Optical and microwave control of germanium-vacancy center spins in diamond

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A solid-state system combining a stable spin degree of freedom with an efficient optical interface is highly desirable as an element for integrated quantum optical and quantum information systems. We demonstrate a bright color center in diamond with excellent optical properties and controllable electronic spin states. Specifically, we carry out detailed optical spectroscopy of a Germanium Vacancy (GeV) color center demonstrating optical spectral stability. Using an external magnetic field to lift the electronic spin degeneracy, we explore the spin degree of freedom as a controllable qubit. Spin polarization is achieved using optical pumping, and a spin relaxation time in excess of 20 µs is demonstrated. Optically detected magnetic resonance (ODMR) is observed in the presence of a resonant microwave field. ODMR is used as a probe to measure the Autler-Townes effect in a microwave-optical double resonance experiment. Superposition spin states were prepared using coherent population trapping, and a pure dephasing time of about 19 ns was observed. Prospects for realizing coherent quantum registers based on optically controlled GeV centers are discussed.

Over the last few decades significant effort has been directed towards the exploration of solid-state atom-like systems such as quantum dots or color centers in diamond owing to their potential application in quantum information processing [1–4]. The nitrogen vacancy (NV) center in diamond has become prominent due to its optical spin initialization and readout [5], and the ease of spin control by microwave fields [6]. However the small Debye-Waller factor of this defect [7] and its spectral instability [8] hinder the realization of an efficient quantum-optical interface [9], motivating an ongoing search for new candidates. Here we investigate the recently discovered germanium vacancy (GeV) center in diamond [9,10], demonstrating its outstanding spectral properties devoid of measurable spectral diffusion. We show spin–½ Zeeman splitting which confirms this is the negative charge state of this defect. We use two-photon resonance to optically prepare coherent dark spin superposition states, and show microwave spin manipulation via optically-detected magnetic resonance (ODMR). The spin coherence time is found to be $T_2^* = 19 \pm 1$ ns, which is concluded to be limited by phonon-mediated orbital relaxation as in the closely-related silicon-vacancy (SiV) center [12,13]. Optical and microwave control of GeV spin, combined with the possibility of GeV centers in nanophotonic devices [14], make it a promising platform for quantum optics and quantum information science applications.

The GeV center can be produced in diamond during crystal growth and by ion implantation, and it fluoresces strongly with a zero-phonon line at 602 nm accompanied by a weak phonon sideband (PSB) containing about 40% of the fluorescence [9,10]. Isotopic shifts of the fluorescence spectrum established that the defect contains a single germanium atom [11,15], and ab initio calculations suggest that it is formed by the Ge atom taking the place of two carbon atoms and relaxing its position to split off the adjacent vacancy [9,10]. The resulting geometry is aligned along a (111) axis and has inversion-symmetric $D_{4h}$ symmetry as illustrated in Figure 1(a). This structure is identical to the SiV center in diamond [17,18] and leads to $^2E_g$ and $^2E_u$ ground and excited states (respectively). These have 2-fold degeneracy in both spin and orbit, which is partially lifted by spin-orbit interaction to produce levels labelled 1, 2 (ground) and 3, 4 (excited) in order of increasing energy. Transitions between these lead to a four-line fine structure of the zero-phonon-line (ZPL) as shown in Figure 1(a) [10]. At low temperatures the large spin-orbit splitting of the excited state results in thermal depopulation of level 4, apparent in the weaker 1-4 and 2-4 peaks relative to peaks 1-3 and 2-3 in the photoluminescence spectrum.

