Measuring central-spin interaction with a spin bath by pulsed ENDOR: Towards suppression of spin diffusion decoherence

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We present pulsed electron-nuclear double resonance (ENDOR) experiments which enable us to characterize the coupling between bismuth donor spin qubits in Si and the surrounding spin bath of 29Si impurities which provides the dominant decoherence mechanism (nuclear spin diffusion) at low temperatures (< 16 K). Decoupling from the spin bath is predicted and cluster correlation expansion simulations show near-complete suppression of spin diffusion, at optimal working points. The suppression takes the form of sharply peaked divergences of the spin diffusion coherence time, in contrast with previously identified broader regions of insensitivity to classical fluctuations. ENDOR data suggest that anisotropic contributions are comparatively weak, so the form of the divergences is largely independent of crystal orientation.

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I. INTRODUCTION

Quantum decoherence presents a fundamental limitation to the realization of practical quantum computing and of other technological devices which actively exploit quantum phenomena. In 2002, a ground-breaking study established the usefulness of so-called optimal working points (OWPs). These are parameter regimes where the system becomes - to first order - insensitive to fluctuations of external classical fields. We consider here the effect of OWPs in a system where decoherence of a central spin system arises from interactions with a fluctuating bath of surrounding spins - a scenario that is of considerable significance in the field of quantum information.2–4

A promising approach for silicon-based quantum-information processing (QIP) involves combined electron and nuclear spins of donor atoms in Si, which are amenable to high-fidelity manipulation by means of electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR), respectively. Most studies have considered phosphorus (31P) donors in Si.11–22 More recently, several different groups have investigated another Group V donor, 209Bi. These studies not only showed that bismuth donors have similar properties to Si:P, such as long electron spin coherence times T2 of the order of several ms at low temperatures (< 16 K),23–24 but that they also offer new possibilities for QIP. For example, strong optical hyperpolarization was demonstrated25–27 allowing for efficient initialization of the nuclear spin. The Si:Bi spin system has an electron spin S = 1/2 and a large nuclear spin I = 9/2 as well as an atypically strong hyperfine coupling constant, A/2π = 1.4754 GHz. The strong state-mixing occurring for magnetic fields B ≃ 0.1 – 0.6 T where the hyperfine interaction competes with the electronic Zeeman energy allows transitions which are forbidden at high magnetic fields26,27 observed recently in Ref. 28. In Refs. 23,27 a set of minima and maxima were found in the f – B parameter space of dipole-allowed transitions at frequencies f. These df/dB ≈ 0 points were identified as OWPs: Line narrowing and reduced sensitivity to temporal and spatial noise in B over a broad region of fields (closely related to df/dB = 0 extrema) were found. However, to date, their effectiveness for reducing decoherence in the real environment of a spin bath remains untested.

In natural Si, 4.67% of lattice sites are occupied by the nuclear spin-half 29Si isotope, rather than the spinless 28Si. Flip-flopping of the 29Si spins provides the dominant mechanism of decoherence for both Si:P and Si:Bi systems at low temperatures. The decay of the donor Hahn spin echo for these systems is typically fitted to exp[−t/T2 − (t/TSD)n], where TSD < 1 ms characterizes the nuclear spin diffusion, with n ≃ 2 – 3.28 Other relaxation processes, such as those arising from donor-donor interactions, are represented by T2. Since T2 ≫ TSD, nuclear spin diffusion remains the main channel of decoherence at low temperatures.29,30

In this work, we investigate the nature of the Bi–29Si interaction by means of pulsed electron-nuclear double resonance (ENDOR).2 To obtain an ENDOR spectrum, an EPR spin echo is detected as a function of a radio frequency (rf) excitation. When the rf radiation is resonant with an NMR transition, changes are seen in the EPR signal if the EPR spin echo is detected as a function of a radio frequency (ENDOR).

This model has been used
with considerable success to model central spin decoherence in Si:P.\cite{24,25,26} In Ref. \cite{24} weak state-mixing in Si:Bi was investigated by simply allowing for the variation of an effective gyromagnetic ratio. Here we adapt the CCE simulations to include, for the first time, the strong state-mixing seen near the OWPs. A key finding is the demonstration of near-complete suppression of nuclear spin diffusion, even in natural Si: This occurs in extremely narrow regions, where $T_{\text{SD}}$ is in effect divergent,\cite{27,28} in contrast to the broader effect expected from the form of $df/dB$\cite{29} $A$. A successful means of controlling decoherence is to employ isotopically enriched samples. In addition to the CCE and using $\pi$-pulses, the disparity between the electronic Zeeman and hyperfine frequencies for the donor and Si spins, respectively.

