

Nuclear spin diffusion in dynamic nuclear polarization of crystalline nanoscale silicon particles

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Hyperpolarized nanoparticles offer high polarization levels with room-temperature relaxation times exceeding half an hour. In this work, we demonstrate that the achievable hyperpolarization enhancement and relaxation (decay) time at room temperature are largely independent of the particle size contrary to previous assumptions. This is explained through first-principles spin-diffusion coefficient calculations and finite-difference polarization simulations. The simulated zero-quantum (flip-flop) linewidth governing the spin diffusion is found to agree with the experimentally accessible single-quantum (single spin flip, e.g., radio-frequency pulse) linewidth. The transport of hyperpolarization from strongly hyperfine-coupled spins toward the bulk is believed to be responsible for the slow polarization dynamics including the long room-temperature decay time. The linewidth and spin-diffusion simulations are extended to other cubic crystal structures and analytical expressions, which only require insertion of the gyromagnetic ratio, lattice constant, isotope abundance, and measured spectral density distribution (nuclear linewidth). The presented simulations can be adjusted to study spin diffusion in other materials.

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Recent advances in hyperpolarization have been stimulated by growing interest in its application to enhance the sensitivity of ^{13}C organic compounds, specifically in the context of metabolic magnetic resonance imaging (MRI) [1]. Small organic molecules, however, suffer from short spin-lattice relaxation times T_1 in solution on the order of few tens of seconds. Short T_1 limits the time window available for imaging and imposes additional constraints on the sample transfer such as the need for fast dissolution [2], minimization of time for quality control, and short shuttling distances between polarizer and imaging magnet. Hyperpolarized (crystalline) nanoparticles can exhibit long T_1 times at room temperature [3–12], biocompatibility, and sufficient *in vivo* clearance [13–20]. Particles are typically hyperpolarized at liquid-helium temperatures and few tesla magnetic fields using dynamic nuclear polarization (DNP), before the sample is extracted from the polarizer and transferred to the imaging scanner at room temperature to exploit the long T_1 times for imaging. Possible applications include perfusion imaging not limited by the hyperpolarized T_1 time, targeted imaging (molecular targeting), and possible combination with therapeutics [4,18,21].

Nanoparticles with a few tens of nanometers in diameter are preferred given their faster clearance to avoid *in vivo* accumulation [22]. However, previous reports showed shorter T_1 times and lower enhancements for smaller particles [4,11,23–25]. For diamond nanoparticles, the increased relaxation for smaller particles was associated with the larger ratio of surface to bulk defects [24,25]. Surface dangling bonds appeared rather inefficient for DNP [26,27] while causing strong relaxation. In contrast, bulk substitutional nitrogen defects (P1 or C centers) can create DNP enhancements of several hundred [11,24,25] even at room temperature [28–30]. An increased relaxation by surface defects in nanodiamonds combined with an unchanged DNP injection from the bulk defects leads to a reduced steady-state polarization as shown using a rate-equation model [31,32] (cf. Sec. S4 of the Supplemental Material [33] for a summary of the model).

Silicon particles naturally form a surface oxide with defects (P_b centers) at the interface to the crystalline core, which has been investigated for decades with a brief summary in terms of results for DNP given in Ref. [10]. The relevance of P_b centers for DNP and relaxation in silicon particles has been investigated [5,10,23,34–38] and, hence, the particles should be described in terms of an outer part containing the P_b centers and an inner crystalline part without strong DNP or relaxation sources (core-shell geometry). Based on this structure, it was proposed that the long relaxation times (>30 min) observed in microparticles arise [23,34,35] from most of the polarization being stored in the slowly relaxing bulk, which is weakly connected via spin diffusion to the fast-relaxing shell containing the paramagnetic P_b defects. This explanation for the long T_1

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times of silicon came under scrutiny with measurements of room temperature $T_1 \geq 40$ min and enhancements $\varepsilon \geq 100$ in 50 nm bulk particles [5,6] as well as highly porous silicon (PSi, crystallite sizes between 10 and 60 nm) particles [10].

In this work, we report on 20 nm silicon particles with a room temperature $T_1 \approx 40$ min and DNP enhancements around 100 at 3.4 T (3.4 K). This raises the question of how to explain the long relaxation times as the estimated spin-diffusion constant in silicon [34,39] would suggest T_1 's on the order of a few seconds.