The experiments were performed on two identical samples polished in the {100} and {111} planes. These diamonds were grown by high pressure high temperature synthesis in a Mg-Ge-C system, and the GeV centers were incorporated during this process [10,15]. Solid immersion lenses were fabricated on the diamonds by fo-
FIG. 1. Stable narrow optical transitions. (a) PL spectrum of GeV at 18 K and 35 K, demonstrating the four-line ZPL structure with thermalization of the high-energy transitions. (Inset) Molecular structure of the GeV center in diamond showing a Ge atom taking the place of two adjacent carbon atoms. (b) SEM image of a solid immersion lens fabricated on the sample surface. (c) Fluorescence image of a single GeV center located off-center under the SIL, recorded with a long-pass filter (sideband only) and without any filter on the detector. (d) In the low-intensity limit, linewidths as narrow as 42 MHz were recorded. The GeV transitions were stable in frequency for measurements of several hours. (e) Saturation curve for a single GeV center recorded under resonant excitation (only photons from phonon side band are recorded). The inset shows a single-sweep PLE spectrum recorded without long pass filter (entire emission band is recorded), yielding up to 0.6 Mc/s at saturation intensity.

cused ion beam milling (Figure 1(b)) to increase fluorescence collection efficiency [19, 21]. Individual GeV defects were excited resonantly by a tunable dye laser and addressed in a confocal microscope at cryogenic temperature ($T \approx 2.2$ K) as shown in Figure 1(c). An optical long pass filter with cut-on edge at 610 nm was placed in the detection channel to reject scattered laser light, meaning that only photons associated with the phonon sideband were detected. Measurements were controlled and coordinated using the Qudi software suite [22].

A resonant laser was scanned across the transition between the lower branches of ground and excited state (transition 1-3) and a linewidth of 42 MHz was measured as shown in Figure 1(d). This is less than double the 26 MHz transform-limit imposed by the excited state lifetime of 6 ns [14], indicating the stability of the transition over the measurement duration of 40 s. Subsequent measurements at intervals over 4 hours demonstrated the line to be stable at longer time scales (Figure 1(e)).

The linewidth and stability were probed at lower laser excitation intensities to avoid power broadening. Figure 1(f) presents a saturation measurement on the optical transition, yielding more than 200 kc/s detected in the sideband. The off-center position of this GeV center in the SIL meant that laser scatter was collected only weakly, allowing a signal-to-noise ratio of 5:1 even after removing the filter from the detection path (Figure 1(c)). Photoluminescence excitation (PLE) spectra are typically measured on a carefully filtered sideband to eliminate the dominant laser scatter. The high contrast observed here without any filter is evidence of a strong optical transition. Collecting the whole fluorescence band in this manner yielded up to 0.6 Mc/s as shown inset to Figure 1(f). These data exhibit a blinking phenomenon that was observed to intensify for higher excitation intensities. Blinking has also been observed for SiV centers in certain diamond samples [23, 24] but not others [15]. It is therefore anticipated that blinking is not intrinsic to the GeV center itself and can be controlled using superior sample preparation techniques.

The {100} sample was mounted over neodymium magnets producing a field of about 0.3 T aligned roughly in the plane of the diamond surface as illustrated in Figure 2(a). Figure 2(b, c) show the Zeeman-split PLE spectra for transitions 1-3 and 2-3 of an individual GeV center aligned almost perpendicular to the field. For this center the ground state splitting between levels 1 and 2 was found to be about 170 GHz, indicating the presence of transverse strain inducing an additional splitting of about 20 GHz [14]. The measurement temperature of 2.2 K was cold enough to reduce the thermal population in level 2 compared to level 1, and so the absolute intensity is less for transition 2-3 than for 1-3. Transitions to state 4 are of less interest because of rapid thermalization into state 3 [13], and were not measured here in PLE. The four-fold Zeeman splitting patterns suggest electronic spin-1/2 splitting of each of the states, as illustrated in Figure 2(d). This is consistent with the 602 nm emission line attributed to the GeV center.
FIG. 2. Optical lambda-schemes. (a) The diamond sample was mounted over neodymium magnets, giving a field in the plane of the \{100\} surface. (b) PLE spectrum shows transition 2-3 split into four peaks, with the outer two being strongest. (c) PLE spectrum shows transition 1-3 split into four peaks, with the inner two being strongest. (d) The magnetic field lifts the spin degeneracy and produces doublets from each of the ground and excited state branches (A and B subscripts describe two spin states). (e) CPT was performed on the 1A-3A-1B \Lambda\text{-scheme}, demonstrating coherent optical spin manipulation. Inset depicts the narrowest dip, which was found to be 8.6 ± 0.5 MHz wide corresponding to a coherence lifetime of 19 ± 1 ns.

