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Spin relaxation and donor-acceptor recombination of Se^+ in 28-silicon

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Selenium impurities in silicon are deep double donors and their optical and electronic properties have been recently investigated due to their application for infrared detection. However, a singly-ionised selenium donor (Se^+) possesses an electron spin which makes it a potential candidate as a silicon-based spin qubit, with significant potential advantages compared to the more commonly studied group V donors. Here we study the electron spin relaxation (T_1) and coherence (T_2) times of Se^+ in isotopically purified 28-silicon, and find them to be up to two orders of magnitude longer than shallow group V donors at temperatures above ~ 15 K. We further study the dynamics of donor-acceptor recombination between selenium and boron, demonstrating that it is possible to control the donor charge state through optical excitation of neutral Se^0 .

I. INTRODUCTION

The electron and nuclear spins of Group V donors in silicon, such as phosphorus, have been actively studied as potential quantum bits^{1,2}. Recent advances in this field include the manipulation and read-out of individual electron and nuclear spins by integrating donors into nano-electronic devices³⁻⁵, and the demonstration that donor spin coherence times can be as long as 3 seconds for the electron spin⁶ and up to 3 hours for the nuclear spin⁷. In contrast to such work on shallow donors in silicon as qubits, there has been relatively little experimental attention on the chalcogens, which are deep double donors in silicon. Nevertheless, they possess several attributes of potential relevance to donor-based spin qubits — we focus here on selenium as an example.

First, neutral selenium (Se^0) possesses two bound electrons which form a singlet ground state, and has a binding energy of 307 meV⁸. This makes it ideal for spin readout methods using spin-to-charge conversion that require that the two-electron state on the donor is well bound⁹⁻¹¹. In phosphorus, for example, the two-electron state (P^-) has a very weak binding energy of only 2 meV. Second, the singly-ionised state, Se^+ , is isoelectronic with the neutral Group V donors and possesses a bound $S = 1/2$ electron spin. Compared to shallow donors, Se^+ has a much larger thermal ionisation energy (593 meV)¹² such that it can retain a bound electron even at room temperature. Third, the large energy separation between the donor ground state, $1s(A_1)$, and first excited valley state, $1s(T_2)$ is of order 429 meV (more than an order of magnitude greater than for the shallow Group V donors) and could be expected to result in a significantly longer electron spin relaxation time.

Here we present a study of the electron spin proper-

ties of Se^+ in isotopically purified 28-silicon, including timescales for electron spin relaxation (T_1) and decoherence (T_2), and their mechanisms. Isotopically purified ^{28}Si was used to suppress decoherence due to interactions with the nuclear spin of the ^{29}Si isotope (which has 5% natural abundance), as has been previously demonstrated¹³. We find that the electron spin relaxation times are as much as two orders of magnitude longer than phosphorus, for a given temperature, and that electron spin decoherence times can be reasonably expected to be as long as those measured for phosphorus (up to seconds¹³). We go on to investigate donor-acceptor (DA) recombination following above band gap illumination (1047 nm), by monitoring the electron spin echo intensity, using the same method previously applied to phosphorus donors¹⁴. This demonstrates an optical mechanism for placing the donors in the neutral Se^0 state, thus removing the hyperfine interaction between the electron and the nucleus. We find DA recombination is slow (minutes to hours) given the concentrations of selenium ($\sim 5 \times 10^{15} \text{ cm}^{-3}$) and boron ($\sim 5 \times 10^{13} \text{ cm}^{-3}$) used here¹⁴ and the rate at which charge equilibrium is re-established can be enhanced by selectively ionising the Se^0 via optical illumination at 4 μm .