In the present work, we estimate the (isotropic) nuclear spin-diffusion coefficient D from first principles for different cubic lattices. The calculated D is used to fit the buildup and room-temperature decay with a finite-difference approach [40,41] to show that the long measured relaxation times are related to the slow nuclear spin diffusion near P_b centers.

I. NUCLEAR SPIN DIFFUSION

Microscopically, nuclear spin diffusion results from the internuclear dipolar couplings

$$d_{ij} = \frac{\mu_0}{4\pi} \frac{\hbar \gamma_i \gamma_j}{r_{ij}^3} \frac{3 \cos^2 \theta_{ij} - 1}{2}, \quad (1)$$

where r_{ij} and θ_{ij} are the distance and angle between spins i and j with respect to the main magnetic field; γ_i is the gyromagnetic ratio of spin i . The dipolar coupling between the two spins leads to an exchange rate W_{ij} that might be suppressed if the two spins have different resonance frequencies/energies (see below). W_{ij} can be computed by evaluation of the dipolar couplings on a lattice including a (normalized) spectral density function modulating the coupling [42–44]. In particular, we use [44]

$$W_{ij} = \frac{\pi}{2} d_{ij}^2 p_{\text{ZQ}}(0), \quad (2)$$

where $p_{\text{ZQ}}(0)$ is the normalized zero-quantum (ZQ) line evaluated at zero frequency. This approach entails energy-conserving flip-flops. The ZQ line describes the energy-level distribution of spin-spin flip-flops, which constitute the fundamental process of nuclear spin diffusion. The factor $\frac{\pi}{2}$ arises from a Fermi's golden rule approach (2π) combined with the notion that $-\frac{1}{2}d_{ij}(I_i^+ I_j^- + I_i^- I_j^+)$ (part B of the dipolar alphabet) is responsible for the flip-flops (providing an additional prefactor of 1/4).

In the following, we will discuss two different approaches for how to calculate the spin-diffusion coefficient D .

A. Nearest-neighbor approach

Assuming that spin diffusion is a process of nearest-neighbor (NN) spin flip-flops, the spin-diffusion coefficient D can be calculated using [45,46]

$$D_{\text{NN}} = \frac{1}{2} W r_{\text{NN}}^2, \quad (3)$$

with W being the spin flip-flop rate and r_{NN} the distance between NN nuclear spins. This approximation was used in previous estimates of the spin diffusion in silicon [34,39] and relies on the experimentally measured single-quantum (SQ) line (T_2^*) describing the frequency/energy distribution if a

single spin is flipped (see below). Specifically, the spin-diffusion coefficient D in the nearest-neighbor approximation of cubic lattices is given by [39,46]

$$D_{\text{NN}} \approx \frac{\Delta \nu_{\text{dd}}}{30} r_{\text{NN}}^2, \quad (4a)$$

$$r_{\text{NN}} \approx N_n^{-1/3} = \left(f \frac{8}{a^3} \right)^{-1/3}, \quad (4b)$$

where $\Delta \nu_{\text{dd}}$ is the dipole-dipole contribution to the SQ linewidth [39], r_{NN} is the statistical nearest-neighbor distance between ^{29}Si atoms, N_n is the spatial density of ^{29}Si atoms, f is the ^{29}Si isotope abundance, and the 8 stems from the eight lattice sites in the cubic conventional unit cell of silicon (diamond cubic structure) with the lattice constant $a = 5.43$ Å. The nearest-neighbor distance r_{NN} may be modified by a factor of ~ 0.55 to account for the statistical occupation of the lattice (Poisson distribution; cf. Appendix VII of Ref. [47]), which would be relevant for not too high isotope abundances. However, for high isotope abundances, this would result in an unrealistic nearest-neighbor distance smaller than the distance between neighboring lattice sites. We note that Eq. (4a) rather approximates a simple cubic monocrystalline lattice as already discussed by Khutsishvili [46]. A diamond cubic structure is a face-centered cubic (fcc) lattice with a diatomic basis.

B. Lattice approach

A Taylor series expansion of the nuclear spin field yields the spin-diffusion coefficient D [48,49]

$$D_{\text{lat}} = \sum_j \frac{1}{2} W_{ij} r_{ij}^2, \quad (5)$$

with lattice site indices i and j .

