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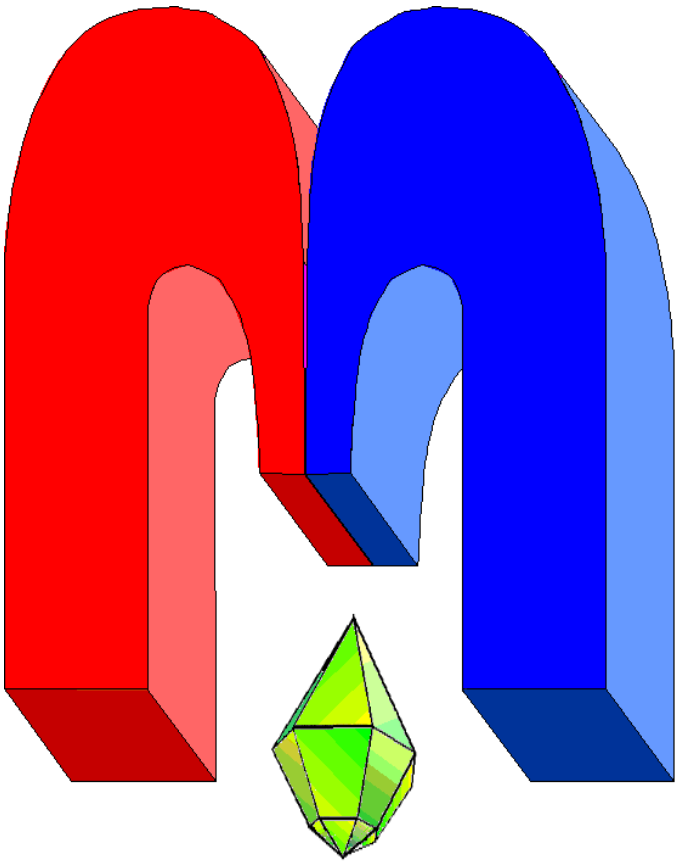

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* Address: "Magnetic Resonance in Solids. Electronic Journal", Kazan Federal University; Kremlevskaya str., 18; Kazan 420008, Russia

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

Coherence of optically addressable spin centers created in hexagonal boron nitride by proton irradiation

M.A. Sadovnikova, G.V. Mamin, R.V. Yusupov, P.P. Kobchikova, F.F. Murzakhanov*

Kazan Federal University, Kremlevskaya 18, Kazan 420008, Russia

**E-mail: murzakhanov.fadis@yandex.ru*

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Spin-carrying defects possessing optically addressable ground states in semiconductors allow the development of solid-state quantum technologies. Recently such type of defect has been found in hexagonal boron nitride (hBN) and identified as a negatively charged boron vacancy (V_B^-). Here we investigate the possibility to create V_B^- centers in hBN by irradiation with high-energy protons ($E_P = 15$ MeV), and probe the spin-coherence of the defects. Electron paramagnetic resonance methods show that such irradiation generates the V_B^- centers. Spin-relaxation times (T_1 and T_2) of V_B^- spin ensembles created by proton irradiation are determined to be 20 μs and 4 μs, respectively.

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Keywords: Electron paramagnetic resonance, hexagonal boron nitride, Van der Waals material

1. Introduction

High-spin states ($S > 1/2$) of defects possessing spin-dependent inter-system crossing transitions in optical excitation-recombination cycle in wide bandgap semiconductors are considered as one of the important building blocks in the solid-state based quantum technologies. This spin-dependent cycle allows one to selectively initialize the defects' spin states by optical means. Efficient manipulation and control over the spin are possible by microwave (MW) or radiofrequency (RF) pulses resonant with the splitting of the defects' ground (and/or excited) state. Intensive studies have been put forward to find and identify such defects, establish their main spin and optical properties followed by the development of efficient protocols to implement the properties in quantum technologies. NV^- defect in diamond [1], silicon-carbon divacancies [2,3], and negatively charged silicon vacancies in Silicon Carbide [4–7] are just a few examples. Moderate GHz or MHz (depending on the defect type) values of the zero-field splitting (ZFS), appearing due to the spin-spin interaction, allow to control the defects' spin down to the single defect level [7–9]. These all together allows implementing these defects for the development of quantum networks, as well as quantum sensors and room temperature operated masers [10–12].

