

Electron–Nuclear Coherent Coupling and Nuclear Spin Readout through Optically Polarized V_B^- Spin States in hBN

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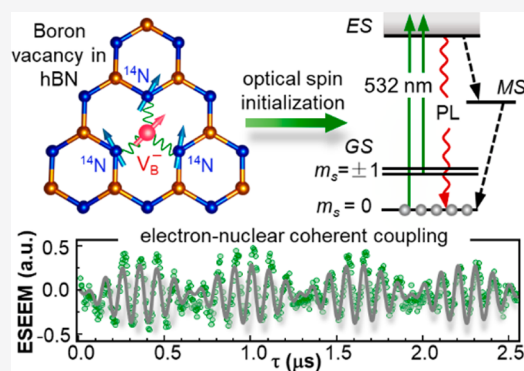
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Supporting Information

ABSTRACT: Coherent coupling of defect spins with surrounding nuclei along with the endowment to read out the latter are basic requirements for an application in quantum technologies. We show that negatively charged boron vacancies (V_B^-) in hexagonal boron nitride (hBN) meet these prerequisites. We demonstrate Hahn-echo coherence of the V_B^- spin with a characteristic decay time $T_{\text{coh}} = 15 \mu\text{s}$, close to the theoretically predicted limit of $18 \mu\text{s}$ for defects in hBN. Elongation of the coherence time up to $36 \mu\text{s}$ is demonstrated by means of the Carr–Purcell–Meiboom–Gill decoupling technique. Modulation of the Hahn-echo decay is shown to be induced by coherent coupling of the V_B^- spin with the three nearest ^{14}N nuclei via a nuclear quadrupole interaction of 2.11 MHz. DFT calculation confirms that the electron–nuclear coupling is confined to the defective layer and stays almost unchanged with a transition from the bulk to the single layer.

KEYWORDS: hexagonal boron nitride, boron vacancy, optical spin polarization, electron–nuclear coherent coupling



Optically addressable high spin states ($S \geq 1$) of defects in a semiconducting host are fundamental for the development of solid-state quantum technologies and serve as a tool to probe a plethora of novel physical phenomena.^{1,2} Quantum sensing down to the nanoscale,^{3–5} quantum informational processing,^{1,6} and realization of exotic states of matter² are just a few examples. Mainly two solid-state platforms have been intensively explored within this respect. Namely, diamond with negatively charged nitrogen-vacancy centers (NV^-) and silicon carbide (SiC) comprising several silicon vacancy-related defects.^{1–9} Both 3D crystals are formed by sp^3 -hybridized atoms of nearly nonmagnetic (i.e., low-abundant magnetic) nuclei. Thus, they are rather similar with respect to their structural and chemical properties.

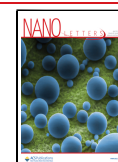
A completely different class of host materials for defect spins has been recognized only recently by referring to the van der Waals materials family, such as hexagonal boron nitride (hBN), after successful demonstration of optical and microwave control over the spins bounded to defects in its lattice by means of optically detected magnetic resonance in zero and low magnetic fields (ZF-ODMR).^{10–14} hBN is formed by 2D atomic layers of sp^2 -hybridized nitrogen–boron atoms that are coupled through weak vdW interactions. Its ultrawide-bandgap ($E_g \approx 6 \text{ eV}$)¹⁵ combined with two-dimensional screening mechanisms and natural hyperbolic properties in the mid-infrared range make such a kind of layered material particularly interesting for quantum technologies.¹⁶ Defects in hBN are

deeply explored from the perspective of quantum photonics,^{16–20} quantum sensing,^{21–24} and qubits.^{10–14,25–27} However, so far only one defect possessing ODMR has been rigorously identified and its microscopic structure is well understood. This defect is the negatively charged boron vacancy (V_B^-), a missing boron atom having three equivalent nitrogen atoms as nearest neighbors, as schematically shown in Figure 1a.^{10,25,26,28} V_B^- possesses a spin-triplet ($S = 1$) ground state, whereby the spin–spin interaction between the unpaired spins induces energy-level splitting ($D \cong 3.6 \text{ GHz}$) even in the zero magnetic field. A spin-dependent recombination channel in its optical excitation–recombination cycle (Figure 1b) allows to polarize the $m_s = 0$ ground state sublevel and to realize its readout via ODMR or electron spin resonance (ESR).¹⁰ Taking into account (i) the demonstrated integration of V_B^- defects into advanced photonic cavities,²⁹ (ii) the high readout contrast of its ODMR signal, comparable with those of NV^- centers in diamond,³⁰ and (iii) the developed robust mechanisms of defect generation in hBN,^{10,31–33} V_B^- centers

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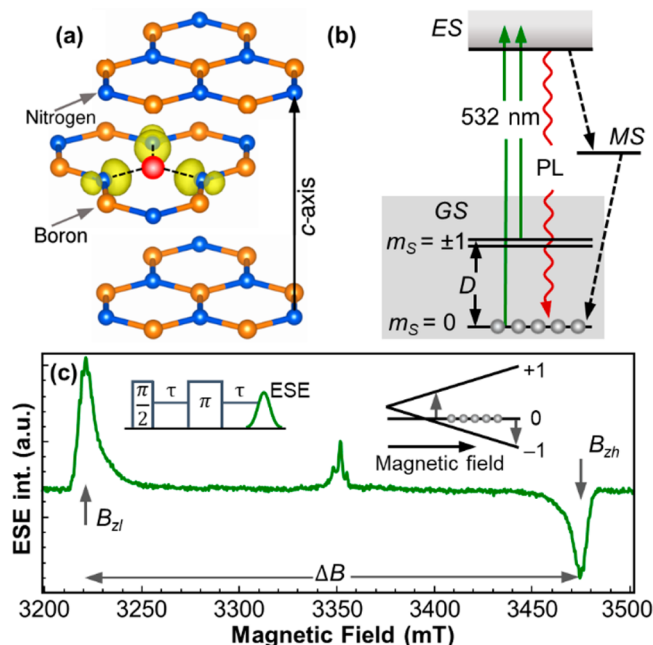