For a given central spin i , W_{ij} is summed over all surrounding lattice sites [48,49]. Combining Eqs. (2) and (5) gives

$$D_{\text{lat}} = \sum_j \frac{\pi}{4} d_{ij}^2 r_{ij}^2 p_{\text{ZQ}}(0). \quad (6)$$

In this work, we focus on crystalline lattices consisting of a single atomic species (silicon). Hence, we can approximately calculate the ZQ line using a three-spin model: (1) a central spin, (2) a second spin that we designate as the target spin for the spin flip-flop, and (3) a third background spin modifying the energy levels of the first two spins. The second and third spins (target and background spins) take random positions with respect to the central spin and, in principle, we need to sum over all possible three-spin systems.

In this three-spin system, we study the zero- and single-quantum (ZQ and SQ) processes of the system. The SQ line describes the experimentally measured linewidth with a single spin flipped by a radio-frequency (RF) pulse. The ZQ line describes the spin exchange processes with a net-zero change of spin angular momentum (spin flip-flop) occurring during nuclear spin diffusion. We note that the ZQ and SQ lines can have different values. Therefore, calculating the spin-diffusion coefficient D based on the experimentally observed SQ line ($\sim 1/T_{2,\text{SQ}}$) might give erroneous results for the spin-diffusion coefficient.

In this work, we compute the SQ and ZQ lines with an approach based on Van Vleck moments [50–52]. We assume a Gaussian line such that the SQ and ZQ linewidths for the full width at half maximum (FWHM) are given by $\text{FWHM} = 2\sqrt{2\ln(2)}M_2$, with M_2 being the second moment. The lengthy expressions for M_2 of the three-spin model are provided in a Mathematica (Wolfram Research, USA) notebook together with the experimental data (cf. Data availability). However, it should be noted that the expressions for M_2 of SQ and ZQ lines only contain d_{ij}^2 , which will be used to define an effective cutoff distance to accelerate the lattice calculations. Furthermore, the relevant part of the dipolar coupling for M_2 is $2d_{ij}I_i^zI_j^z$ (part A of the dipolar alphabet), giving an additional factor of 2 in the ZQ/SQ line calculation.

II. METHODS

A. Samples and characterization

The samples were purchased from US Nano Research (USA) and used without further modification. For the 50 nm sample, the previously reported characterization of the sample was used [5,6]. For the 20 nm particles, the average particle size (APS) was measured with a transmission electron microscope (TEM) [6]. The 20 nm particles were characterized with X-band electron paramagnetic resonance (EPR; Magnetech MiniScope MS5000, Bruker Corp.) following the experimental approach and analysis presented in Ref. [10]. In particular, the density of paramagnetic centers was calculated with a reference TEMPO sample and the EPR spectrum was fitted with a combination of anisotropic P_b^{111} and isotropic P_b^{iso} centers using EasySpin 6.0.6. More details about the EPR measurements and analysis can be found in Ref. [10].

The Si crystalline sizes were measured with x-ray powder diffraction (XRPD; D8 Discover, Bruker Corp.) in Bragg-Brentano geometry. Si crystalline sizes were then calculated from the diffraction pattern using Rietveld refinement method in TOPAS[®] 4.6 software taking into account the instrumental broadening.

B. Dynamic nuclear polarization

The DNP profiles and buildup curves were measured using home-built polarizers operated at 3.4 and 7 T [53] and a temperature of 3.4 K unless otherwise stated. The 3.4 T system was equipped with an OpenCore NMR [54–56] (142 MHz ¹H Larmor frequency) spectrometer and the 7 T with a Bruker Avance III console (Bruker BioSpin, Switzerland, 299 MHz ¹H Larmor frequency). Both setups were equipped with a 200 mW microwave (MW) source [from ELVA-1, Estonia for 3.4 T and Virginia Diodes (VDI), USA for 7 T] unless otherwise stated. DNP profiles at 3.4 T (cf. Sec. S2 of the Supplemental Material [33]) were performed with a 400 mW VDI source. The 7 T setup was equipped with an in-house electroplated low-loss waveguide yielding approximately doubled MW power at the sample space compared to a stainless steel waveguide (around 65 mW at the sample) [57]. The MW power was set to the maximum output unless explicitly stated. The MW was frequency modulated to further improve the polarization (cf. Sec. S2 of the Supplemental Material [33]) [5,6]: A sawtooth modulation with 1 kHz (10 kHz) frequency

and ~150 (300) MHz bandwidth at 3.4 (7) T was used. The other details of the setup are described elsewhere [53,57]. The experiments at 3.4 T were performed with small flip angles (~1.5°) and long repetition times (20 min), while at 7 T about 7° pulses every 6 min were used. Perturbations of the signal intensity by the monitoring RF pulses were corrected [31].

