Coherent Storage of Photoexcited Triplet States Using ^{29}Si Nuclear Spins in Silicon

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Pulsed electron paramagnetic resonance spectroscopy of the photoexcited, metastable triplet state of the oxygen-vacancy center in silicon reveals that the lifetime of the $m_s = \pm 1$ sublevels differs significantly from that of the $m_s = 0$ state. We exploit this significant difference in decay rates to the ground singlet state to achieve nearly $\sim$100% electron-spin polarization within the triplet. We further demonstrate the transfer of a coherent state of the triplet electron spin to, and from, a hyperfine-coupled, nearest-neighbor ^{29}Si nuclear spin. We measure the coherence time of the ^{29}Si nuclear spin employed in this operation and find it to be unaffected by the presence of the triplet electron spin and equal to the bulk value measured by nuclear magnetic resonance.

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Nuclear spins in solids are promising candidates for quantum bits (qubits) as their weak coupling to the environment often leads to very long spin coherence times [1–4]. However, performing fast manipulation and controlling interaction between nuclear spin qubits is often more challenging than in other, more engineered, quantum systems [5–7]. The use of an optically driven mediator spin has been suggested as a way to control coupling between donor electron spins in silicon: the donor spins exhibit weak direct coupling, but mutually couple through the optically excited state of the mediator [8]. Such ideas could similarly be applied to couple nuclear spins, and, if the mediator spin is a photoexcited triplet with a spin-zero single ground state, it would have the added advantage that it avoids long-term impact on the nuclear spin coherence [9–11].

Photoexcited triplets are optically generated electron spins ($S = 1$) which often exhibit large (positive or negative) spin polarization, thanks to preferential population of each of the triplet sublevels following intersystem crossing and/or the differing decay rates of these sublevels to the ground singlet state [12,13]. Nuclear spins, in contrast, have weak thermal spin polarization at experimentally accessible conditions, due to its small magnetic moment. Highly polarized electron-spin triplets can be used to polarize surrounding nuclear spins, through continuous wave microwave illumination (under processes termed dynamic nuclear polarization) [14,15], or using microwave pulses [16]. Triplet states can also be used to mediate entanglement between mutually coupled nuclear spins [9], on time scales much faster than their intrinsic dipolar coupling [17].

Oxygen-vacancy (O-V) complexes can be formed in silicon by electron beam or γ-ray irradiation of oxygen-rich silicon crystals [18,19], and can be excited to the triplet state (termed an SL1 center) using illumination of above band gap light [20]. Magnetic resonance studies including electron paramagnetic resonance (EPR), electrically or optically detected magnetic resonance, spin dependent recombination, and electrically detected cross relaxation [20–25] have revealed that the SL1 has orthorhombic symmetry with nonequilibrium triplet electron-spin polarization and strong hyperfine coupling with the nearest-neighbor ^{29}Si nuclear spins. The triplet spin polarization of SL1 centers can be incoherently transferred to bulk ^{29}Si nuclear spins in the lattice by all-optical methods [26] or dynamic nuclear polarization [27,28]. Previous electron-spin echo studies on SL1 performed at zero magnetic field have revealed that the populating rates of the triplet sublevels are equal, and the spin polarization arises instead from a difference in the decay rates to the singlet ground state [29]. In this Letter we use the high spin polarization of the triplet system and its strong coupling with the nearest-neighbor ^{29}Si nuclear spins to demonstrate coherent state transfer between the electron and nuclear spin degrees of freedom, and examine the nuclear spin coherence in the presence of the triplet.

Czochralski-grown, single-crystal natural silicon (4.7% ^{29}Si, $I = 1/2$) was exposed to 1 MeV e-beam irradiation (dose $\approx 10^{18}$ cm^{-2}) at room temperature to form O-V complexes (an interstitial oxygen already present in the silicon traps a monovacancy generated due to the e-beam irradiation). Pulsed EPR measurements were carried out at X band (9.72 GHz) on a Bruker Elexsys580 spectrometer equipped with a helium-flow cryostat. Photoexcitation of the SL1 was achieved using a 1064 nm pulsed Nd:YAG laser (pulse width $\sim$7 ns, 1 mJ/pulse) with a 10 Hz repetition rate.