II. MATERIALS AND METHODS

The $^{28}\text{Si}:\text{Se}$ samples used here have been previously measured by IR absorption spectroscopy¹⁵, and consist of ^{28}Si doped with selenium, and partially compensated with boron in order to produce a significant concentration of Se^+ , as described by Ludwig¹⁶. The starting silicon material had a composition of 99.991% ^{28}Si , with 75 ppm ^{29}Si and 15 ppm ^{30}Si , and a residual boron concentration

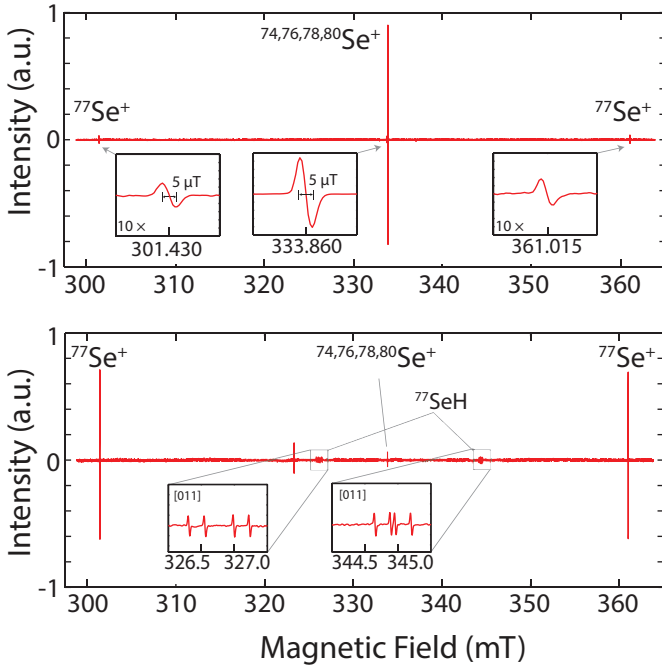


FIG. 1: X-band cw-ESR of Se^+ in ^{28}Si at X-band for $^{28}\text{Si}:\text{natSe}$ (upper) and $^{28}\text{Si}:^{77}\text{Se}$ (lower). The natural abundance of ^{77}Se is 7.5%, with the remaining isotopes (92.5% abundance) possessing zero nuclear spin. The ^{77}Se -doped sample shows predominantly the hyperfine-split lines arising from coupling to the $I = 1/2$ nuclear spin of ^{77}Se , while addition features in the spectrum correspond to residual isotopes of Se and the presence of SeH pairs. Microwave frequency = 9.38 GHz; temperature = 23 K.

$[\text{B}] \sim 5 \times 10^{13} \text{ cm}^{-3}$. This was then doped with selenium by thermal diffusion⁸. We studied two samples, one with natural abundance selenium, and the other made using ^{77}Se with an isotopic enrichment of 97.1 %. The concentration of selenium impurities of $\sim 5 \times 10^{15} \text{ cm}^{-3}$ was determined by measuring the free carrier at room temperature using the Hall effect, combined with simulations based on the Fermi-Dirac statistics for double donors¹⁷. ESR measurements were carried out using a Bruker Elexsys 580 spectrometer at X-band (9.7 GHz).

III. CONTINUOUS WAVE ESR

The ESR properties of Se^+ in silicon have been previously investigated by Grimmeiss *et al.*^{8,18}. The electronic g -factor is $g = 2.0057$. All stable Se isotopes $^X\text{Se}^+$ ($X=74, 76, 78, 80$) have zero nuclear spin, apart from ^{77}Se which has $I = 1/2$ and an isotropic hyperfine coupling of $A = 1.6604 \text{ GHz}$ with the donor electron spin. The electron and nuclear spin properties of Se^+ are described by the spin Hamiltonian (in frequency units):

$$\mathcal{H}_0 = \omega_e S_z - \omega_n I_z + A \mathbf{S} \cdot \mathbf{I} \quad (1)$$