Widely studied in 3-dimensional (3D) crystals characterized by sp^3-hybridized atoms, such as diamond and silicon carbide, defects possessing spin-dependent optical recombination have recently been found in 2D material formed by atomic planes of sp^2-hybridized atoms, interconnected through van der Waals (vdW) forces, namely hexagonal Boron Nitride (hBN) [13–15]. Hexagonal Boron Nitride is the ultra-wide (UW) bandgap (≈ 6 eV) [16] material which has been recently shown to accommodate the large variety of atomic impurities (or point defects), that give rise to optical transitions, well below its bandgap [17]. These properties combined with the possibility to create atomically thin 2D layers due to the weakness of the interlayer coupling in vdW materials allows studying properties of spin-related phenomena at the limit of the condensed state of matter. While spin-dependent optical recombination has been observed for several types of defects in hBN [13–15], so far only one has been rigorously identified and its microscopic structure has been established by means of electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) techniques [14]. Namely, this defect is the

negatively-charged boron vacancy (V_B^-) which is nothing but a missing boron atom having three equivalent nitrogen atoms as the nearest neighbor schematically shown in Figure 1a. This defect forms a spin-triplet ($S = 1$) ground state (GS) characterized by the zero-field splitting value $D = 3.5$ GHz [14, 18, 19]. Optical excitation with green light leads to a predominant population of the $m_s = 0$ spin sublevel through spin-dependent recombination pathway via metastable state (MS) in its excitation-recombination cycle.

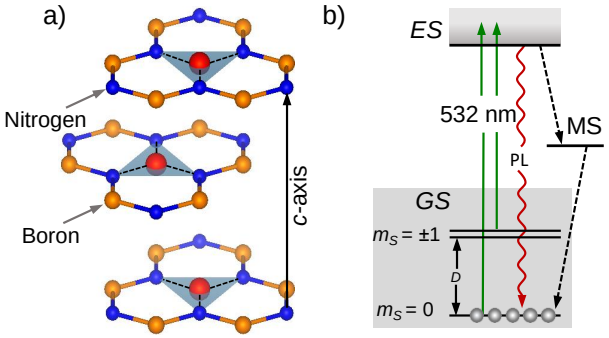

Figure 1. (a) Schematic representation of the hBN crystal structure together with the Boron vacancies shown as the red balls. Nitrogen and boron are shown in blue and yellow colours, respectively. 2D planes of sp^2-hybridized nitrogen-boron atoms staked along the c hexagonal axis, are shown in grey. (b) V_B^- defect energy levels diagram in the absence of external static magnetic field and the scheme of optical pumping cycle of the ground state (GS) ($m_s = 0$) spin sublevel. Excitation (green) transfer the system into the excited state (ES). Radiative recombination (purple) and spin-dependent nonradiative intersystem crossings decay to the GS via metastable state (MS) (dashed lines). D denotes the zero-field splitting (ZFS).

To further study and explore the optical and spin properties of V_B^- centers, methods of its creation in a reliable way have to be developed. Up to date several types of irradiation techniques have been approved for creation of V_B^- centers in hBN lattice. Namely they are neutron irradiation [14, 20], irradiation with a focused beam of different ions [14, 21] and irradiation with the femtosecond laser pulses [22]. In this article, we explore the possibility to create these centers by means of high-energy proton ($E_P = 15$ MeV) irradiation. This type of irradiation technique allowing to avoid clustering of defects is widely used for the creation of a high homogeneous distribution of point defects in solids. Utilizing EPR techniques, we have identified the defect as boron vacancies in the negative charge state and established the proton irradiation to be a robust way to create the paramagnetic centers – V_B^- in hBN crystals.

2. Methods and materials

Commercially available crystals of hexagonal boron nitride (hq Graphene manufacturer) were irradiated with protons on an isochronous cyclotron with the proton energy $E_P = 15$ MeV and total radiation dose $6 \cdot 10^{16}$ cm^{-2}. The sample was irradiated for 4 hours. The temperature range of the sample during proton irradiation was in $20 - 100$°C. EPR studies were carried out on a commercial EPR spectrometer manufactured by Bruker Elexsys E680 in the W-band (frequency 94 GHz). Electron spin echo-detected (ESE) EPR spectra and relaxation times were obtained using a standard Hahn-echo pulse sequence $\pi/2$–τ–π– ESE, where $\pi/2 = 40$ ns, $\pi = 80$ ns, $\tau = 240$ ns. Simulations of the measured EPR data was performed using EasySpin software [23].