The results reported in this work were measured together with porous silicon (PSi) experiments reported in Ref. [10]. In particular, both reports rely on the same thermal-equilibrium measurements (see below) and the identical setups allowed for a direct comparison of the absolute polarizations/enhancements. Measuring the thermal equilibrium for silicon is complicated by the long relaxation times and the low signal. Therefore, we used the averaged signal measured with a fully ²⁹Si-labeled sample at room temperature, following previous work [5,6]. At 3.4 T, the averaged signal of a saturation recovery experiment with a single data point (after ~3.8 h) was extrapolated to infinite time with a T_1 from a hyperpolarized decay experiment. At 7 T, multiple thermal buildup (saturation recovery) experiments were averaged and the fitted value was taken for the thermal signal.

The room-temperature relaxation time was measured with a 9.4 T small animal MRI scanner (Bruker BioSpin, Germany) employing a solenoid coil wound around the sample cup [5,6]. The polarization before the room-temperature relaxation relied on a different cryostat inset [58] together with a 1 W MW amplifier (QuinStar, USA) inserted after the frequency-modulated MW source. Due to the absence of a flip angle calibration, it was not possible to correct the room-temperature relaxation measurement for the perturbations by the RF pulses.

All data processing was performed with in-house developed Matlab (MathWorks Inc., USA) scripts. Uncertainties in the processed experimental data are expressed as 95% fit intervals. Experimental instabilities such as slight changes in the MW output or temperature fluctuations as well as uncertainties in the thermal-equilibrium measurement were considered negligible.

C. ZQ/SQ line and spin-diffusion simulations

To accelerate the ZQ/SQ and spin-diffusion simulations, a spatial cutoff distance for the respective couplings (d_{ij}^2 and $d_{ij}^2r_{ij}^2$) was set on 100 randomly generated lattices per isotope abundance. The simulation box for the ZQ/SQ line and spin diffusion spanned 30 lattice constants (around 150 Å) in every direction from the central unit cell giving a cube of 61³ unit cells with eight sites per unit cell.

In the SQ/SQ line and spin diffusion simulations, the identified cutoff distances (cf. Fig. 3 for silicon and Fig. S12 of the Supplemental Material [33] for the generalized spin-diffusion simulations of cubic lattices) were used to accelerate the calculations with a moderate sacrifice in accuracy as at least 95% of the relevant coupling was chosen to be within the cutoff. The exact cutoff values are given in the simulation files and are available online (cf. Data availability). The secondary spins (target spins for flip-flop with the central spin) consist of all spins (except the central spin) for the ZQ and SQ simulations within one cutoff distance. For the background spins, all spins (except the chosen secondary and central spins) within twice

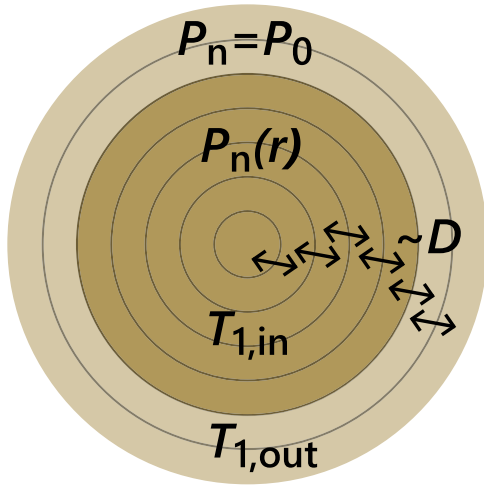


FIG. 1. Sketch of the radial finite-difference buildup simulations in a core-shell geometry motivated by P_b centers forming at the interface between the naturally forming surface oxide and silicon crystalline bulk (cf. Introduction). Hence, the outer (shell) and inner (core) particle parts are characterized by different relaxation times $T_{1,in}$ ($T_{1,out}$) and polarization levels P_n . In the inner part of the particle, the polarization depends on the radial segment [$P_n(r)$]. During the buildup, the polarization in the outer part is fixed at the steady-state polarization due to constant DNP transfer from the P_b centers to nuclei. Spin diffusion is assumed to be isotropic and transport polarization between neighboring segments denoted by the arrows in the sketch (cf. main text for more details).

the cutoff distance contribute in the simulations. Averaging over all secondary spins was applied in the SQ and ZQ line calculations. For the ZQ/SQ line simulations, around 1600 orientations were averaged (cf. Fig. S10 of the Supplemental Material [33]). For the spin diffusion simulations in the lattice approach, the crystal lattice was rotated in 1° steps between 0 and 360° and all orientations of $d_{ij}^2 r_{ij}^2$ were averaged (cf. Fig. S11 of the Supplemental Material [33]). For both the ZQ/SQ line and the spin diffusion simulations, the results of 100 randomly generated lattices were averaged for each isotope abundance. The dipolar cutoff, ZQ/SQ line and spin-diffusion simulations were carried out with in-house developed Matlab scripts.