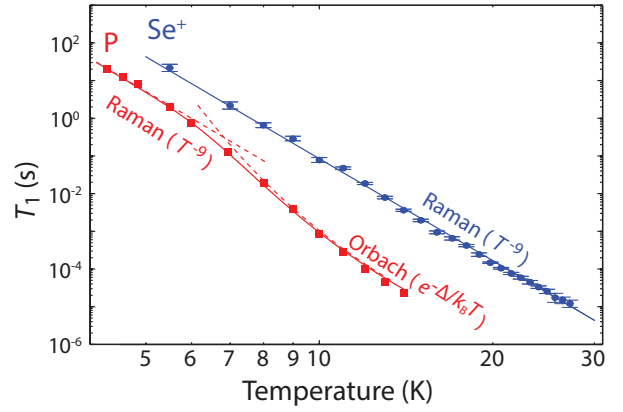


FIG. 2: Temperature dependence of electron spin relaxation T_1 in $^{28}\text{Si}:^{77}\text{Se}^+$ and Si:P at $B \sim 0.34 \text{ T}$. Solid lines are fits to the experimental data, made up of contributions (dashed lines) from different relaxation mechanisms. Data for Si:P is from Ref²⁰.

where $\omega_e = g\beta B_0/\hbar$ and $\omega_n = g_n\beta_n B_0/\hbar$ are the electron and nuclear Zeeman frequencies and B_0 is the static magnetic field applied along the z axis. Neutral Se^0 has a spin singlet ground state and thus gives no contribution to the ESR signal. Figure 1 shows continuous wave ESR spectra for $^{28}\text{Si}:\text{natSe}$ and $^{28}\text{Si}:^{77}\text{Se}$. The values we obtain for A and g confirm previously reported results¹⁸, though the transitions have a much smaller linewidth ($< 5 \mu\text{T}$) due to silicon isotopic purification. The relative intensity of the central line (around $g = 2$, corresponding to Se isotopes with zero nuclear spin) and hyperfine-split lines (corresponding to ^{77}Se) in each sample is consistent with their expected isotopic composition. The remaining features in the $^{77}\text{Se}^+$ ESR spectrum have been characterised by angular dependent cw-ESR and ENDOR and confirmed to be due to SeH pairs, previously measured in natural Si and referred as Si-NL60¹⁹. The presence of the hydrogen in this defect centre reduces the ^{77}Se hyperfine coupling by a factor of ~ 3 and gives it a slight anisotropy.

IV. ELECTRON SPIN RELAXATION

We studied the electron spin relaxation time (T_1) of Se^+ by pulsed ESR, using an inversion-recovery sequence ($\pi - T - \pi/2 - \tau - \pi - \tau$ -echo, where T is varied). The results, shown in Figure 2, show that $(1/T_1)$ is well fit by $1/T_1 = CT^9$ with $C = 1.2 \times 10^{-8} \text{ s}^{-1}\text{K}^9$, in the temperature range of 5 – 35 K, and is independent of the projection of selenium nuclear spin ($m_I = 0, \pm 1/2$). A comparison with P donors in silicon shows that T_1 is between one to two orders of magnitude longer for Se^+ in this temperature range.

The temperature dependence of the electron spin T_1 has been well studied for shallow donors²⁰, with differ-

Donor	Raman temperature range (K)	C (s^{-1}K^9) CT^9	Δ (meV)	Reference
P	2.6 - 6	10×10^{-8}	10.5	20
As	5 - 11	2×10^{-8}	19.7	20
Bi	5 - 26	6.6×10^{-8}	33.8	23
Se ⁺	5 - 35	1.2×10^{-8}	429	this work

TABLE I: Comparison of the strengths of the T^9 Raman electron spin relaxation process for various shallow donors and Se⁺ in silicon, including the temperature range at which this mechanism dominates T_1 at X-band. Only a weak dependence is observed between the strength of the process, C , and the energy separation (Δ) between the ground $1s(A_1)$ and first excited state ($1s(T_2)$) of the donor.