Figure 1. (a) hBN lattice with the V_B^- defect (red ball). The c -axis is shown with the solid arrow. Nitrogen dangling bonds are shown with dashed lines. (b) Scheme of the V_B^- spin initialization through spin-dependent recombination pathway (dashed lines) from the excited state (ES) into the ground state (GS, with occupied $m_S = 0$ sublevels and ZFS denoted by D) via metastable state (MS) under $\lambda = 532$ nm excitation (green lines) and radiative decay (PL) from the ES to the GS (red curve). (c) ESR spectrum of the V_B^- defects at a temperature $T = 50$ K under $\lambda = 532$ nm excitation, obtained using Hahn-echo microwave pulse sequence (top inset) with static magnetic field $B_0 \parallel c$. Vertical arrows indicate allowed ESR transitions (B_{zl} and B_{zh}) separated by ΔB .

provide a promising platform to probe and extend the quantum technologies concepts on defect spins confined in a two-dimensional atomic layer. However, both N and B are 100%-magnetic nuclei (99.9% ^{14}N , $I = 1$; 19.9% ^{10}B , $I = 3$, 80.1% ^{11}B , $I = 3/2$) rendering a detailed understanding of the electron–nuclear coupling a prerequisite for spintronic applications.

In this article, we study the coherent coupling of optically polarized V_B^- electron spin with surrounding nuclei by tracking the oscillation behavior of Hahn-echo coherence followed by an analysis of the coherence behavior through density functional theory (DFT). Understanding the interactions allowed us to implement a standard double resonance technique (ENDOR) to demonstrate the nuclear spin readout through nuclear population transfer onto electron spin sublevels, which forms the fundamentals for quantum information processing.^{34,35} The demonstrated, quite long coherence time of the V_B^- defect shows its applicability for quantum sensing.^{3,21–24}

The sample used in this study was a commercially produced (HQ Graphene company) hBN single crystal which has been irradiated at room temperature with 2 MeV electrons to a total dose of $6 \times 10^{18} \text{ cm}^{-2}$ in order to produce the V_B^- defects.³² All experiments were done in the W-band ($\cong 94$ GHz) commercial pulsed ESR spectrometer Bruker Elexsys 680. The ESR technique is the method of choice to study structural and in particular dynamical properties of spin defects.^{9,36,37} The sample is inserted in the microwave cavity and an external

static magnetic field B_0 is applied to produce a net magnetization vector. Pulsed ESR spectra are recorded using a standard Hahn-echo sequence $\pi/2 - \tau - \pi - \tau$ –electron spin echo with $\pi = 48$ ns and $\tau = 300$ ns by sweeping the external magnetic field B_0 and detecting an integral intensity of electron spin echo (ESE) for each B_0 value. The first $\pi/2$ -pulse creates a transverse magnetization that decays over the delay time τ due to the local field inhomogeneities. The second π -pulse refocuses the decomposed spin packets and leads to the recovery of the transverse magnetization after delay time τ , resulting in the spin–echo signal.³⁸

First, we measure the field swept ESE detected ESR spectrum of the V_B^- defects using Hahn-echo pulse sequence (inset in Figure 1c). Two pronounced ESR lines in the magnetic fields labeled B_{zl} and B_{zh} correspond to the allowed magnetic dipole transitions between the triplet spin manifold (see also right inset in Figure 1c). The splitting between these lines is $\Delta B \cong 255 \text{ mT} = 2D/\gamma_e$, where $D = 3.57 \text{ GHz}$ and $\gamma_e = 28 \text{ GHz/T}$ is the electron gyromagnetic ratio, corresponding to the spectroscopic signatures of the spin-triplet ($S = 1$) V_B^- centers.¹⁰ The spectrum also demonstrates that 532 nm excitation initialize the $m_S = 0$ ground-state spin sublevel of the defect through spin-dependent intersystem-crossing (as illustrated in Figure 1b). The latter follows from phase reversal of the ESR signals, that is, the B_{zh} transition ($m_S = 0 \rightarrow -1$) exhibits emission rather than absorption of the microwave power.

We then probe the coherence of the optically polarized V_B^- spin ensemble measuring a decay of the Hahn-echo magnitude by incrementing the delay time τ after the first microwave $\pi/2$ -pulse (Figure 2a). The decay curve measured on the B_{zl} resonance is well described by a stretched exponent of the form $I(2\tau) = I_0 \times \exp\{-(2\tau/T_{\text{coh}})^n\}$ with $T_{\text{coh}} = 15.1 \mu\text{s}$ and a moderate stretching parameter $n = 1.4$. From this, two

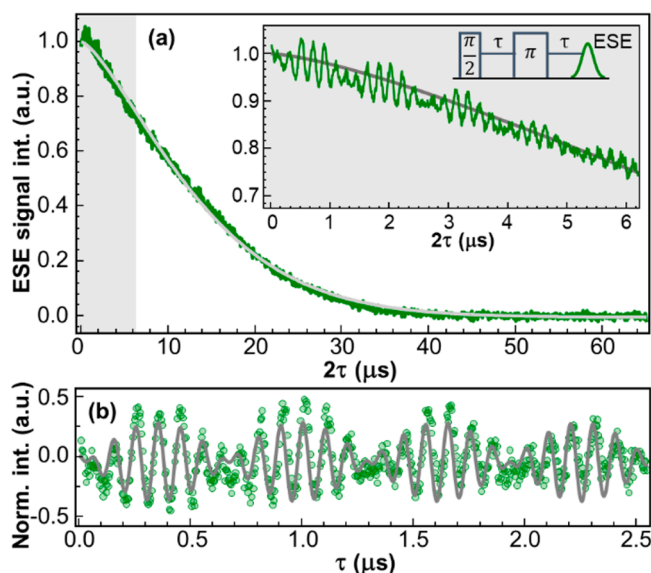


Figure 2. (a) Hahn-echo ESE decay curve (green) measured on the optically polarized V_B^- spins as a function of the time delay τ between the mw pulses. Stretched exponential fit (gray line) demonstrates a characteristic decay time $T_{\text{coh}} = 15.1 \mu\text{s}$. Inset shows the gray-shaded segment in an enlarged scale. (b) Experimentally observed modulation (green) after subtraction of the corresponding decay curve; fit functions (gray, see text).