Here, $\omega_0 = \mu B/\hbar$ is the electronic Zeeman frequency ($\mu = 1.857 \times 10^{-23}$ JT$^{-1}$) while $\delta_{\text{Si}} = 2.486 \times 10^{-4}$ and $\delta_{\text{Si}} = 3.021 \times 10^{-4}$ are the ratios of the nuclear to electronic Zeeman frequencies for the donor and Si spins, respectively.

The spin-bath interaction term

$$\hat{H}_{\text{int}} = \sum_n \hat{I}_n \cdot \mathbf{J}_n \hat{S},$$

represents the SHF couplings between the donor and bath spins, in general of tensor form (for anisotropic couplings).

Finally, dipolar coupling between each pair of Si spins is represented by the bath term

$$\hat{H}_{\text{bath}} = \sum_{n<m} \hat{I}_n \cdot \mathbf{D}(\mathbf{r}_{nm}) \hat{I}_m,$$

where $\mathbf{r}_{nm}$ denotes the relative position vector of bath spins at lattice sites $n$ and $m$. Writing $\mathbf{r}_{nm} \equiv \mathbf{r}$ for a pair of spins, the components of the dipolar tensor $\mathbf{D}$ are given by

$$D_{ij}(\mathbf{r}) = \left( \frac{\mu_0 \mu_2 \mu^2}{4 \pi n^3} \right) \delta_{ij} - \frac{3 r_i r_j}{r^3},$$

with $\mu_0 = 4\pi \times 10^{-7}$ N A$^{-2}$ and $i, j = x, y, z$.

III. ENDOR MEASUREMENTS

The experimental ENDOR studies reported here served to investigate and characterize the isotropic/anisotropic character of the spin-bath interaction term, namely a set of distinct $\mathbf{J}_n$ values - SHF couplings - in Eq. (3), corresponding to occupancy of inequivalent lattice sites by $^{29}$Si impurities. Pulsed ENDOR experiments were performed using the Davies ENDOR pulse sequence $25,26$ We applied the pulse sequence $\pi_{\text{mw}} - \tau_1 - \pi_{\text{rf}} - \tau_2 - \pi_{\text{mw}} - \tau_3 - \pi_{\text{mw}} - \tau_4$-echo, where the microwave (mw) frequency is chosen to excite one EPR transition and the rf is stochastically varied between 2 - 12 MHz or 2 - 7 MHz to excite all nuclear spin transitions in this region. We used 256 ms long $\pi_{\text{mw}}$-pulses and a 128 ns long $\pi_{\text{rf}}$-pulse. For optimal signal-to-noise ratio and resolution, we used a $\pi_{\text{rf}}$-pulse of 10 $\mu$s. Pulse delays were set to $\tau_1 = 1 \mu$s, $\tau_2 = 3 \mu$s, and $\tau_3 = 1.5 \mu$s and a shot repetition time of 1.3 ms was employed to give a good signal-to-noise ratio. All experiments were carried out at 15 K on an E580 pulsed EPR spectrometer (Bruker Biospin) equipped with pulsed ENDOR accessory (E560-DP), a dielectric ring ENDOR resonator (EN4118X-MD4), a liquid helium flow cryostat (Oxford CF935), and an rf amplifier (ENI A-500W). We used a donor concentration of $3 \times 10^{15}$ cm$^{-3}$ and the magnetic field was directed perpendicular to the [111] plane.

While not offering the higher frequency resolution attainable with continuous-wave ENDOR,\cite{29,30} the pulsed ENDOR measurements permit us to adequately constrain and to demonstrate the reliability of the numerical simulations. In particular, we established that isotropic couplings to the spin bath dominate the decoherence dynamics. While not the focus of this study, a further motivation is to investigate the feasibility of an alternative possibility for QIP: to simultaneously manipulate the $^{29}$Si atoms as spin-half qubits, along with the donors.\cite{31}