ent mechanisms dominating in different regimes of temperature and magnetic field. The Orbach two-phonon relaxation process^{21,22} depends exponentially on the energy gap, $\Delta = 1s(T_2) - 1s(A_1)$, between the ground state and first excited state of the donor: $T_1 \propto \exp(\Delta/k_B T)$. Therefore, though the Orbach process is the dominant T_1 mechanism for phosphorus donors at X-band and at temperatures above ~ 8 K, the large value of $\Delta = 429$ meV for Se⁺ makes the Orbach process irrelevant here. A T^9 Raman process dominates the phosphorus donor electron spin relaxation in the range 2 – 6 K at X-band²², arising from two-phonon scattering via a continuum of excited states. It has been observed in the shallow donors (see Table I) that this process has only a weak dependence on Δ , which dictates the spin mixing through a spin-orbit coupling. Our results on Se⁺ are consistent with this observation — despite the much larger value of Δ , the strength of the T^9 Raman process is only marginally weaker than for the shallow donors. Nevertheless, the electron spin T_1 for Se⁺ in silicon remains longer than any of the shallow donors across the full temperature range studied here, suggesting that it may also offer the longest spin coherence times.

Electron spin coherence times (T_2) of $^{77}\text{Se}^+$ were measured using a Hahn echo sequence ($\pi/2 - \tau - \pi - \tau - \text{echo}$) and are shown in Figure 3. We find that T_2 is limited by spin relaxation (T_1) for temperatures above ~ 12 K. Below this temperature, T_2 in these samples is limited by dipole coupling between Se⁺ electron spins which are not refocussed by the Hahn echo sequence (a mechanism termed instantaneous diffusion (ID)^{13,23}). This effect can be mitigated by reducing the angle of the θ_2 pulse in the Hahn sequence ($\pi/2 - \tau - \theta_2 - \tau - \text{echo}$)^{13,24}, providing both a measure of the concentration of Se⁺ electron spins, as well as a value of T_2 in the absence of ID. The concentration of Se⁺ we obtain is $4 \times 10^{13} \text{ cm}^{-3}$, in good agreement with level of boron in this sample (noting that boron is required to ionise the selenium). The extended value of T_2 in the absence of ID, can be well described by a combination of spectral diffusion arising from T_1 -induced spin flips of neighbouring Se⁺

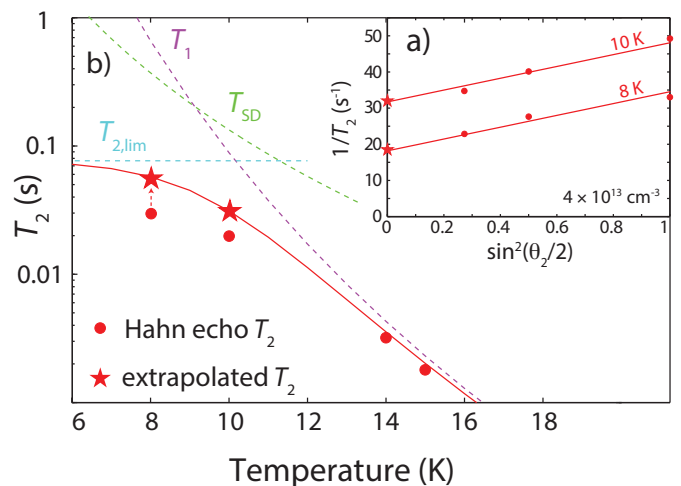


FIG. 3: Measured and extrapolated T_2 in $^{28}\text{Si}:^{77}\text{Se}^+$ at $B \sim 0.34$ T. a) $1/T_2$ as function of the refocusing pulse rotation angle θ_2 . The intercept of the linear fit gives the extrapolated T_2 corresponding to the suppression of the instantaneous diffusion (ID), while the slope gives a Se⁺ concentration of $4 \times 10^{13} \text{ cm}^{-3}$. b) The value of T_2 is limited by T_1 above ~ 12 K. Below this temperature, the extrapolated value of T_2 (in the absence of ID) can be well described by a combination of spectral diffusion arising from T_1 -induced spin flips of neighbouring Se⁺ spins, combined with a temperature-independent mechanism that limits T_2 to about 80 ms. The details of the fit of T_2 and its temperature dependence are described in the Supplementary Material.