important conclusions follow: (i) The measured coherence time T_{coh} in this electron-irradiated sample is approximately 7 times longer than the Hahn-echo coherence of about 2 μs previously measured on the neutron-irradiated hBN sample^{12,27} and is longer than 10 μs , that is, the upper bound of V_{B}^- spin ensembles coherence estimated from the Rabi nutations.¹⁰ The W-band echo decay measured on the V_{B}^- spin ensemble in neutron irradiated sample used in the studies^{10,12} is presented in Supporting Information Figure S1, and demonstrates $T_{\text{coh}} = 5.14 \mu\text{s}$. This value is close to previous pulsed ZF-ODMR measurements and demonstrates that the high magnetic fields used in the present study do not have a significant impact on the V_{B}^- coherence time. Remarkably, the V_{B}^- coherence in electron-irradiated sample is close to the 18 μs upper limit, theoretically predicted for spin defects in hBN using a cluster expansion method and assuming that decoherence is mainly caused by the entanglement between the electron spin and the nuclear spin bath of the host atoms.³⁹ It is thus within the common range of the coherence for high-density spin defects in diamond^{40,41} and SiC,^{42,43} though well below the millisecond range established for single defects in these materials.^{1,44} (ii) The observed stretched exponential decay indicates that the total coherence time, in addition to spin-spin relaxation, is determined by spectral diffusion, which is commonly characterized by a typical value of n between 1 and 4 depending on the regime of spectral diffusion.⁴⁵ The latter indicates coherent interaction of the V_{B}^- defect spin with the random and temporally fluctuating local (effective) magnetic field associated with the dipolar-interaction induced flip-flops of nuclear spin pairs⁴⁶ of ^{10}B , ^{11}B , and ^{14}N .

The impact of spectral diffusion on the coherence time can be significantly reduced by the Carr–Purcell–Meiboom–Gill (CPMG) decoupling technique, where a multiple number (N) of π_y refocusing pulses are applied after a Hahn echo sequence, namely $(\pi/2)_x - (\tau - \pi_y - \tau - \text{ESE})^N$. By this, the CPMG approach limits time-dependent effects that are responsible for the decay by reducing the refocusing time τ .^{38,47} The CPMG data measured for two values ($\tau = 1 \mu\text{s}$ and $\tau = 4 \mu\text{s}$) are presented in Supporting Information Figure S2. The single exponential decay of the CPMG echo traces corresponds to an enhancement of the V_{B}^- coherence time to $T_{\text{CPMG}} = 36 \mu\text{s}$ and demonstrates partial suppression of spectral-diffusion induced decoherence. It is worth mentioning here that the coherence time can potentially be further improved by reducing the refocusing time τ together with increasing the number of π_y pulses.

The decay curve reveals its oscillatory behavior especially pronounced at the very beginning of the transient curve (inset to Figure 2a). Such oscillations refer to electron spin echo envelop modulation (ESEEM)^{48,49} and manifest the presence of coherent coupling of the V_{B}^- electron spin with magnetic moments of nuclei available in the hBN lattice. The modulation is generated by high-intense microwave pulses inducing a mixture of “forbidden” and “allowed” ESR transitions. As a result, the decay curve is modulated by frequencies corresponding to nuclear magnetic resonance (NMR) transitions within nuclear-spin manifolds bound to the current electron spin, whereby both sublattices, N as well as B, are potentially contributing.

To further elucidate the origin of these modulations we first analyze them in the time domain after removal of the exponential contribution. The corresponding fit $f(\tau) = A_0 \times \cos(2\pi\tau f_1 + \varphi_1) \times \cos(2\pi\tau f_2 + \varphi_2)$ presented in Figure 2b

shows that the modulation pattern is well described by a product of a slow-oscillating envelope function ($f_2 = 0.789 \pm 0.001 \text{ MHz}$) and a fast-oscillating one ($f_1 = 9.99 \pm 0.09 \text{ MHz}$), whereby the latter (i.e., the average of contributing NMR frequencies) coincides with the Larmor frequency of ^{14}N nuclear magnetic moments ($\nu_{\text{L}}(^{14}\text{N})$) for the given magnetic field via $\nu_{\text{L}} = \gamma_{\text{N}} B_{\text{z}} \approx 9.92 \text{ MHz}$, where $\gamma_{\text{N}} = 3.077 \text{ MHz/T}$ ⁵⁰ is the ^{14}N nuclear gyromagnetic ratio. The observed modulation can be thus naturally explained by coherent coupling of the V_{B}^- electron spin with nuclear spins of the nitrogen sublattice.

To identify the particular ^{14}N atoms giving rise to this coupling, and in order to establish the interaction type we determine the parameters of the electron–nuclear coupling and compare them with the predictions from DFT calculations. For this purpose, we consider the following spin-Hamiltonian

$$H = \gamma_{\text{e}} B_0 S_z + D \left(S_z^2 - \frac{1}{3} S(S+1) \right) + \mathbf{SAI} - \gamma_{\text{n}} I_z B_0 + \mathbf{IPI}$$

with electron Zeeman (Z_{e}), zero-field splitting (ZFS), hyperfine (HF), nuclear Zeeman (Z_{N}), and quadrupole (QI) interactions, where $\mathbf{A}$ and $\mathbf{P}$ are the HF and QI tensors, respectively. A static magnetic field B_0 is applied parallel to the c -axis, that is, the principal z -axis of the axially symmetric ZFS tensor, expressed by the D -value. For simplicity, we consider here a single interaction energy for the three nearest nitrogen nuclei exclusively. Because of the trigonal symmetry of the ground state configuration these nuclei are indeed equivalent, and the respective nitrogen dangling bonds are in the defective 2D B–N sp^2 plane (see also defect model in Figure 1a). The localization of the electron-spin density in a single BN 2D layer (see Figure 3a) is supported by the fact that the calculated hyperfine parameters of V_{B}^- defect in hBN bulk (this work) and those reported in ref 26 for a single BN layer are essentially identical (see also Supporting Table 1). This implies that the symmetry axes of the HF and QI interactions are perpendicular to the c -axis and possess axial symmetry along the dangling bonds, that is, HF and QI interactions are fully described by $A = a + b(3 \cos^2 \theta - 1)$ and $\text{QI} = P(3 \cos^2 \theta - 1)$, respectively. Here a and b are isotropic and anisotropic part of the HF, respectively, and $P = \frac{3eQ_{\text{N}}V_{\text{zz}}}{4I(2I-1)}$ is related to the electric field