D. Finite-difference buildup and decay simulations

Due to the core-shell geometry of the silicon particles with DNP and relaxation mostly caused by the P_b centers on the outside of the particles, we could adapt the finite-difference buildup and decay simulations from published work [40,41] and implement it in Matlab. Figure 1 sketches the approach. A particle radius of 10 nm (25 nm) was assumed with an outer (shell) part of 3 nm thickness containing the defects responsible for DNP. The thickness of the outer shell is motivated by the difference between the APS of the 50 nm particles and crystalline size (XRD) of 43 nm. The hyperpolarization buildup was modeled by setting the nuclear polarization in the outer part (shell) to be equal to the experimentally measured steady-state value, since this value is constantly replenished by DNP from the electrons. The particle was discretized in

1000 radial segments. The spin-diffusion value was chosen based on the ZQ line and spin-diffusion simulations. For simplicity, the spin diffusion in the outer part of the particles and in its core was assumed to be identical. Moreover, to simplify the differential equations, spin diffusion was only considered between neighboring radial segments in line with previous works [40,41]. Possible quenching of spins and a different spin concentration in the outer shell were ignored in the absence of a good estimate. The nuclear polarization relaxation times $T_{1,in}$ and $T_{1,out}$ of the inner (core) and outer (shell) parts of the particle were fitted in a least-squares grid search, while all other parameters were fixed. We assume a homogeneous relaxation time $T_{1,out}$ for the outer shell that absorbs a number of effects that are inhomogeneous over the outer shell: (1) the dependence of the paramagnetic relaxation as a function of the distance (and orientation) to the paramagnetic center and (2) the dependence of the spin-diffusion rate constant on the distance (and orientation) to the paramagnetic center due to frequency detuning.

III. RESULTS AND DISCUSSION

A. Experiments

Figure S1 of the Supplemental Material [33] shows the TEM image of the 20 nm particles and the particle size distribution, giving an APS of 20 ± 12 nm. The estimated crystalline sizes from XRPD were 25.8 ± 0.4 nm with an indication for an oxide phase (Fig. S2 of the Supplemental Material [33]).

The comparison of the hyperpolarization buildups corrected for the perturbations of the monitoring RF pulses [31] is displayed in Fig. 2(a) for the 20 and 50 nm particles (43 nm mean crystalline size [6]) at 3.4 and 7 T (3.4 K at both fields). Both samples reached the same fitted nuclear steady-state polarizations (enhancements ε , cf. Fig. S7 of the Supplemental Material [33]) at the two fields: $2.3\% \pm 0.2\%$ ($\varepsilon = 112 \pm 9$) and $3.7\% \pm 0.1\%$ ($\varepsilon = 89 \pm 2$) at 3.4 and 7 T, respectively. The polarizations/enhancements are similar to those reported for PSi particles [10], although the best-performing PSi samples provided higher enhancements at 3.4 T and lower at 7 T (both datasets are calibrated with the same thermal-equilibrium measurements; see Sec. II). We note the good reproducibility of DNP results and thermal-equilibrium measurements as the 50 nm sample was reported with an enhancement of 97 ± 29 at 3.4 T in independent experiments [6]. At both fields, the 20 nm particles show a faster buildup time (2.7 ± 0.4 and 5.6 ± 0.3 h at 3.4 and 7 T, respectively) than the 50 nm sample (6.3 ± 0.6 and 12.4 ± 0.5 h). This difference is discussed in Sec. S4 of the Supplemental Material [33] in terms of rate-equation parameters [31], which show a (partial) limitation of the achievable polarization levels by the MW-induced relaxation enhancement [10,32]; i.e., the MW irradiation reduces the electron polarization at the irradiation frequency, which increases the rate of triple spin flips (electron-electron-nuclear flip-flop-flips) causing nuclear relaxation.