3. Results and Discussion

The ground state of the V_B^- centers, excluding hyperfine interactions with the nuclei of ^{14}N nitrogen and ^{10,11}B boron sublattices, is described by the spin Hamiltonian (see Eq. 1), including the terms of Zeeman interaction and zero-field splitting of spin sublevels. The presence of ZFS leads to the appearance of a fine structure (doublet lines) in the EPR spectrum due to the partial removal of spin degeneracy:

$$H = g\mu_B \mathbf{BS} + D(S_z^2 - 2/3) + E(S_x^2 - S_y^2), \quad (1)$$

where $S = 1$ is the total spin, μ_B is the Bohr magneton, $\mathbf{B}$ is the static magnetic field, D and E describe the zero-field splitting interaction, S_z, S_x and S_y the total spin-triplet operators, z-axis is collinear with the hexagonal c-axis.

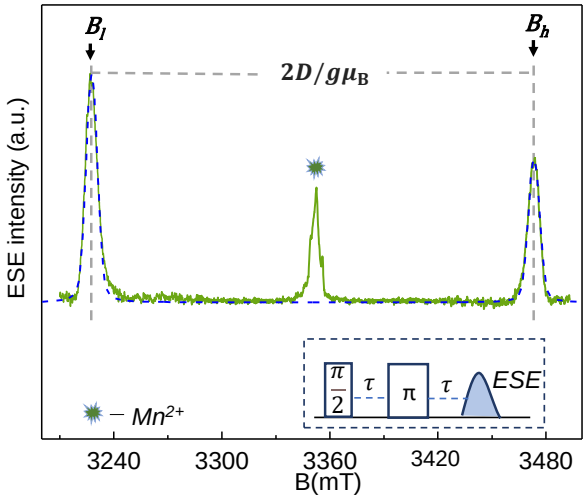

Figure 2. W-band EPR spectrum (green) registered in the proton-irradiated hBN sample at $T = 297$ K under $\lambda = 532$ nm excitation at $\mathbf{B} \parallel \mathbf{c}$. The simulation of the EPR spectrum (blue dashed line) is also shown, taking into account the manifestation of the fine structure and the population redistribution of the triplet center. The bottom inset shows the Hahn pulse sequence used for ESE detection. The star highlights the side signal from the Mn^{2+} centers in the resonator.

Figure 2 shows the EPR spectrum registered in the primary spin echo (pulse) mode for the hBN sample irradiated with protons. The hBN crystal was oriented so that its hexagonal axis **c** was directed parallel to the static magnetic field **B** ($\mathbf{B} \parallel \mathbf{c}$, $\theta = 0°$). The EPR spectrum was recorded at room temperature $T = 297$ K under optical excitation using the line at $\lambda = 532$ nm (2.33 eV) of the Nd: YAG laser. The doublet of lines in the magnetic fields indicated in Figure 2 as B_l and B_h reflects the presence of splitting in zero magnetic field (D), caused predominantly by spin-spin interaction. Thus, this pair of lines, spaced relative to each other by a distance $\Delta B = 2D/g\mu_B = 245.9$ mT, corresponds to the allowed EPR transitions $\Delta m_s = \pm 1$ between spin sublevels of the triplet, as shown schematically in the inset in Figure 2. The inhomogeneous broadening of EPR line is due to an unresolved hyperfine structure with three equivalent nitrogen nuclei with splitting $A_{||} = 47$ MHz. The number (N) of lines is in correspondence with the number (n) of equivalent nuclei and given by $N = 2nI + 1$, where $I = 1$. The simulation of the EPR spectrum (see the dashed line in Figure 2) was carried out using the spin Hamiltonian (see Eq. 1) and with the parameters $g_{||} = 2.0042$, $D = 3.4$ GHz, and $E = 50$ MHz corresponding to the spectroscopic parameters of the V_B^- centers in earlier works [14, 24]. Owing to the presence of a metastable intermediate level in the spin-dependent excitation-recombination channel (see

Figure 1) of paramagnetic centers, laser excitation leads to a redistribution of the populations of all three spin levels. In this case, the thermodynamic Boltzmann equilibrium state is violated, where the nonmagnetic level $m_s = 0$ becomes more populated. This effect leads that the low-field component B_l of the fine structure in the EPR spectrum manifests itself as an absorption line, and the high-field component B_h in the form of radiation (inverted signal) [25]. However, in the present study, a complete inversion of the high-field component does not occur, but only a decrease in its intensity (see Figure 2). In the region $g = 2.003$ (the center of gravity of the EPR spectrum of a boron vacancy), a weakly structural signal is observed. This broadened line refers to the isotropic hyperfine interaction of Mn^{2+} (marked with a frame in Figure 2), which is associated with the experiment at room temperature. These manganese ions are not related to the hBN sample. The central EPR lines are signals from the resonator that do not respond to laser irradiation. Since the nature of the vacancy type centers is quite complex in hBN, one of the EPR resonance sources can be boron or nitrogen vacancies with a neutral charge state (there is no reaction to laser irradiation with $\lambda = 532\,\text{nm}$). Identification and analysis of these new centers are beyond the scope of this work and will be studied in the following scientific papers.