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Figure 1(a) illustrates the SL1 center in silicon under two representative orientations of the static magnetic field B_0. Under one orientation, termed $SL1^0$, the magnetic field lies in the plane, marked (110), comprising the oxygen atom and two vacancy-trapping silicon atoms (i and j lattice sites). An alternative orientation ($SL1^{90}$) has the magnetic field in an orthogonal plane ($1\bar{1}0$) with respect to the same center. Both planes are equivalent by symmetry for the crystal as a whole, so both orientations are visible in the EPR spectrum.

Figure 1(b) shows the triplet energy sublevels in the presence of a static magnetic field (T_+, T_0, and T_-), each of which decays with a characteristic rate to the ground singlet state [24,30]. The hyperfine coupling with one of the two nearest-neighbor ^{29}Si nuclear spins (occupying i or j lattice site) further splits the $T_\pm$ sublevels, while the T_0 state ($m_s = 0$) has no first-order hyperfine interaction, thus the nuclear spin splitting in this sublevel is close to the Zeeman energy of ^{29}Si. The EPR spectrum obtained by monitoring the electron-spin echo intensity as a function of magnetic field at 12 K with $B_0 \| \langle 110 \rangle$ is shown in Fig. 1(c), labeled with electronic transitions identified by previous cw EPR studies [20]. The satellite peaks accompanying each main peak are due to the hyperfine interaction with the ^{29}Si nuclear spins situated at i or j lattice sites. The phase difference of the spin echo (i.e., dips or peaks) is indicative of the nonequilibrium polarization within the electron-spin triplet.

To investigate the origin of this nonequilibrium polarization, we studied the decay kinetics of the triplet by measuring the electron-spin echo at a variable time T after the optical excitation ($h\nu$-T-$\pi/2$-τ-π-τ-echo), as shown in Fig. 2(a). The zero echo intensity at $T = 0$ indicates equal initial filling of the three triplet sublevels upon creation of the triplet. The echo intensity proceeds to grow as T is increased. This can be attributed to a difference in the

