by strong exchange interaction. In this case, the spin Hamiltonian can be written in the following form:

$$\hat{\mathcal{H}} = g(\theta) B_0 S_z + \sum_{i,j} \left[J_{iso} S_{z,i} S_{z,j} + \frac{1}{2} J_{dd} (S_{x,i} S_{x,j} + S_{y,i} S_{y,j}) \right], \quad (2)$$

where $g(\theta)$ is the g -factor described in Equation (1), and J_{iso} and J_{dd} represent the isotropic and anisotropic parts of the exchange interaction, respectively. The summation is performed over all possible pairs of indices i and j . In Figure 3B, the calculated dependence of the g -factor for interacting centers, obtained using the EasySpin package [15], is shown as a dashed line with parameters $g_{\parallel} = 2.05$, $g_{\perp} = 2.7$, $J = J_{iso} = J_{dd} = 80$ GHz. It should be noted that when $J_{iso} = J_{dd}$, the parameter J has a negligible effect on the line positions if it greatly exceeds the spectrometer frequency.

Next, let us calculate the local magnetization of such centers, taking into account the population of energy levels, the number of states, and the magnetic moment of each state like [16]. For simplicity, we assume the levels are equally spaced with an energy separation equal to J .

$$M = \frac{e^{\frac{1.5J}{T}} + e^{\frac{0.5J}{T}} - e^{\frac{-0.5J}{T}} - e^{\frac{-1.5J}{T}}}{6 \cosh\left(\frac{0.5J}{T}\right) + 2 \cosh\left(\frac{1.5J}{T}\right)} \quad (3)$$

In Figure 5B, the calculated g -factor dependence of the spectral line position on temperature (shown as a dashed line) is based on the g -factor parameters from Table 1 (at 16 K) and $J = 115$ K (2.4 THz, 10 meV). As can be seen, the temperature dependence of the g -factor shift

is in good agreement with this law within the 15–20 K range. The observed local magnetization can also explain the influence of light on the sample. In the case of light exposure where a quantum can be promoted to the conduction band, the upper energy levels become populated, causing the local magnetization to decrease, which leads to the effects shown in Figure 6. Thus, lines 1–3 belong to a single paramagnetic complex formed by three or more paramagnetic centers with spin $\frac{1}{2}$ and an exchange interaction between them on the order of 100 K. As mentioned above, lines 4 must belong to a center with non-local compensation in the *ab*-plane of the crystal, similar to the centers described in reference [9].

4. Summary

Thus, for h-BN crystals doped with beryllium via high-temperature diffusion, the orientational and temperature dependences of the paramagnetic complexes formed upon beryllium introduction were measured. The first type of complex arises from three or more paramagnetic defects coupled by an exchange interaction of the order of 100 K. The second type corresponds to a single paramagnetic defect with non-local compensation lying within the *ab*-plane of the crystal.

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