FIG. 3. Microwave manipulation of GeV spin. (a) Excitation of the spin-conserving transition 1A-3A polarizes the spin due to optical pumping into 1A. The time-resolved fluorescence for an excitation pulse shows spin polarization of 59% (limited by laser intensity). (b) Microwaves resonant to 1A-1B return population to 1A and restore the higher fluorescence, enabling optically detected magnetic resonance (ODMR). The width of the ODMR peak is 9 MHz corresponding to a dephasing time of about 19 ns. The ODMR contrast of about 35% is limited by the 59% contrast possible from spin polarization. (c) Autler-Townes effect is observed upon laser power increase. The splitting of the ODMR signal scales linearly with the square root of laser intensity.

The presence of all four lines in the Zeeman-split spectrum of transition 1-3 indicates that lambda-schemes are accessible optically. These provide an opportunity to investigate coherence properties through optically-prepared superpositions of the ground states [25]. We make use of coherent population trapping (CPT), in which a dark superposition state is produced when driving optical fields are resonant to both transitions of the \Lambda\text{-scheme}. The state is dark due to quantum interference, resulting in a dip in the excitation spectrum with a width limited by the lifetime of the superposition. Both excitation frequencies for CPT were generated from a single laser using a high-bandwidth electro-optic amplitude modulator with the carrier on transition 1B-3A as pump, and a sideband tuned across transition 1A-3A as probe. The CPT linewidths in Figure 3(b) are therefore insensitive to laser frequency noise, and the narrowest dip-width observed was 8.6 ± 0.5 MHz corresponding to a coherence time of 19 ± 1 ns.

The optical \Lambda\text{-schemes} identified in the GeV electronic structure also provide a mechanism for polarizing the spin. Resonantly exciting the spin-conserving transition 1A-3A led to optical pumping into the spin-B levels of the ground state as illustrated in Figure 3(a). Time-resolved fluorescence measurements indicate an optical pumping contrast of 59%, which is the spin polarization...
(normalised population difference \( P_B - P_A / P_{\text{total}} \)) [29]. This spin polarization is a function of the optical pumping rate compared to the spin relaxation rate, and can be increased with higher laser powers. Since it is necessary to spectrally resolve the Zeeman-split transitions, excitation intensity (and hence spin polarization) is limited by the need to avoid power broadening beyond the Zeeman splitting.

A 25 µm wire placed across the sample surface was used to apply microwaves at a frequency of 1530 MHz corresponding to the \( 1_A-1_B \) transition, and a sharp increase in the steady-state fluorescence was observed (Figure 3(b)). This optically-detected magnetic resonance (ODMR) is a result of the microwaves returning population to the \( 1_A \) level, and provides a simple direct way to manipulate the spin state. Avoiding power broadening on the microwave and optical transitions produced an ODMR linewidth of 9.0 ± 0.5 MHz (Figure 3(b)), corresponding to a dephasing time of 19 ± 1 ns. The ODMR contrast of about 35% is limited by the spin polarization. ODMR occurred at a microwave frequency exactly matching the two-photon detuning for laser fields producing CPT (Figure 2(e)), proving that the ODMR response is due to microwave manipulation of the ground state levels \( 1_A \) and \( 1_B \). The ODMR linewidth and CPT dip width were also identical within the accuracy of the measurement, presenting a consistent picture regarding the coherence time of the Zeeman split levels.