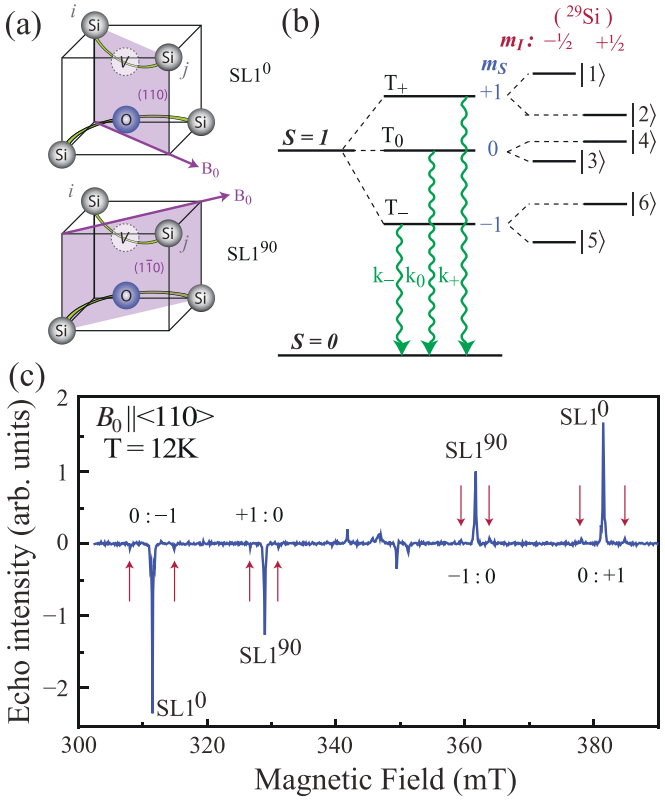

FIG. 1 (color online). (a) Structures of the oxygen-vacancy center in silicon, illustrating the $SL1^0$ and $SL1^{90}$ orientations with respect to the externally applied magnetic field B_0. (b) The SL1 triplet ($S = 1$) state is Zeeman split by B_0 into levels T_+, T_0, and T_-. These states decay with different rates (k_+, k_0, and k_-, respectively) to the ground singlet ($S = 0$) state. The hyperfine coupling to the ^{29}Si ($I = 1/2$) nuclear spin at lattice site i or j further splits the triplet states. (c) Electron-spin echo-detected EPR spectrum of the SL1 center at 12 K with $B_0 \| \langle 110 \rangle$. The satellite peaks (red arrows) arise from hyperfine coupling to ^{29}Si.

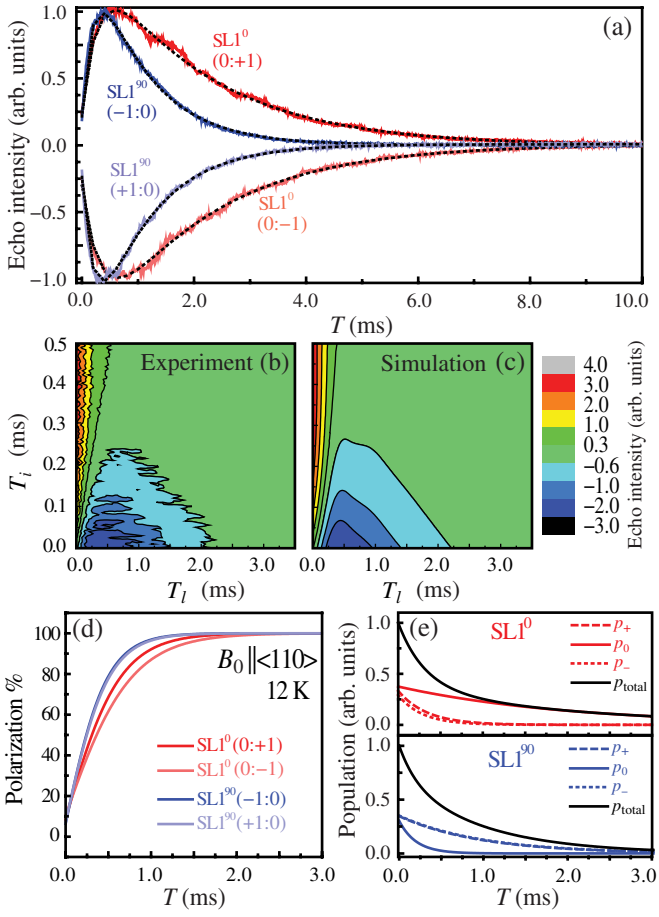

FIG. 2 (color online). (a) Decay traces obtained by the flash delay ($h\nu$-T-$\pi/2$-τ-π-τ-echo) pulse sequence, used to extract the triplet decay rates shown in Table I. (b) Experimental and (c) simulated 2D plots of the decay characteristics observed with the pulse sequence $h\nu$-T_l-π-T_i-$\pi/2$-τ-π-τ-echo. (d) The polarization buildup and (e) triplet population as a function of waiting time T after the laser pulse.

TABLE I. Lifetime of triplet sublevels, for two orientations of SL1 centers, obtained from fitting to the flash delay curve.