Measured ENDOR spectra at $f \approx 9.755$ GHz are presented in Fig. 1 together with a list of SHF couplings. For the magnetic field range $B = 0.1 - 0.6$ T in Fig. 1 there is significant mixing of the high-field Si:Bi energy eigenstates $|m_S, m_I\rangle$. The mixed eigenstates, $|\pm, m\rangle$, correspond to doublets (at most) of constant $m = m_S + m_I$:

$$|\pm, m\rangle = a_m^\pm |\pm \frac{1}{2}, m \pm \frac{1}{2}\rangle + b_m^\pm |\mp \frac{1}{2}, m \pm \frac{1}{2}\rangle,$$

$$|a_m^\pm|^2 - |b_m^\pm|^2 = \frac{\Omega_m(\omega)}{\sqrt{(\Omega_m(\omega) + 25 - m^2)}} = \gamma_m(\omega),$$

where $\Omega_m(\omega) = m + \frac{1}{2} |1 + \delta_{\text{Si}}|$ and $m$ is an integer, $-5 \leq m \leq 5$. Such mixing leads to a complex EPR spectrum for bismuth with $df/dB = 0$ extrema. The minima correspond to transitions between states corresponding to adjacent avoided level crossings, of which there are four. The disparity between the electronic Zeeman and hyperfine energy scales and SHF energy scales means that the tensor coupling in Eq. 3 reduces to simpler form

$$\hat{H}_{\text{int}, \ell} = \alpha_\ell \hat{I}_\ell^z + \beta_\ell \hat{I}_\ell^x \hat{S}_z,$$

written for a coupling to a single $^{29}$Si at site $I$, where $\alpha_\ell = [(a_{\text{iso}, \ell} - T_I) + 3T_J^2 \cos^2 \theta_I]$ and $\beta_\ell = 3T_J \sin \theta_I \cos \theta_I$ with $a_{\text{iso}, \ell}$ and $T_I$ the isotropic and anisotropic parts of the
molecular-frame SHF tensor, respectively, and \( \vartheta_l \) the angle between the external field and the line connecting the bismuth site and site \( l \). Nonsecular terms involving \( S^z \) and \( S^y \) can be neglected. Diagonalization of the resulting 2-dimensional Hamiltonian, and setting \( I_l = 0 \) for a purely isotropic coupling leads to a simple expression for the ENDOR resonance frequency for donor level \( |\pm, m\rangle \):

\[
\Delta_{iso, l}^{\pm, m}(\omega_0) = \frac{1}{2\pi} \omega_0 \delta_{Si} \pm \left( \frac{a_{iso, l}}{2} \right) \gamma_m(\omega_0). \tag{9}
\]

The above expression is in perfect agreement with full numerical diagonalization. The couplings in Fig. 1 were extracted from the measured spectra by fitting to the data Gaussians of equal width and using Eq. (9). The same expression and a single set of couplings gave excellent agreement with data at 10 different fields. In particular, the observed pattern of half a dozen highest frequency lines and a single set of couplings gave excellent agreement with data at 10 different fields. In particular, the observed pattern of half a dozen highest frequency \( ^{29}\text{Si} \) resonances moving to a minimum at \( B \approx 0.2 \text{ T} \), then increasing again, is directly attributable to mixing of the states of the bismuth donor: i.e., here \( \gamma_m(\omega_0) \) has a minimum.

Ten out of the twelve couplings extracted from data were found to be purely isotropic. The highest-field spectrum was measured for a range of crystal orientations and only three weak intensity lines showed orientation-dependent frequencies and hence anisotropy. Two are indicated by \( X_1 \) and \( X_2 \) in Fig. 1. The corresponding two couplings with nonzero anisotropy were found to have \( (a_{iso, X_1} \approx 2.8, T_{X_1} \approx 2.4 \text{ MHz} \) and \( (a_{iso, X_2} \approx 0.4, T_{X_2} \approx 2.8 \text{ MHz} \) by fitting the more general form of Eq. (9) with nonzero \( T \). A previous ESEEM (electron spin echo envelope modulation) study identified a single anisotropic coupling \( \Xi \) attributed to E-shell (nearest neighbor) \( ^{29}\text{Si} \). The third line we identify is fitted by coupling constants consistent with the anisotropic coupling in Ref. 12. For most crystal orientations, this line is masked by much higher intensity lines arising from isotropic couplings.