gradient V_{zz} in the direction of the nitrogen dangling bond and the nuclear electric quadrupole moment Q_{N} . θ is the angle between B_0 direction and the symmetry axis of the HF and QI and thus $\theta = 90^\circ$. The corresponding NMR resonance conditions for nuclear spin flips in such system and thus potentially expected in the echo envelope are labeled in Figure 3b as ν_1 to ν_4 . These frequencies are $\nu_{1,2} = \nu_{\text{L}} \pm P/2$ and $\nu_{3,4} = A - \nu_{\text{L}} \pm P/2$, where the absolute value of A in $B_0 \parallel c$ configuration has been established previously to be 47 MHz.¹⁰ It is seen, that ν_3 and ν_4 correspond to the nuclear spin-flips between hyperfine- and quadrupole-split $m_{\text{S}} = +1$ Zeeman level, while ν_1 and ν_2 frequencies couple purely quadrupole-split nuclear states in the $m_{\text{S}} = 0$ sublevel. The latter two frequencies are symmetrically placed around the $\nu_{\text{L}}(^{14}\text{N})$ frequency and are thus in accordance with the experimentally observed modulation.

To analyze these $\nu_{1,2}$ frequencies precisely, we conduct three-pulse ESEEM experiments. Compared with the 2-pulse technique, a three-pulse method allows to reveal the basic frequencies of nuclear-spin flips, and eliminates observation of the frequencies given as sums and differences of the basic NMR transitions. A Fourier-transform (FT) spectrum of such a measured echo modulation is presented in Figure 3c. The

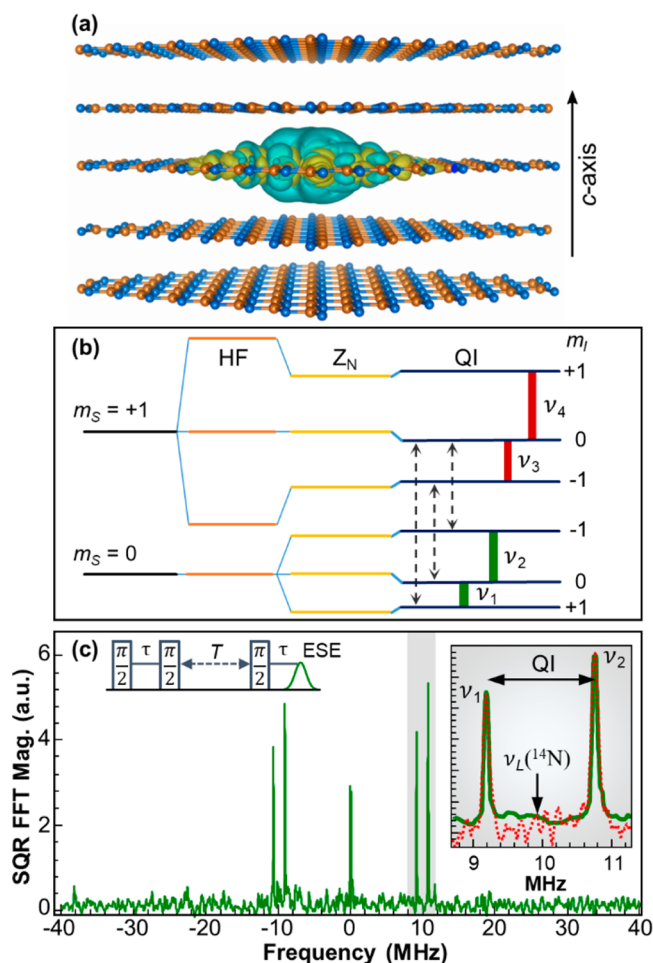


Figure 3. (a) Electron-spin density around the V_B defect confined to the respective defect-containing BN layer. (b) Energy-level scheme of the V_B ground state including Z_{eff} , ZFS, HF, Z_{N} , and QI interactions with one ^{14}N nucleus. Electron and nuclear levels are indexed by corresponding quantum numbers m_S and m_I . NMR transitions $\nu_1 - \nu_4$ are denoted by green and red vertical bars. (c) FT spectrum of the three-pulse ESEEM, obtained using the pulse sequence (left inset). Right inset shows FT frequencies in enlarged scale together with the FT spectrum (red dots) of the modulations from Figure 2b; $\nu_L(^{14}\text{N})$ denoted with a vertical arrow.

resonance frequencies labeled ν_1 and ν_2 are observed exactly as expected for the QI-induced splitting of the $m_S = 0$ sublevel. The value of the QI determined as the difference between the frequencies $|\nu_1 - \nu_2| = 2f_2$ is 1.58 MHz corresponding to the nuclear quadrupole interaction constant defined as $C_q = eQ_N V_{zz} = 2.11$ MHz. Notably, this value is around 10 times larger than recently determined $C_q \approx 200$ kHz for the electric quadrupole moment of ^{14}N nuclei interacting with the native electric field gradient of hBN.⁵¹ On the other hand, it is close to previously determined C_q for the three-fold coordinated nitrogen nucleus involved in the prototypical nitrogen-vacancy (NV^-) spin-qubits in diamond⁵² and SiC.⁵³

We further support this finding by performing DFT calculations. A single V_B center is embedded in a periodically repeated hBN supercell containing 800 atoms ($10 \times 10 \times 2$ unit cells with 4 BN layers). The calculations utilize the GIPAW module of the Quantum ESPRESSO software,^{54,55} Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional,⁵⁶ standard norm-conserving pseudopotentials,⁵⁷ and a

plane-wave basis set with 600 eV kinetic energy cutoff. Our calculation confirms that the ground state provides trigonal symmetry, whereby the spin density is perfectly confined in the defective BN-layer, as shown in Figure 3a. We find nice agreement with the characteristic EPR fingerprints of the center provided in the caption of Figure 4; the ZFS and the