spins, combined with a temperature-independent mechanism that limits T_2 to about 80 ms. At the spin concentration used here, indirect flip-flop of neighbour electron spins is expected to limit T_2 to about $\sim 1 \text{ s}^{13}$. We therefore postulate the temperature independent-mechanism observed arises from charge tunnelling in the sample, due to the high impurity concentration and compensation in the material, which alters the Se ionisation state. Therefore, for lower donor concentrations and using alternative means of ionising the Se, we anticipate the coherence times will be at least as long as those obtained for P (and indeed, longer, for the same temperature, given the longer T_1 of Se⁺). The red solid line in Figure 3 gives the temperature dependence of the extended value of T_2 (in the absence of ID). The model is obtained by taking into account the combined effects of the three mechanisms described above: i) spin relaxation of the central spin, yielding an echo decay of the form $\exp[-(2\tau/T_1)]$; ii) a temperature-independent process of the form $\exp[-(2\tau/T_{2,\text{lim}})]$ with $T_{2,\text{lim}} = 80$ ms; and iii) a spectral diffusion process caused by spin relaxation of nearest neighbours, of the form $\exp[-(2\tau/T_{SD})^2]$ with $T_{SD}^2 = K T_1/[Se^+]$ and $K = 7.6 \times 10^{12} \text{ s/cm}^{317}$.

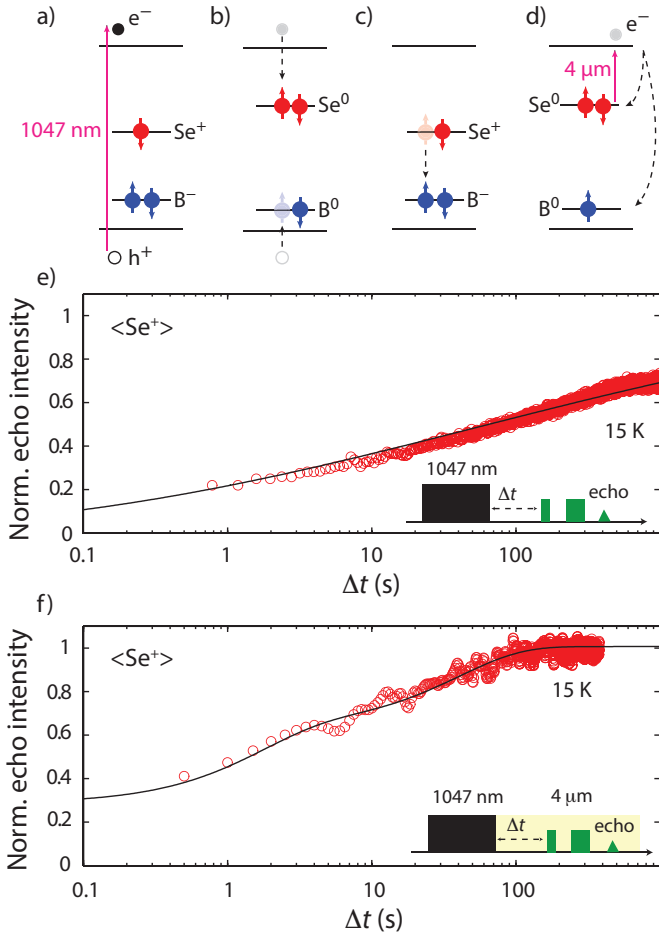


FIG. 4: Schematic representation of the recombination mechanisms in selenium doped silicon after above band gap illumination: (a) At the thermal equilibrium one of the electron from a selenium impurity moves to the acceptor B forming the DA pair (Se^+B^-). Under 1047 nm illumination electron-hole pairs are formed. (b) The excess of conduction carriers recombines through the impurities levels forming a non-equilibrium state. (c) The process of DA recombination re-establish the thermal equilibrium. (d) Under 4 μm illumination an electron from Se^0 is continuously pumped into the conduction band enhancing the rate at which the thermal equilibrium is re-established. The normalised concentration of selenium in the Se^+ state ($\langle\text{Se}^+\rangle$) is monitored by plotting the normalised electron spin echo intensity, as a function of wait time, after a pulse of above band gap illumination, (e) in the dark, or (f) in the presence of 4 μm illumination. Red circles show normalised electron spin echo intensity and black lines are fits (see main text).