EPR transition	Lifetime
$0 \rightarrow +1$, $SL1^0$	$(1/k_0)^0 = 2000(4)\ \mu s$, $(1/k_{+1})^0 = 280(2)\ \mu s$
$0 \rightarrow -1$, $SL1^0$	$(1/k_0)^0 = 1970(4)\ \mu s$, $(1/k_{-1})^0 = 330(2)\ \mu s$
$-1 \rightarrow 0$, $SL1^{90}$	$(1/k_{-1})^{90} = 960(2)\ \mu s$, $(1/k_0)^{90} = 200(1)\ \mu s$
$+1 \rightarrow 0$, $SL1^{90}$	$(1/k_{+1})^{90} = 987(2)\ \mu s$, $(1/k_0)^{90} = 205(1)\ \mu s$
$k_x = 1.6(3)\ ms^{-1}$, $k_y = 4.93(6)\ ms^{-1}$, $k_z = 0.50(4)\ ms^{-1}$	

decay rates of the triplet sublevels to the ground state, creating a buildup in spin polarization (positive or negative) across the EPR transition being measured.

Based on the simple decay model shown in Fig. 1(b), the population difference between a given pair of sublevels follows a biexponential behavior where the two time constants represent the lifetimes of the two sublevels involved in the EPR transition. The time constants obtained from biexponential fitting to the flash delay curves are given in Table I—the assignment of rates to particular energy levels is enabled by electron nuclear double resonance experiments described further below. As the transition from the triplet to the ground singlet is determined by the amount of singlet admixture to the triplet via spin-orbit coupling, the lifetimes are expected to depend on the defect orientation with respect to the magnetic field. The composition of triplet levels $T_{+,0,-}$ can be expressed in terms of the zero-field eigenstates ($T_{x,y,z}$), and similarly the observed decay rates from these levels can be traced back to a corresponding mixture of zero-field decay rates ($k_{x,y,z}$), as shown in Table I. These values are in good agreement with times measured using zero-field EPR [29].

Our model assumes that there is negligible spin-lattice relaxation within the triplet sublevels, and this is consistent with the lack of temperature dependence we observe in the relaxation dynamics below 20 K. Nevertheless, in order to probe the dynamics in more detail, we can introduce an additional inversion π pulse to the sequence: ($h\nu$-T_l-π-T_i-$\pi/2$-τ-π-τ-echo). Figure 2(c) shows the 2D plot of the echo intensity for this sequence, as both T_l (the delay after the laser pulse) and T_i (the delay after the inversion pulse) are varied. The simulation of this experiment, based on the model described above, is in good agreement with the observed behavior, supporting our assumption that spin-lattice relaxation can be neglected.

Based on the observed decay rates, we can extract both the polarization buildup [Fig. 2(d)] and the triplet population [Fig. 2(e)] for the two SL1 orientations ($SL1^0$ and $SL1^{90}$) as a function of time T after the laser pulse. The maximum electron polarization reaches >99% after about 1.5 ms following the laser pulse. Below we investigate the coherent transfer of such well-prepared electron-spin states to a neighboring ^{29}Si nuclear spin.

For the following electron nuclear double resonance (ENDOR) experiments, we focus on four selected levels [labeled $|1\rangle$, $|2\rangle$, $|3\rangle$, and $|4\rangle$ in Fig. 1(b)] of $SL1^{90}$. We studied the hyperfine coupling strength between the ^{29}Si nuclear spin and triplet electron spin using the Davies ENDOR pulse sequence [Fig. 3(a)]. For $SL1^{90}$, T_0 decays more quickly than $T_\pm$ (see Table I), thus the states $|3\rangle$ and $|4\rangle$ are mostly unpopulated in ~700 μs. A selective microwave π pulse between $|1\rangle$ and $|3\rangle$ creates a polarization across the nuclear spin transitions, which can be driven using a radio frequency (ν_{rf}) pulse. The ENDOR signal is obtained by monitoring the electron-spin echo on the $|1\rangle \rightarrow |3\rangle$ transition as a function of ν_{rf}. Figure 3(a) shows the $|1\rangle \rightarrow |2\rangle$ transition frequency dominated by the strong hyperfine interaction. Thus, with resonant rf pulses we can selectively address ^{29}Si nuclear spins at specific lattice sites i and j. These nuclear spins can be coherently manipulated as illustrated by the Rabi oscillations in Fig. 3(b), in addition to being prepared and measured using the triplet electron spin.