Figure 2(b) compares the room-temperature relaxation of the 20 and 50 nm samples recorded at a 9.4 T small animal MRI. These data are not corrected for the perturbations of

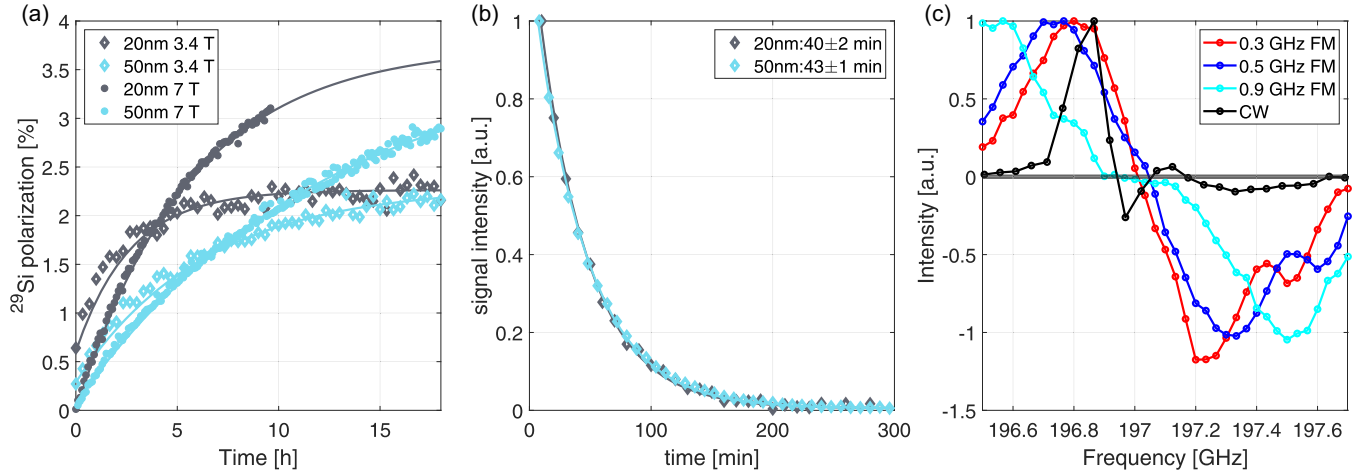


FIG. 2. (a) Buildup comparison of 20 and 50 nm particles at 3.4 and 7 T with MW modulation. (b) Decay at room temperature in a 9.4 T scanner after polarization for around 24 h at 3.4 T. (c) DNP profiles of the 20 nm particles with different FM widths (cf. Sec. S2 of the Supplemental Material [33] for more details). For the CW MW irradiation, only a very weak negative DNP enhancement can be observed. With frequency modulation, the positive and negative parts of the DNP profile have similar amplitude and shape. A comparison with the DNP profile of the 50 nm particles, an EPR profile, and further discussion are given in Sec. S2 of the Supplemental Material [33]. The 20 and 50 nm samples show identical enhancements and room-temperature relaxation while differing in their buildup times and DNP profiles.

the monitoring RF pulses [31] as the exact flip angles of the different experiments are not known (cf. Sec. II). The 20 and 50 nm particles show nearly identical relaxation times of 40 ± 2 and 43 ± 1 min at room temperature.

Differences between the two samples are evident in the DNP profiles, which will be summarized below and discussed in more detail in Sec. S2 of the Supplemental Material [33]. The 50 nm sample shows a nearly symmetric DNP profile [6] (cf. Fig. S5 of the Supplemental Material [33]) even without MW frequency modulation (FM), in agreement with other samples [6,10,34]. In contrast, the DNP profile of the 20 nm sample is asymmetric [cf. Fig. 2(c)] with the DNP lobe of negative enhancement nearly vanishing for the continuous wave (CW) MW irradiation. Furthermore, instead of a wide negative DNP lobe, a weak narrow positive DNP enhancement is observed around 197.2 GHz in Fig. 2(c). A similar asymmetry, although possibly for different reasons, has been observed [59] in nanoparticles with different surface terminations. If MW irradiation is frequency modulated, the DNP profile of the 20 nm particles appears nearly symmetric. The asymmetry of the CW DNP profile and its nearly symmetric shape with FM are not understood as of now and require further study.

In summary, the 20 nm particles show identical enhancements and room temperature T_1 compared to 50 nm particles and μm particles [6,20]. The buildup times, however, show clear differences for different sizes of the particles.