At fields where \( \gamma_m(\omega_0) \) becomes small (this occurs close to the \( df/dB = 0 \) minima as shown in Refs. 26–28., Eq. (9) tends to the \( ^{29}\text{Si} \) Zeeman frequency \( \delta_{Si} \omega_0 \). It is straightforward to extend Eq. (9) to the anisotropic case and show that the latter statement also holds for anisotropic couplings. In effect, at these points, the donor might be said to approximately decohere from the bath. For example, for the EPR transition |12⟩ → |9⟩ (labeling the eigenstates \( |n = 1, 2, \ldots 20 \rangle \) in increasing order of energy), \( \gamma_m(\omega_0) = 0 \) at \( B = 157.9 \text{ mT} \) for level |12⟩ and \( B = 210.5 \text{ mT} \) for |9⟩. We note that there is however no \( B \)-field value where both the upper and lower levels have \( \gamma_m(\omega_0) = 0 \). As we see below, this is not actually essential for complete suppression of spin diffusion. The actual OWP is at \( B = 188.0 \text{ mT} \), where \( \gamma_{-3}(\omega_0) = -\gamma_{-4}(\omega_0) \). This is extremely close to where \( df/dB = 0 \), which occurs when

\[
\gamma_{-3}(\omega_0) + \gamma_{-4}(\omega_0) - \frac{2\delta_{Bi}}{1 + \delta_{Bi}} = 0. \tag{10}
\]
the \( \hat{L}_S(t) \) is obtained in terms of the \( L_S(t) \) and the \( \hat{L}_C(t) \) in subsets \( C \) of \( S \),
\[
\hat{L}_S(t) = L_S(t)/ \prod_{C \subset S} \hat{L}_C(t).
\]

The problem of calculating \( L(t) \) is reduced into independent components each for a distinct cluster of bath spins. The exact solution to \( L(t) \) is obtained if the \( \hat{L}_S(t) \) from all clusters are combined using Eq. (11) and the approximation to \( L(t) \) up to a maximum cluster size of \( k \) is defined as
\[
L^{(k)}(t) = \prod_{|S| \leq k} \hat{L}_S(t),
\]
which involves calculating reduced problems for all clusters each containing at most \( k \) spins. The \( L^{(k=2)}(t) \) (2-cluster) calculation is a good approximation to \( L(t) \) when considering only dipolar interactions in the bath affecting the spin echo, as these are at most a few kHz and hence perturbative compared to the SHF interactions in the MHz range involving the donor electron. The CCE is exact, but not always convergent. We calculated the 2-cluster \( (k = 2) \) approximation to the CCE and obtained convergence for up to \( k = 3 \).

The Hahn echo sequence evolves the combined system-bath state to time \( t = 2\tau \):
\[
|\psi(t = 2\tau)\rangle = e^{-iH\tau}(\hat{\sigma}_x \otimes \mathds{1}_B)e^{-iH\tau}|\psi(t = 0)\rangle,
\]
where \( \hat{\sigma}_x \) is the Pauli-X gate acting on the donor and \( \mathds{1}_B \) denotes the bath identity. We assume that the time taken for a \( \pi \)-pulse is small compared to \( \tau \). The initial state was written as a product of the initial donor and bath states, the former chosen as an equal superposition of states \( |12 \rangle \) and \( |9 \rangle \). The donor subsystem is recovered after tracing over the bath and the modulus of the normalized off-diagonal element of the donor reduced density matrix is proportional to the intensity of the echo at time \( t = 2\tau \). The reduced problem of the 2-cluster bath was solved for each of the four initial 2-product bath states and the average intensity obtained. 2-clusters were formed by pairing \( ^{29}\text{Si} \) spins separated by up to the 3rd nearest neighbor distance in a diamond cubic lattice of side length 160 Å. Convergence was obtained as the lattice size and the separation between the two bath nuclei were extended. It was assumed that \( B \) was large enough to conserve the total \( ^{29}\text{Si} \) Zeeman energy. Thus, the dipolar interaction between the two bath spins took the form of a combination of Ising \((\hat{I}_1 \hat{I}_2)\) and flip-flop \((\hat{I}_1^2 \hat{I}_2 + \hat{I}_1 \hat{I}_2^2)\) terms. The Kohn-Luttinger electronic wavefunction was used to calculate the isotropic Fermi contact SHF strength with an ionization energy of 0.069 eV for the bismuth donor. Calculated couplings were of the same order as those obtained from data. The data suggest that isotropic couplings predominate; hence anisotropic couplings were neglected and the simulations were largely insensitive to orientation. Finally, we obtained the average \( L^{(k=2)}(t) \) over 100 spatial configurations of \( ^{29}\text{Si} \) occupying 4.67% of lattice sites. The resulting decay curves were fitted to \( \exp[-t/(2T) - (t/T_{SD})^n] \), obtaining \( T_2 \gg T_{SD} \) and values of \( n \approx 2 - 3 \).