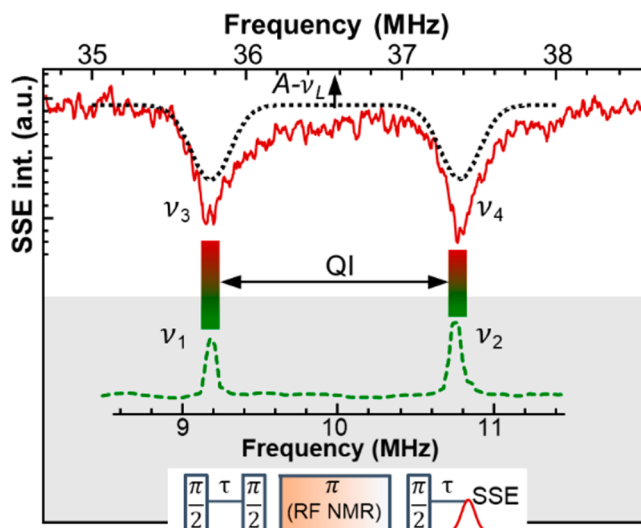


Figure 4. Readout of the ν_3 and ν_4 NMR transitions between quadrupole-split hyperfine levels in the $m_S = +1$ state by monitoring the SSE intensity. Pulse sequence used for nuclear-spin readout indicated in the bottom. Calculated spectrum using the spin-Hamiltonian with parameters $D = 3.57$ GHz, $A = 46.52$ MHz, $C_q = 2.12$ MHz is shown with black dashed line. Bottom spectrum reflects the QI in the $m_S = 0$ state, taken from the inset of Figure 3c.

out-of-plane HF (for $\theta = 90^\circ$) are calculated to be $D = 3.47$ GHz and $A = 46.12$ MHz, respectively. Because of the symmetry of the charge density distribution in the vicinity of the V_B^- center, the leading component of the electric field gradient at the nearest-neighbor nitrogen nucleus, V_{zz} , coincides with the direction of the nitrogen dangling bond. The value of $C_q = 2.06 \pm 0.08$ MHz derived from V_{zz} shows very good agreement with experiment (2.11 MHz). The uncertainty in the calculated C_q reflects the spreading of the nuclear quadrupole moment Q_N between 0.0193 and 0.0208 barn reported in literature.⁵⁸ For the other ^{14}N nuclei in the supercell, the calculated NQI is about five times weaker, with C_q of 0.35 ± 0.01 MHz for the next-nearest-neighbor nitrogens and 0.42 ± 0.01 MHz for the most distant ones. By means of DFT calculations, we further study the evolution of the ground state spin-Hamiltonian parameters with the number of the hBN layers. In fact, we are able to show that all parameters reflecting interactions with the nearest nitrogen nuclei stay almost unchanged even for the defect in a single BN layer, as summarized in the Supporting Table 1.

The intricate peculiarity of interaction with more distant ^{14}N shells can be eliminated by direct manifestation of the 1.58 MHz interaction in the hyperfine-split $m_S = +1$ state as the latter originates from the three equivalent nitrogen atoms nearest to the vacancy. In Figure 4, this is demonstrated by probing the population of the hyperfine sublevels through the generation of the stimulated electron spin echo (SSE) following the driving of appropriate nuclear magnetic resonance transitions. The pulse sequence used in this experiment (Mims-ENDOR⁵⁹) is shown in the inset of Figure

4. The first two $\pi/2$ mw pulses invert the electron spin population; the third $\pi/2$ pulse generates the stimulated ESE. Between the second and the third mw pulses, a radiofrequency (RF) pulse is applied to invert the population of the nuclear spin sublevels, that is, inducing NMR transitions. The resulting spectrum of B_{2I} transitions is presented in Figure 4. It possesses the doublet of lines labeled as ν_3 and ν_4 in accordance with the energy level diagram for the $m_S = +1$ state. The center of gravity of these frequencies is on the value $A - \nu_L$. Their splitting $|\nu_3 - \nu_4|$ mimicks again the 1.58 MHz QI modulating the FT ESEEM spectrum of the $m_S = 0$ state, cf. gray-shaded bottom in Figure 4. This reinforces our aforementioned conclusion that the modulating 1.58 MHz are induced by ^{14}N quadrupole interaction from the three nitrogen dangling bond atoms.

To conclude, in this Letter we perform an in-depth analysis of the V_B^- spin ensembles in hBN. We demonstrate their coherent coupling with atoms of the nitrogen sublattice, identify the origin of this coupling and unambiguously reveal it to be induced by nuclear quadrupole interaction of the three neighboring ^{14}N dangling bond atoms. We find that the magnitude of this interaction is about 1 order of magnitude larger than those for the more distant host nitrogen atoms. The 15 μs spin-coherence time directly measured via Hahn-echo decay is apparently longer than previously reported for the V_B^- spin ensemble in neutron-irradiated samples. It is thus within the common range of the coherence for high-density spin defects in diamond^{40,41} and SiC^{42,43} though well below the millisecond range established for single defects in these materials.^{1,44} Given the 100% magnetic nuclei of the host material, the achieved coherence time is remarkable, suggesting that some decoherence-reducing effects are already active. These effects should be identified in near future work, in order to enhance them afterward. In this context, we reveal that the coherence of the V_B^- defect possess nontrivial stretched-exponential behavior pointing to the presence of coherent interactions of the V_B^- defect spin with fluctuating spin bath generated by distant nuclei. By means of CPMG technique, we show that decoupling from the nuclear spin bath is possible and reach 36 μs spin ensemble coherence. These all-together make the V_B^- defect spin confined in the two-dimensional boron nitride layer an intriguing object for implementations in quantum technologies and potentially in the discovery of the novel quantum states in the limits of condensed matter.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.1c04610>.