Using a sequence based on Davies ENDOR, it is possible to coherently transfer a state of the electron spin to a coupled nuclear spin (pulse sequence is essentially the same as the one shown in Fig. 2a of Ref [4]). We apply this to transfer the highly polarized triplet electron-spin coherence to, and from, the nearest-neighbor ^{29}Si nuclear spin [see Fig. 4(a)]. The decay of the recovered spin coherence as a function of the storage time in the nuclear spin ($2\tau_n$) is shown in Fig. 4(b), with an exponential decay of time constant 0.9(1) ms. The measured decay is dominated by the relaxation of the T_+ sublevel back to the ground singlet state ($1/k_+ = 987\ \mu s$), rather than ^{29}Si

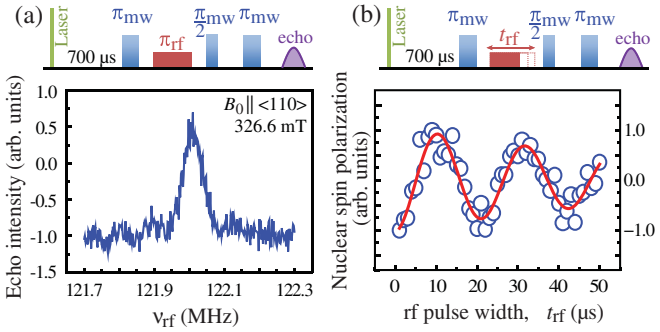

FIG. 3 (color online). (a) Davies ENDOR spectrum illustrating the hyperfine coupling between the triplet and nearest-neighbor ^{29}Si for the $SL1^{90}$ center. (b) Rabi oscillation of the ^{29}Si nuclear spin, driven between the states $|1\rangle$ and $|2\rangle$, detected by monitoring the electron-spin echo intensity.

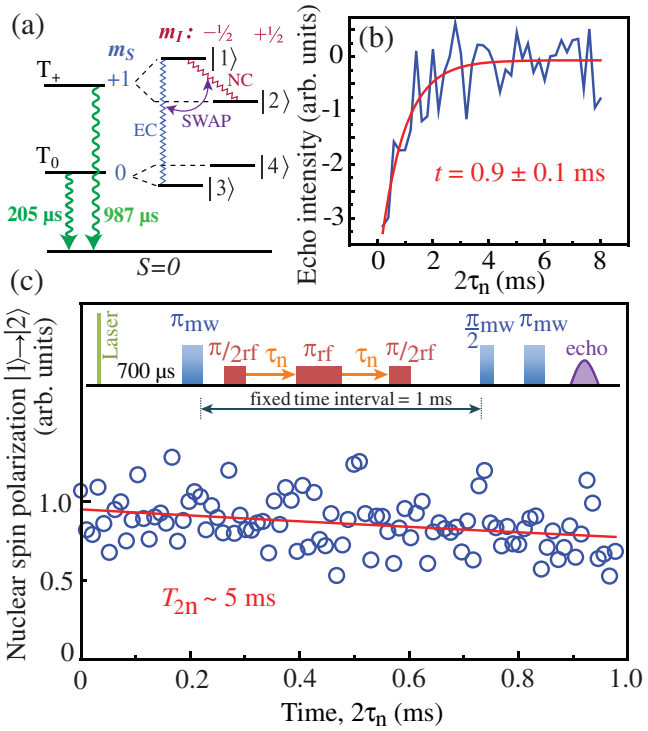

FIG. 4 (color online). (a) The electron-spin coherence (EC) of the triplet is transferred to, and from, a ^{29}Si nuclear coherence (NC). (b) The retrieved electron-spin echo intensity (blue line) decays as a function of the ^{29}Si nuclear storage time, $2\tau_n$. A fit to an exponential decay (red line) yields a time constant of 0.9(1) ms, apparently limited by the lifetime (0.99 ms) of the T_+ state. (c) By fixing the experimental time window to ~1 ms, the intrinsic coherence time of the nuclear spin can be measured. To confirm here that the measured electron spin echos arose solely from nuclear spin coherences, rf pulses were phase cycled.

nuclear decoherence. This confirms our assignment of the decay rates shown in Table I. By subtracting k_+ from the decay in Fig. 4(b) we can estimate T_2 of ^{29}Si to be several milliseconds, however, it is possible to make a more accurate measurement as described below.