FIG. 2: (Color online) Suppression of \(^{29}\text{Si} \) spin bath decoherence for the \( |12 \rangle \rightarrow |9 \rangle \) EPR transition. (a) Simulated ENDOR and nuclear spin diffusion coherence times \( T_{SD} \) as a function of magnetic field \( B \), showing collapse of the superhyperfine couplings and a sharp increase in \( T_{SD} \) as the field approaches the \( B = 188.0 \text{ mT optimal working point (OWP)} \). The dashed line is a fit. (b) Simulated ENDOR at the \( B = 188.0 \text{ mT OWP} \) (upper panel) and experimental spectrum at 9.755 GHz (lower panel). (c) Calculated donor Hahn spin echo decays from which coherence times in Fig. 2(a) were extracted.
V. SUPPRESSION OF NUCLEAR SPIN DIFFUSION

The results of our CCE simulations are presented in Fig. 2. Figure 2(a) shows the behavior around the $B = 188.0$ mT OWP, associated with the $|12\rangle \rightarrow |9\rangle$ EPR line. The calculated coherence time $T_{SD}$ (orange dashed line) is superposed on a color map showing the SHF spectrum: The latter shows ENDOR spectra simulated as a function of $B$, using Eq. (9) and centered about the $29$Si nuclear Zeeman frequency. Strikingly, as $B$ approaches the OWP, the "comb" of SHF lines narrows to little more than the width of a single line. This suggests a drastic reduction in the value of the SHF couplings, indicating that the bismuth has become largely decoupled from the $29$Si spin bath.

The collapse in the SHF couplings is illustrated further in Fig. 2(b). The lower panel shows the measured spectrum at 9.755 GHz. Using our experimentally determined SHF couplings, the corresponding spectrum at the OWP is shown in the upper panel of Fig. 2(b), demonstrating clearly the narrowing of the spectrum [corresponding to the same parameters as Fig. 2(a) but at the precise field value of the OWP].

The behavior of $T_{SD}$ is also quite striking and unexpected: The coherence time predicted by CCE simulations increases asymptotically at the OWP by several orders of magnitude. Away from the OWP, the results agree well with experimentally measured values of approximately 0.7 ms. In Ref. 24, in a regime of weak state-mixing, simulations using an effective gyromagnetic ratio indicated that $T_{SD}$ was slightly reduced (by about 5%) in a regime corresponding to lower $df/dB$. The present study, on the other hand (which in contrast to Ref. 24 employed a full treatment of the quantum eigenstate mixing), shows rather an effect very sharply peaked about the OWP: Nuclear spin diffusion is predicted to be largely suppressed, but over an extremely narrow magnetic field range.

Figure 2(c) shows a sample of CCE spin echo decays from which $T_{SD}$ times were extracted, and also serves to further illustrate the sharp increase in $T_{SD}$. Similar suppression is present for other OWP in Si:Bi. There are $df/dB = 0$ minima for the $|15\rangle \rightarrow |6\rangle$, $|14\rangle \rightarrow |7\rangle$, $|13\rangle \rightarrow |8\rangle$, $|12\rangle \rightarrow |9\rangle$, and $|11\rangle \rightarrow |8\rangle$ transitions in the frequency range 5 – 7.5 GHz and two maxima for $|12\rangle \rightarrow |11\rangle$ and $|9\rangle \rightarrow |8\rangle$ close to 1 GHz. The decoupling from the spin bath is also expected to lead to suppression of decoherence arising from the interaction with a bath of donors.

VI. CONCLUSIONS

In conclusion, we present measurements of the SHF couplings between a bismuth donor and a bath of $29$Si impurities which suggest that isotropic couplings dominate. We further demonstrate the suppression of couplings at OWP. Finally, the spin echo decay of the donor is calculated as a many-body problem and sharp divergence of the spin diffusion time is found at an OWP. Our study motivates experimental EPR studies in the range 5 – 7.5 GHz corresponding to the regions of suppressed decoherence.

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