It contains Hahn-echo decay curve measured on the V_B^- spin ensemble in the neutron-irradiated hBN sample, and CPMG decay curves measured with two different delay times $\tau = 1$ and 4 μs on the V_B^- spin ensemble in the electron-irradiated sample. Both experiments are conducted in the W-band ($\cong 94$ GHz) commercial pulsed ESR spectrometer (Bruker Elexsys 680) under 532 nm optical excitation of the sample at a temperature $T = 50$ K. The hyperfine and nuclear quadrupole coupling constants calculated for the nearest-neighbor ^{14}N nucleus in bulk hBN ($10 \times 10 \times 2$ unit cells with four BN layers) and in a single BN layer (10×10 unit cells) by means of DFT (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Awschalom, D.; Hanson, R.; Wrachtrup, J.; Zhou, B. B. Quantum technologies with optically interfaced solid-state spins. *Nat. Photonics* **2018**, *12*, 516–527.
- (2) Choi, S.; Choi, J.; Landig, R.; Kucsko, G.; Zhou, H.; Isoya, J.; Jelezko, F.; Onoda, S.; Sumiya, H.; Khemani, V.; von Keyserlingk, C.; Yao, N. Y.; Demler, E.; Lukin, M. D. Observation of discrete time-crystalline order in a disordered dipolar many-body system. *Nature* **2017**, *543*, 221–225.
- (3) Degen, C. L.; Reinhard, F.; Cappellaro, P. Quantum sensing. *Rev. Mod. Phys.* **2017**, *89*, 035002.
- (4) Michl, J.; Steiner, J.; Denisenko, A.; Bühlau, A.; Zimmermann, A.; Nakamura, K.; Sumiya, H.; Onoda, S.; Neumann, P.; Isoya, J.; Wrachtrup, J. Robust and accurate electric field sensing with solid state spin ensembles. *Nano Lett.* **2019**, *19* (8), 4904–4910.
- (5) Balasubramanian, P.; Osterkamp, C.; Chen, Y.; Chen, X.; Teraji, T.; Wu, E.; Naydenov, B.; Jelezko, F. DC - magnetometry with engineered nitrogen-vacancy spin ensembles in diamond. *Nano Lett.* **2019**, *19* (9), 6681–6686.
- (6) Humphreys, P. C.; Kalb, N.; Morits, J. P. J.; Schouten, R. N.; Vermeulen, R. F. L.; Twitchen, D. J.; Markham, M.; Hanson, R. Deterministic delivery of remote entanglement on a quantum network. *Nature* **2018**, *558*, 268–273.
- (7) Childress, L.; Walsworth, R.; Lukin, M. Atom-like crystal defects: From quantum computers to biological sensors. *Phys. Today* **2014**, *10*, 67.
- (8) Astakhov, G. V.; Simin, D.; Dyakonov, V.; Yavkin, B. V.; Orlinskii, S. B.; Proskuryakov, I. I.; Anisimov, A. N.; Soltamov, V. A.; Baranov, P. G. Spin centres in SiC for quantum technologies. *Appl. Magn. Reson.* **2016**, *47*, 793–812.
- (9) von Bardeleben, H. J.; Cantin, J.-L.; Gerstmann, U.; Schmidt, W. G.; Biktagirov, T. Spin Polarization, Electron–Phonon Coupling, and Zero-Phonon Line of the NV Center in 3C-SiC. *Nano Lett.* **2021**, *21* (19), 8119–8125.
- (10) Gottscholl, A.; Kianinia, M.; Soltamov, V.; Orlinskii, S.; Mamin, G.; Bradac, C.; Kasper, C.; Krambrock, K.; Sperlich, A.; Toth, M.; Aharonovich, I.; Dyakonov, V. Initialization and read-out of intrinsic spin defects in a van der Waals crystal at room temperature. *Nat. Mater.* **2020**, *19*, 540–545.
- (11) Chejanovsky, N.; Mukherjee, A.; Geng, J.; Chen, Yu.-C.; Kim, Y.; Denisenko, A.; Finkler, A.; Taniguchi, T.; Watanabe, K.; Dasari, D. B. R.; Auburger, P.; Gali, A.; Smet, J. H.; Wrachtrup, J. Single-spin resonance in a van der Waals embedded paramagnetic defect. *Nat. Mater.* **2021**, *20*, 1079–1084.
- (12) Gottscholl, A.; Diez, M.; Soltamov, V.; Kasper, C.; Sperlich, A.; Kianinia, M.; Bradac, C.; Aharonovich, I.; Dyakonov, V. Room temperature coherent control of spin defects in hexagonal boron nitride. *Sci. Adv.* **2021**, *7*, 14.
- (13) Stern, H. L.; Jarman, J.; Gu, Q.; Barker, S. E.; Mendelson, N.; Chugh, D.; Schott, S.; Tan, H. H.; Sirringhaus, H.; Aharonovich, I.; Atatüre, M. Room-temperature optically detected magnetic resonance of single defects in hexagonal boron nitride. *Nat. Commun.* **2022**, *13*, 618.
- (14) Guo, N.-J.; Yang, Y.-Z.; Zeng, X.-D.; Yu, S.; Meng, Yu.; Li, Z.-P.; Wang, Z.-A.; Xie, L.-K.; Xu, J.-S.; Wang, J.-F.; Li, Q.; Liu, W.; Wang, Y.-T.; Tang, J.-S.; Li, C.-F.; Guo, G.-C. Coherent control of an ultrabright single spin in hexagonal boron nitride at room temperature. 2021, DOI: 10.48550/arXiv.2112.06191 (accessed Dec 12, 2021).
- (15) Cassabois, G.; Valvin, P.; Gil, B. Hexagonal boron nitride is an indirect bandgap semiconductor. *Nat. Photonics* **2016**, *10*, 262.
- (16) Caldwell, J. D.; Aharonovich, I.; Cassabois, G.; Edgar, J. H.; Gil, B.; Basov, D. N. Photonics with hexagonal boron nitride. *Nat. Rev. Mater.* **2019**, *4*, 552–567.