Using the pulse sequence shown in Fig. 4(c), we shift the rf pulses within a fixed experimental window of 1 ms in order to remove the effect of the triplet relaxation and directly measure the ^{29}Si coherence time [31]. The sequence is based on Davies ENDOR described above, but with the single rf π pulse replaced with a nuclear Hahn echo sequence, whose delay time τ_n is swept. In the absence of nuclear spin decoherence, the applied rf pulses form a net 2π rotation. In contrast, when the nuclear spin is fully decohered, the nuclear spin polarization across the $|1\rangle \rightarrow |2\rangle$ transition falls to zero. Fitting the data to an exponential decay gives the nuclear coherence time of 5(1) ms, which should be interpreted as a lower bound. The bulk value for T_{2n} of ^{29}Si in natural silicon has been measured by NMR and found to be 5.6 ms, limited by ^{29}Si dipolar coupling [32]. The hyperfine coupling to the triplet can both suppress decoherence from ^{29}Si dipolar coupling as well as introduce additional decoherence mechanisms of its own, though the net result is a measured T_{2n} which is at least as long as the bulk value.

In conclusion, we utilized the coupling between nuclear spin and the photoexcited electron-spin triplet in silicon to demonstrate the coherent storage and retrieval of triplet electron-spin coherence in the ^{29}Si nuclear spin. In the future, given well-developed silicon isotope engineering [33,34] it will be possible to investigate more than one nuclear spin strongly coupled to the single electron spin in the photoexcited triplet state and explore optical control of the interaction between the nuclear spins.

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[1] T. D. Ladd, J. R. Goldman, F. Yamaguchi, Y. Yamamoto, E. Abe, and K. M. Itoh, Phys. Rev. Lett. **89**, 017901 (2002).
[2] K. M. Itoh, Solid State Commun. **133**, 747 (2005).
[3] T. D. Ladd, D. Maryenko, Y. Yamamoto, E. Abe, and K. M. Itoh, Phys. Rev. B **71**, 014401 (2005).
[4] J. J. L. Morton, A. M. Tyryshkin, R. M. Brown, S. Shankar, B. W. Lovett, A. Ardavan, T. Schenkel, E. E. Haller, J. W. Ager, and S. A. Lyon, Nature (London) **455**, 1085 (2008).
[5] J. R. Petta, A. C. Johnson, J. M. Taylor, E. A. Laird, A. Yacoby, M. D. Lukin, C. M. Marcus, M. P. Hanson, and A. C. Gossard, Science **309**, 2180 (2005).
[6] K. C. Nowack, M. Shafiei, M. Laforest, G. E. D. K. Prawiroatmodjo, L. R. Schreiber, C. Reichl, W. Wegscheider, and L. M. K. Vandersypen, Science **333**, 1269 (2011).
[7] T. Obata, M. Pioro-Ladriere, Y. Tokura, Y. Shin, T. Kubo, K. Yoshida, T. Taniyama, and S. Tarucha, Phys. Rev. B **81**, 085317 (2010).
[8] A. M. Stoneham, A. J. Fischer, and P. T. Greenland, J. Phys. Condens. Matter **15**, L447 (2003).
[9] M. Schaffry, V. Filidou, S. D. Karlen, E. M. Gauger, S. C. Benjamin, H. L. Anderson, A. Ardavan, G. A. D. Briggs, K. Maeda, K. B. Henbest, F. Giustino, J. J. L. Morton, and B. W. Lovett, Phys. Rev. Lett. **104**, 200501 (2010).
[10] E. M. Gauger, P. P. Rohde, A. M. Stoneham, and B. W. Lovett, New J. Phys. **10**, 073027 (2008).
[11] M. Schaffry, B. W. Lovett, and E. M. Gauger, Phys. Rev. A **84**, 032332 (2011).
[12] J. H. van der Waals, Appl. Magn. Reson. **20**, 545 (2001).
[13] M. Deimling, H. Brunner, K. P. Dinse, K. H. Hausser, and J. P. Colpa, J. Magn. Reson. **39**, 185 (1980).
[14] P. Bachert, H. Brunner, K. H. Hausser, and J. P. Colpa, Chem. Phys. **91**, 435 (1984).
[15] K. Takeda, K. Takegoshi, and T. Terao, J. Phys. Soc. Jpn. **73**, 2319 (2004).