V. DONOR-ACCEPTOR RECOMBINATION DYNAMICS

Pulsed ESR studies of donors at low temperatures often employ optical excitation to generate free carriers, as a way to ‘reset’ the electron spin to its thermal equilibrium state, allowing experiments to be repeated on

timescales much faster than the intrinsic T_1 . However, for a compensated Se-doped sample, the free electron-hole pairs generated by the optical excitation are readily captured by the Se^+ and B^- , and the ESR signal will only be recovered after charge equilibrium is reached through DA recombination.

To study the dynamics of DA pairs, we measure the Se^+ electron spin echo as it recovers back to thermal equilibrium following above band-gap illumination (1047 nm). This method has been previously used to study DA recombination of highly compensated phosphorus-doped silicon¹⁴ showing that the recombination time can be as long as $\sim 10^3$ s. Figure 4 gives a schematic representation of the DA recombination process after above band gap illumination. In this case, the system is brought out of equilibrium by the creation of free carriers via illumination (a). Due to the fast capture of such free carriers into the impurities levels, a non-equilibrium state is created after illumination (b). Thermal equilibrium is then re-established by DA recombination (c).

We first measured the photoconductivity directly following illumination to obtain a photo-induced carrier lifetime of 40 ms at 15 K (process (b) in Figure 4). DA recombination, a much slower process, was then measured by observing the electron spin echo intensity following the laser pulse, as shown in Figure 4(e). A pulse of 100 mW for about 1 s was sufficient to ensure almost all the selenium and boron impurities were in the neutral state (i.e. zero initial spin echo signal)³². After ~ 1000 seconds following the laser pulse, 60-70% of the echo intensity had recovered indicating that the majority of selenium-boron pairs had recombined. However, obtaining the full echo intensity required a waiting time of $\sim 10^4$ s — such non-exponential behaviour is consistent with a random distribution of donor-acceptor nearest-neighbour distances.

The problem of DA recombination has been solved analytically for shallow donors by Thomas *et al.*²⁵ and has been adapted here to selenium in the case of low compensation ($[\text{Se}] \gg [\text{B}]$). In this case, the relative distance between donors and acceptors is much larger than the Bohr radius of both electron and hole bound to impurities and the wavefunctions in the ground state may be considered unperturbed. For instance, for concentrations of $\sim 10^{15} \text{ cm}^{-3}$ and low compensation, the most probable distance between DA nearest-neighbours is about 50 nm which is much larger than $a_H^* = 4.2 \text{ nm}$, the effective Bohr radius of the bound hole in silicon. Under this approximation, the calculation of the recombination rate (W) for each individual DA pair only involves the optical matrix element M between the wavefunctions of the donor and acceptor in the neutral condition and we have $W(r) = |M|^2$. The optical matrix element can be then taken to be proportional to the value of the hole wavefunction at the donor site, giving

$$W(r) = W_0 \exp \left\{ -\frac{2r}{a_H^*} \right\}, \quad (2)$$

where W_0 has been determined to be between 10^5 s^{-1} and 10^3 s^{-1} . The effect of an ensemble of selenium impurities surrounding the acceptor can be seen as set of independent recombination channels with a certain distribution of recombination rates. By integrating over a random distribution of donors, the dynamics can be shown to follow:

$$\frac{\langle B^0(t) \rangle}{[B]} = \exp \left[4\pi[\text{Se}] \int_0^\infty \left\{ e^{-W(r)t} - 1 \right\} r^2 dr \right], \quad (3)$$

$$\frac{\langle \text{Se}^+(t) \rangle}{[B]} = 1 - \frac{\langle B^0(t) \rangle}{[B]} \quad (4)$$

where $\langle \text{Se}^+(t) \rangle$ and $\langle B^0(t) \rangle$ are the concentrations of Se^+ and B^- respectively. We simulated the dynamics of the recombination process using the equations above, taking the known concentration of selenium impurities, and find a good fit to the experimental data. The value of the relaxation rate W_0 used in the fit was 10^4 s^{-1} , at 15 K, which is consistent with previous values observed for similar samples doped with shallow donors¹⁴.