- (17) Dietrich, A.; Bürk, M.; Steiger, E. S.; Antoniuk, L.; Tran, T. T.; Nguyen, M.; Aharonovich, I.; Jelezko, F.; Kubanek, A. Observation of Fourier transform limited lines in hexagonal boron nitride. *Phys. Rev. B* **2018**, *98* (R), 081414.
- (18) Chejanovsky, N.; Rezai, M.; Paolucci, F.; Kim, Y.; Rendler, T.; Rouabeh, W.; de Oliveira, F. F.; Herlinger, P.; Denisenko, A.; Yang, S.; Gerhardt, I.; Finkler, A.; Smet, J. H.; Wrachtrup, J. Structural Attributes and Photodynamics of Visible Spectrum Quantum Emitters in Hexagonal Boron Nitride. *Nano Lett.* **2016**, *16* (11), 7037–7045.
- (19) Koperski, M.; Vacklavkova, D.; Watanabe, K.; Taniguchi, T.; Novoselov, K. S.; Potemski, M. Midgap radiative centers in carbon-enriched hexagonal boron nitride. *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117* (24), 13214–13219.
- (20) Castelletto, S.; Inam, F. A.; Sato, S.-i.; Boretti, A. Hexagonal boron nitride: a review of the emerging material platform for single-photon sources and the spin–photon interface. *Beilstein J. Nanotechnol.* **2020**, *11*, 740–769.
- (21) Gottscholl, A.; Diez, M.; Soltamov, V.; Kasper, C.; Krauß, D.; Sperlich, A.; Kianinia, M.; Bradac, C.; Aharonovich, I.; Dyakonov, V. Spin defects in hBN as promising temperature, pressure and magnetic field quantum sensors. *Nat. Commun.* **2021**, *12*, 4480.
- (22) Tettienne, J.-P. Quantum sensors go flat. *Nat. Phys.* **2021**, *17*, 1074.
- (23) Comtet, J.; Grosjean, B.; Glushkov, E.; Avsar, A.; Watanabe, K.; Taniguchi, T.; Vuilleumier, R.; Bocqu, M.-L.; Radenovic, A. Direct observation of water-mediated single-proton transport between hBN surface defects. *Nat. Nanotechnol.* **2020**, *15*, 598–604.
- (24) Babar, R.; Barcza, G.; Pershin, A.; Park, H.; Lindvall, O. B.; Thiering, G.; Legeza, O.; Warner, J. H.; Abrikosov, I. A.; Gali, A.; Ivady, V. Quantum sensor in a single layer van der Waals material. 2021, DOI: 10.48550/arXiv.2111.09589 (accessed Nov 18, 2021).
- (25) Abdi, M.; Chou, J. P.; Gali, A.; Plenio, M. B. Color Centers in Hexagonal Boron Nitride Monolayers: A Group Theory and Ab Initio Analysis. *ACS Photonics* **2018**, *5*, 1967–1976.
- (26) Ivady, V.; Barcza, G.; Thiering, G.; Li, S.; Hamdi, H.; Chou, J.-P.; Legeza, O.; Gali, A. Ab initio theory of the negatively charged boron vacancy qubit in hexagonal boron nitride. *npj Comput. Mater.* **2020**, *6*, 41.
- (27) Liu, W.; Li, Z.-P.; Yang, Y.-Z.; Yu, S.; Meng, Y.; Wang, Z.-A.; Guo, N.-J.; Yan, F.-F.; Li, Q.; Wang, J.-F.; Xu, J.-S.; Dong, Y.; Chen, X.-D.; Sun, F.-W.; Wang, Y.-T.; Tang, J.-S.; Li, C.-F.; Guo, G.-C. Rabi oscillation of V_B^- spin in hexagonal boron nitride. 2021, DOI: 10.48550/arXiv.2101.11220 (accessed Jan 18, 2021).
- (28) Baber, S.; Malein, R. N. E.; Khatri, P.; Keatley, P. S.; Guo, S.; Withers, F.; Ramsay, A. J.; Luxmoore, I. J. Excited State Spectroscopy of Boron Vacancy Defects in Hexagonal Boron Nitride Using Time-Resolved Optically Detected Magnetic Resonance. *Nano Lett.* **2022**, *22* (1), 461–467.
- (29) Froch, J. E.; Spencer, L. P.; Kianinia, M.; Totonjian, D. D.; Nguyen, M.; Gottscholl, A.; Dyakonov, V.; Toth, M.; Kim, S.; Aharonovich, I. Coupling Spin Defects in Hexagonal Boron Nitride to Monolithic Bullseye Cavities. *Nano Lett.* **2021**, *21* (15), 6549–6555.
- (30) Gao, X.; Jiang, B.; Llacsahuanga Alcca, A. E.; Shen, K.; Sadi, M. A.; Solanki, A. B.; Ju, P.; Xu, Z.; Upadhyaya, P.; Chen, Y. P.; Bhawe, S. A.; Li, T. High-Contrast Plasmonic-Enhanced Shallow Spin Defects in Hexagonal Boron Nitride for Quantum Sensing. *Nano Lett.* **2021**, *21* (18), 7708–7714.
- (31) Gao, X.; Pandey, S.; Kianinia, M.; Ahn, J.; Ju, P.; Aharonovich, I.; Shivaram, N.; Li, T. Femtosecond Laser Writing of Spin Defects in Hexagonal Boron Nitride. *ACS Photonics* **2021**, *8* (4), 994–1000.
- (32) Murzakhanov, F. F.; Yavkin, B. V.; Mamin, G. V.; Orlinskii, S. B.; Mumdzhi, I. E.; Gracheva, I. N.; Gabbasov, B. F.; Smirnov, A. N.; Davydov, V. Yu.; Soltamov, V. A. Creation of Negatively Charged Boron Vacancies in hexagonal Boron Nitride crystal by electron irradiation and mechanism of inhomogeneous broadening of Boron Vacancy-related spin resonance lines. *Nanomaterials* **2021**, *11*, 1373.
- (33) Guo, N.-J.; Liu, W.; Li, Z.-P.; Yang, Y.-Z.; Yu, S.; Meng, Y.; Wang, Z.-A.; Zeng, X.-D.; Yan, F.-F.; Li, Q.; Wang, J.-F.; Xu, J.-S.; Wang, Y.-T.; Tang, J.-S.; Li, C.-F.; Guo, G.-C. Generation of Spin Defects by Ion Implantation in Hexagonal Boron Nitride. *ACS Omega* **2022**, *7* (2), 1733–1739.