[16] J. Schmidt, D. J. van den Heuvel, A. Henstra, T.-S. Lin, and W. Wenckebach, Pure Appl. Chem. **64**, 859 (1992).
[17] V. Filidou, S. Simmons, S. D. Karlen, H. L. Anderson, F. Giustino, and J. J. L. Morton (to be published).
[18] G. D. Watkins, J. W. Corbett, and R. M. Walker, J. Appl. Phys. **30**, 1198 (1959).
[19] J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).
[20] K. L. Brower, Phys. Rev. B **4**, 1968 (1971).
[21] B. Stich, S. Greulich-Weber, and J. M. Spaeth, J. Appl. Phys. **77**, 1546 (1995).
[22] W. Akhtar, H. Morishita, L. S. Vlasenko, D. S. Poloskin, and K. M. Itoh, Physica (Amsterdam) **404B**, 4583 (2009).
[23] F. P. Wang and B. Monemar, Phys. Rev. B **42**, 7576 (1990).
[24] L. S. Vlasenko, Yu. V. Martynov, T. Gregorkiewicz, and C. A. J. Ammerlaan, Phys. Rev. B **52**, 1144 (1995).
[25] W. Akhtar, H. Morishita, K. Sawano, Y. Shiraki, L. S. Vlasenko, and K. M. Itoh, Phys. Rev. B **84**, 045204 (2011).
[26] L. S. Vlasenko, Physica (Amsterdam) **116B+C**, 281 (1983).
[27] L. S. Vlasenko, M. P. Vlasenko, D. S. Poloskin, R. Laiho, H. Hayashi, T. Itahashi, A. Sagara, and K. M. Itoh, Phys. Status Solidi C **3**, 4376 (2006).
[28] T. Itahashi, H. Hayashi, K. M. Itoh, D. S. Poloskin, and L. S. Vlasenko, Physica (Amsterdam) **404B**, 5054 (2009).
[29] A. M. Frens, M. E. Braat, A. B. van Oosten, and J. Schmidt, Mater. Sci. Forum **117–118**, 195 (1993). They have further shown that in the presence of magnetic field ($\sim$300 mT) at very low temperature (1.2 K), the population rates of the three triplet levels can be different due to formation of radical pairs.
[30] L. S. Vlasenko, I. M. Zaritskii, A. A. Konchits, and B. D. Shanina, Sov. Phys. Solid State **26**, 66 (1984).
[31] P. Hofer, A. Grupp, and M. Mehring, Phys. Rev. A **33**, 3519 (1986).
[32] A. E. Dementyev, D. Li, K. MacLean, and S. E. Barrett, Phys. Rev. B **68**, 153302 (2003).
[33] K. Takyu, K. M. Itoh, K. Oka, N. Saito, and V. I. Ozhogin, Jpn. J. Appl. Phys., Part 2 **38**, L1493 (1999).
[34] K. M. Itoh, J. Kato, M. Uemura, A. K. Kaliteevskii, O. N. Godisov, G. G. Devyatych, A. D. Bulanov, A. V. Gusev, I. D. Kovalev, P. G. Sennikov, H.-J. Pohl, N. V. Abrosimov, and H. Riemann, Jpn. J. Appl. Phys. **42**, 6248 (2003).