B. Simulation of silicon

1. Cutoff distance of nuclear couplings

Figure 3(a) describes the internuclear distance dependence of the sum over d_{ij}^2 and $d_{ij}^2 r_{ij}^2$ normalized to the summed interaction over all spins within $\sim 150 \text{ \AA}$ of a chosen central spin. The dipolar couplings were calculated on a 30% ^{29}Si lattice with the magnetic field implicitly assumed along the (100) direction of silicon's diamond cubic structure. Please note that we use the term “lattice site” for the crystallographic lattice

throughout this work and reserve “nearest neighbor” for the nearest ^{29}Si to a given ^{29}Si atom. A few aspects of Fig. 3(a) should be noted: The coupling to the nearest neighbor is zero, as this neighbor is at the magic angle. The groups of next-nearest and next-next-nearest neighbors can have a similar coupling to the central spin depending on their position in the randomly generated lattice. For ^{29}Si spins around $10 \text{ \AA}$ (or about two lattice constants) away from the central spin, the sums over d_{ij}^2 and $d_{ij}^2 r_{ij}^2$ become nearly continuous and converge to a finite value. Around 95% of the total coupling of d_{ij}^2 to the central spin originates from spins less than two lattice constants away (around 500 lattice sites). $d_{ij}^2 r_{ij}^2$ shows a slower spatial convergence, and only around 60% of the total coupling is contained within two lattice constants. We remark that spin flip-flops at several lattice constants away are essential to accurately describe spin diffusion with its $d_{ij}^2 r_{ij}^2$ scaling [cf. Eq. (6)].

Figure 3(b) shows the cutoff distances for 95% of the total coupling contained within the cutoff for different ^{29}Si isotope abundances. For low abundances, a larger cutoff value is necessary than for dense ^{29}Si spins. Thus, for low abundance lattices, e.g., 4.7% natural ^{29}Si abundance, flip-flops between spins more than $50 \text{ \AA}$ away from each other still contribute to the total spin diffusion. We note that such a large distance for nuclear flip-flops with respect to the 20 nm average particle size might raise problems with the use of a coarse-grained macroscopic spin-diffusion coefficient D . However, we will estimate D and use it to fit the buildups and decays as the simulations seem to be independent of the exact value of D as will be discussed below.

2. Nuclear SQ and ZQ linewidths

The simulation results of the SQ and ZQ linewidths of the three-spin model evaluated on randomly generated diamond cubic structures for varying ^{29}Si abundances are shown in Fig. 4. The SQ and ZQ linewidths are a result of powder