- (34) Neumann, P.; Beck, J.; Steiner, M.; Rempp, F.; Fedder, H.; Hemmer, P. R.; Wrachtrup, J.; Jelezko, F. Single-shot readout of a single nuclear spin. *Science* **2010**, *329*, 542–544.
- (35) Morton, J. J. L.; Tyryshkin, A. M.; Brown, R. M.; Shankar, S.; Lovett, B. W.; Ardavan, A.; Schenkel, T.; Haller, E. E.; Ager, J. W.; Lyon, S. A. Solid-state quantum memory using the ^{31}P nuclear spin. *Nature* **2008**, *455*, 1085–1088.
- (36) Ochsenbein, S. T.; Gamelin, D. R. Quantum oscillations in magnetically doped colloidal nanocrystals. *Nat. Nanotechnol.* **2011**, *6*, 112–115.
- (37) Baranov, P. G.; Jelezko, F.; Wrachtrup, J. *Magnetic Resonance of Semiconductors and Their Nanostructures: Basic and Advanced Applications*; Springer Series in Material Science; Springer: Heidelberg, 2017.
- (38) Goldfarb, D.; Stoll, S. *EPR spectroscopy: fundamentals and methods*; John Wiley & Sons, 2018.
- (39) Ye, M.; Seo, H.; Galli, G. Spin coherence in two-dimensional materials. *npj Comput. Mater.* **2019**, *5*, 44.
- (40) Jelezko, F.; Gaebel, T.; Popa, I.; Gruber, A.; Wrachtrup, J. Observation of Coherent Oscillations in a Single Electron Spin. *Phys. Rev. Lett.* **2004**, *92*, 7.
- (41) Takahashi, S.; Hanson, R.; van Tol, J.; Sherwin, M. S.; Awschalom, D. D. Quenching Spin Decoherence in Diamond through Spin Bath Polarization. *Phys. Rev. Lett.* **2008**, *101*, 047601.
- (42) Soltamov, V. A.; Yavkin, B. V.; Anisimov, A. N.; Singh, H.; Bundakova, A. P.; Mamin, G. V.; Orlinskii, S. B.; Mokhov, E. N.; Suter, D.; Baranov, P. G. Relaxation processes and high-field coherent spin manipulation in color center ensembles in 6H-SiC. *Phys. Rev. B* **2021**, *103*, 195201.
- (43) Kasper, C.; Klenkert, D.; Shang, Z.; Simin, D.; Gottscholl, A.; Sperlich, A.; Kraus, H.; Schneider, C.; Zhou, S.; Trupke, M.; Kada, W.; Ohshima, T.; Dyakonov, V.; Astakhov, G. V. Influence of Irradiation on Defect Spin Coherence in Silicon Carbide. *Phys. Rev. Applied* **2020**, *13*, 044054.
- (44) Seo, H.; Falk, A. L.; Klimov, P. V.; Miao, K. C.; Galli, G.; Awschalom, D. D. Quantum decoherence dynamics of divacancy spins in silicon carbide. *Nat. Commun.* **2016**, *7*, 12935.
- (45) George, R. E.; Witzel, W.; Riemann, H.; Abrosimov, N. V.; Nötzel, N.; Thewalt, M. L.; Morton, J. J. L. Electron spin coherence and electron nuclear double resonance of Bi donors in natural Si. *Phys. Rev. Lett.* **2010**, *105*, 067601.
- (46) Witzel, W. M.; Das Sarma, S. Quantum theory for electron spin decoherence induced by nuclear spin dynamics in semiconductor quantum computer architectures: Spectral diffusion of localized electron spins in the nuclear solid-state environment. *Phys. Rev. B* **2006**, *74*, 035322.
- (47) Zaripov, R.; Vavilova, E.; Miluykov, V.; Bezkishko, I.; Sinyashin, O.; Salikhov, K.; Kataev, V.; Büchner, B. Boosting the electron spin coherence in binuclear Mn complexes by multiple microwave pulses. *Phys. Rev. B* **2013**, *88*, 094418.
- (48) Mims, W. B. Envelope Modulation in Spin-Echo Experiments. *Phys. Rev. B* **1972**, *5*, 2409.
- (49) Deligiannakis, Y.; Rutherford, A. W. Electron spin echo envelope modulation spectroscopy in photosystem I. *Biochim. Biophys. Acta* **2001**, *1507*, 226–246.
- (50) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. NMR nomenclature: nuclear spin properties and conventions for chemical shifts. IUPAC Recommendations 2001. International Union of Pure and Applied Chemistry. Physical Chemistry Division. Commission on Molecular Structure and Spectroscopy. *Pure Appl. Chem.* **2001**, *73* (11), 1795–1818.
- (51) Lovchinsky, I.; Sanchez-Yamagishi, J. D.; Taniguchi, T.; Bylinskii, A.; Urbach, E. K.; Choi, S.; Fang, S.; Andersen, T. I.; Watanabe, K.; Kim, P.; Kaxiras, E.; Park, H.; Lukin, M. D. Magnetic resonance spectroscopy of an atomically thin material using a single-spin qubit. *Science* **2017**, *355*, 503–507.
- (52) Shin, C. S.; Butler, M. C.; Wang, H.-J.; Avalos, C. E.; Seltzer, S. J.; Liu, R.-B.; Pines, A.; Bajaj, V. S. Optically detected nuclear quadrupolar interaction of N in nitrogen-vacancy centers in diamond. *Phys. Rev. B* **2014**, *89*, 205202.
- (53) Murzakhanov, F. F.; Yavkin, B. V.; Mamin, G. V.; Orlinskii, S. B.; von Bardeleben, H. J.; Biktagirov, T.; Gerstmann, U.; Soltamov, V. A. Hyperfine and nuclear quadrupole splitting of the NV^- ground state in 4H-SiC. *Phys. Rev. B* **2021**, *103*, 245203.
- (54) Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys.: Cond. Mater.* **2017**, *29*, 465901.
- (55) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys.: Cond. Mater.* **2009**, *21*, 395502.
- (56) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (57) Troullier, N.; Martins, J. L. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B* **1991**, *43*, 1993.
- (58) Stone, N. J. Table of nuclear magnetic dipole and electric quadrupole moments. *At. Data Nucl. Data Tables* **2005**, *90*, 75–176.
- (59) Mims, W. B. Pulsed ENDOR experiments. *Proc. R. Soc. London, Ser. A* **2006**, *283*, 452.