The approach to thermal equilibrium (all boron ionised and an equal number of Se^+) can be accelerated over that resulting from DA pair recombination by using infrared radiation at about $4 \mu\text{m}$: an electron is continuously excited from the neutral selenium into the conduction band, whereupon it either returns to re-neutralise the selenium, or is captured by an acceptor (Figure 4(d)). We find that under weak ($10 \mu\text{W}$) illumination at $4 \mu\text{m}$, the rate at which equilibrium charge conditions are established is two orders of magnitude faster than the direct DA recombination. Within the first second after the 1047 nm flash, about 50 % of the echo signal is recovered and thermal equilibrium state is reached after about 100 s. The recombination is well fit by a bi-exponential decay with $\tau_1 = 1.6 \text{ s}$ and $\tau_2 = 40 \text{ s}$. The effect of $4 \mu\text{m}$ illumination is further evidence that the slow observed recombination dynamics are limited by long-lived (i.e. distant) DA pairs. Moreover the illumination sequence ($1047 \text{ nm} + 4 \mu\text{m}$) could be used in order to study the nuclear spin properties of neutral selenium, $^{77}\text{Se}^0$, following analogous methods to those used to study ionised P nuclear spins through electrically detected magnetic resonance²⁶. In shallow donors such as P, the hyperfine interaction with the electron spin strongly limits the nuclear spin coherence, such that nuclear spin coherence times for P^+ are strongly enhanced⁷. Similarly, one could expect the nuclear spin coherence time for neutral selenium (in its singlet ground state) to be comparably long.

VI. CONCLUSIONS

We have found that the electron spin relaxation times of Se^+ are the longest observed for donors in 28-silicon

— this is explicitly demonstrated for temperatures in the range 5–30 K, and is expected to hold true for lower temperatures. The energy splitting, Δ , between the ground and first-excited valley state is an order of magnitude larger in Se^+ than for Group V donors in silicon — this effectively removes the Orbach spin relaxation mechanism, though its effect in reducing the strength of the Raman T^9 process is rather weak, providing motivation for further theoretical work to understand this quantitatively. As a result of this increase in T_1 , the electron spin coherence times in Se^+ are shown to be significantly longer than for Group V donors for temperatures above 10 K, and this trend is likely to extend to lower temperatures for samples with lower Se concentrations than those studied here. The large value of Δ should also result in a dramatically reduced Stark shift²⁷ compared to shallow donors, such that the electron and nuclear spin coherence of Se^+ could be relatively unaffected by charge noise in nano-devices, despite the large value of the hyperfine coupling. It is also possible to spectrally resolve the ground state hyperfine coupling in $^{28}\text{Si}:^{77}\text{Se}^+$ using the $1s(T_2)\Gamma_7$ absorption transition¹⁵, so if a tuneable source were available at $\sim 2.9 \mu\text{m}$ this could be used for fast and efficient hyperpolarization of both the electron and nuclear spin. Finally, we have investigated optical methods to manipulate the donor charge state (from Se^+ to Se^0), examining this through donor-acceptor recombination following above band gap illumination, and showing how Se^0 can be ionised using $4 \mu\text{m}$ illumination. This suggests a possible mechanism to first bring selenium donors into an ESR-active Se^+ state, and subsequently neutralise them leaving a potentially long-lived ^{77}Se nuclear spin.

Acknowledgments

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- ³¹ P. Hu and S. R. Hartmann, *Physical Review B* **9**, 1 (1974).
- ³² We measured no significant change in T_1 measured immediately after the laser pulse, and hence exclude sample heating arising as a significant effect on the observed recombination dynamics