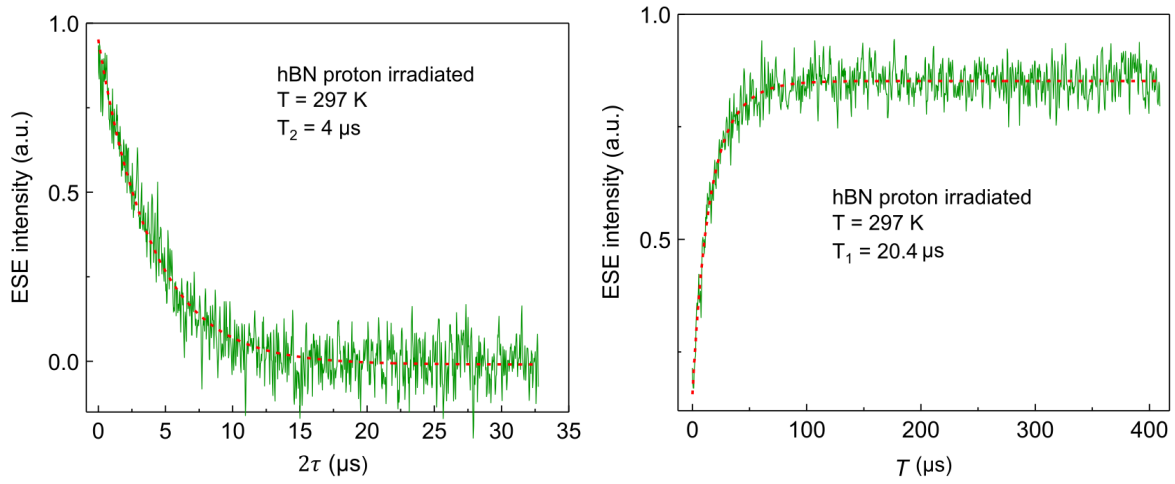

Figure 3. Dynamic characteristics of the boron vacancy at room temperature: spin-spin (left) and spin-lattice (right) relaxation time. The corresponding simulation (red dashed line) is given to estimate the T_1 and T_2 time using a one-exponential function.

Since the observation of EPR signals at room temperature for a boron vacancy is a unique phenomenon, the relaxation characteristics of the defect were investigated in the pulse mode. The relaxation curves together with the simulation are shown in Figure 3. The phase coherence time T_2 for the spin ensembles at room temperature in hBN is equal to $4\,\mu s$ which is slightly longer than previously reported $T_2 = 2\,\mu s$ for the V_B^- spin ensembles created in hBN by means of neutron irradiation [26]. For comparison, the rate of transverse relaxation of boron vacancies at $T = 50\,\text{K}$ in the same matrix hBN $T_2 = 15\,\mu s$ [27], while for the latter the transverse magnetization decay curve shows signs (patterns) of spin diffusion. The time of longitudinal (spin-lattice) relaxation due to room temperature is quite short, which allows the spin system to recover quickly enough and return to the ground state. The relaxation and magnetization recovery curves are described by a one-exponential function, which indicates the absence of other nonequivalent boron vacancies.

4. Conclusion

To summarize, in the present paper we have investigated the possibility to create the defects possessing optically addressable spin states in hexagonal boron nitride by means of proton irradiation. We have shown that such high-energy ($E_P = 15$ MeV) exposure can be used for creation of negatively charged boron vacancies in hBN host. The main spin-Hamiltonian parameters from EPR spectroscopy data at laser excitation ($\lambda = 532$ nm) including g-factor, zero-field splitting D and E, and relaxation (T_1 and T_2) values are unambiguously identified the triplet center under study as boron vacancy V_B^-. Demonstration of the opportunity of conducting EPR experiments under optical pumping significantly advances the possibility of quantum manipulations at room temperature.

Acknowledgments

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