Increasing the resonant excitation intensity on the optical transition \( 1_A-3_A \) led to a broadening and then splitting of the ODMR peak as shown in Figure 3(c). The splitting increased proportionally to the square root of laser intensity, confirming that it arises due to the optical Rabi frequency. For optical Rabi oscillations faster than the excited state lifetime dressed states are resolvable, and the weak microwave field acts as a probe to measure this splitting. This observation of the Autler-Townes effect indicates that coherent Rabi oscillations are achieved on the optical transition for excitation intensities above saturation. It provides further evidence of the stable narrow optical transition for GeV.

Spin relaxation was measured by varying the dark intervals between the \( 1_A-3_A \) excitation pulses of Figure 3(a), yielding \( T_1 = 0.3 \mu s \) as shown in Figure 4(a). Other field alignments were achieved by placing the sample flat on a pole of a disk magnet, producing a field normal to the sample surface. For the \{111\} sample a number of GeV centers were measured to have \( T_1 = 3.3 ± 0.3 \mu s \). The \{100\} sample gives a GeV misalignment of only \( 54° \), and the spin relaxation time was measured to be \( T_1 = 25 ± 5 \mu s \). These results are shown in Figure 4. For SiV centres it was observed that spin \( T_1 \) extends for better aligned fields [12], and the same phenomenon is exhibited here. It is concluded that the GeV centers measured in the \{111\} sample had a misalignment of \( 70° \), and that the arbitrary field used for the ODMR and CPT measurements was misaligned by more than \( 80° \). Improved field alignment increases the spin relaxation time, but it also means the optical transition selection rules become more exclusive to the spin-conserving transitions. It was therefore easier to achieve spin polarization for a misaligned field as shown by the equilibrium \( 1_A \) population (\( \tau \rightarrow 0 \)) in Figure 4 and this effect prevented a measurement of \( T_1 \) for the aligned GeV centres in the \{111\} sample.

The CPT and ODMR measurements indicate that levels \( 1_A \) and \( 1_B \) have a coherence time of about 19 ns, which is considerably shorter than the spin \( T_1 \). The situation is most readily interpreted by analogy with the closely-related negatively-charged SiV center. For SiV it was found that resonant phonons mediated orbital relaxation on a fast timescale of about 40 ns at 5 K, and this limited the spin coherence time [12, 13, 27]. It seems that the same process occurs in the GeV center, however for similar phonon coupling parameters the orbital relaxation rate will be even faster as a result of the increased spin-orbit splitting in the ground state. These energies are within the Debyeapproximate regime for diamond, and so the phonon density of states increases with energy. This is offset by the more extreme thermal reduction in the transition rate out of level 1, but the measurements presented here suggest that the orbital \( T_1 \) lifetime is only about 20 ns at 2 K even for level 1. Although the spin \( T_1 \) increases with reduced transverse field, these phonon-mediated orbital transitions similarly limit the spin coherence time independent of the field alignment. This picture is consistent with the temperature dependence of the transition linewidth and optical Rabi oscillation decay rate [13].

We have established that the GeV centre in diamond combines stable and bright optical transitions with an electronic spin-\( \frac{5}{2} \) degree of freedom. Even for a single centre this spin is accessible optically and by microwave fields, placing the GeV centre in a small class of color centres capable of ODMR. ODMR is a powerful technique for accessing and manipulating solid-state spins [1]. Broad interest in the NV center is based in part on its ODMR
The similarity of SiV and GeV physics indicates there is an entire family of quantum emitters in diamond with favorable optical properties. We have shown that, like in the case of the SiV, GeV spin coherence is limited by phonon dynamics that depend on temperature. Ongoing efforts to break this barrier for SiV by microstructures, sub-500 mK temperature, and strain tuning, should also be beneficial for the GeV electron spin. Combined with efficient optical access to the GeV electron spin reported here, such developments could enable large-scale quantum networks using GeV centers as quantum memory nodes. The demonstrated optical properties of the GeV center make this system worth pursuing as a spin-photon interface.

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