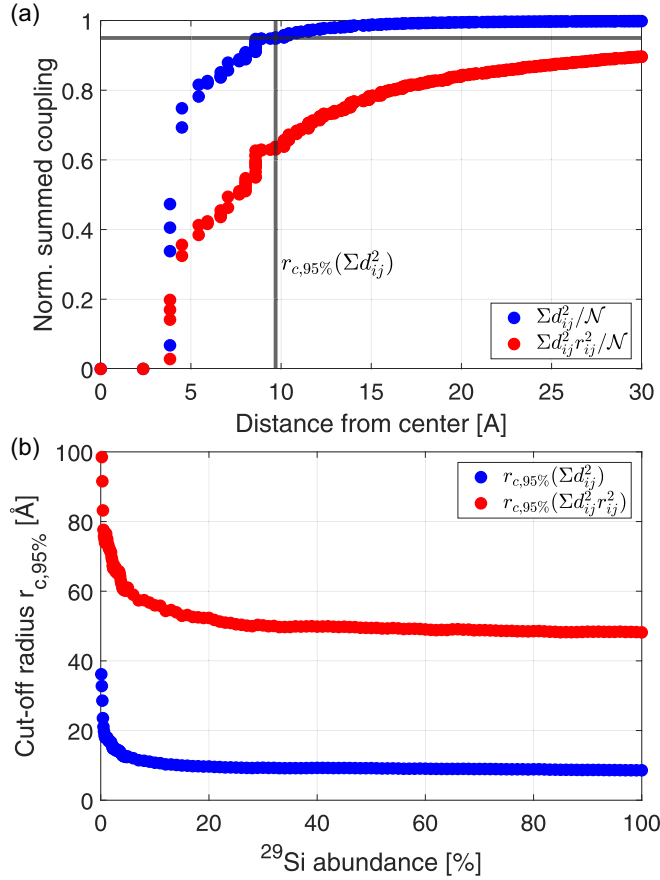


FIG. 3. (a) Normalized internuclear distance dependence of the sum over d_{ij}^2 and $d_{ij}^2 r_{ij}^2$ calculated on a 30% ^{29}Si lattice. The former describes the nuclear dipolar flip-flops, which governs the SQ and ZQ linewidths, while the latter describes spin diffusion [cf. Eq. (6)]. The slow convergence of $\sum_j d_{ij}^2 r_{ij}^2$ indicates the importance of distant spins, i.e., a few nanometers away, for spin diffusion. The sums are normalized over all spins within the simulation box of around 150 Å. (b) cutoff distance $r_{c,95\%}$ to contain 95% of total d_{ij}^2 and $d_{ij}^2 r_{ij}^2$ by ^{29}Si abundance [cf. panel (a)]. These cutoff distances will be used to accelerate the SQ/ZQ line and spin-diffusion simulations as only a limited number of spins need to be considered to obtain accurate results. The magnetic field was assumed parallel to one of the conventional unit cell axes as this direction causes the nearest neighbor to be along the magic angle, yielding a conservative estimate for the cutoff distance (cf. Fig. S9 of the Supplemental Material [33]).

averaging over nearly 1600 orientations with considerable differences depending on the angle, as shown in Fig. S10 of the Supplemental Material [33]. Crucially, the ZQ and SQ lines have very similar widths, which means that experimentally obtained values for the dipolar SQ linewidth can be used to estimate the spin diffusion in silicon.

Compared to the experimental dipolar SQ linewidths reported in Ref. [39], e.g., around 20, 120, and 1700 Hz for 1%, 10%, and 100% ^{29}Si abundance, the simulated linewidths are too large for low, accurate for intermediate, and too small for high ^{29}Si abundances. For low abundances, the experimental NMR line is close to a Lorentzian, while for intermediate ^{29}Si concentrations a nearly single Gaussian line is observed [39]. For a highly ^{29}Si -labeled sample, the line can be approximated

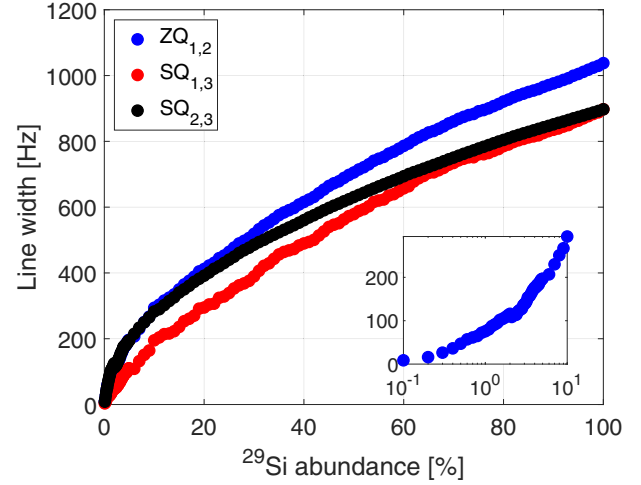


FIG. 4. Simulated SQ and ZQ linewidths for the three-spin system. The inset shows the dependence of the ZQ linewidth for low ^{29}Si abundances. The ZQ and SQ have similar linewidths, justifying the use of experimental SQ lines to estimate the spin diffusion [34,39]. Compared to experimental dipolar SQ linewidths, e.g., around 20, 120, and 1700 Hz for 1%, 10%, and 100% ^{29}Si abundance, the simulated values are too large for low ^{29}Si abundances and too small for high. This is attributed to the assumed Gaussian line shape to convert the M_2 into a linewidth (cf. Sec. I) in the simulation compared to the more complicated line shapes observed experimentally [39]. The small bumps at 2% ^{29}Si abundance are ascribed to changes in the cutoff distance (cf. Sec. II).

by multiple Gaussians [39]. The latter result is consistent with a fully ^{29}Si labeled powder sample measured in our laboratory under identical settings (data not shown). The labeled sample is mostly used to measure the ^{29}Si thermal-equilibrium signal (see Sec. II). In the simulations, we always assumed a Gaussian line, which leads to an overestimation of the SQ/ZQ linewidth for low and an underestimation for high ^{29}Si abundances.

3. Spin-diffusion coefficient

Converting the simulated ZQ linewidth into a spin-diffusion coefficient D with the nearest-neighbor approximation as given in Eq. (4) results in similar values for D_{NN} (cf. Fig. 5 compared to Ref. [39], e.g., for 4.7% natural abundance $1.7 \text{ nm}^2/\text{s}$ [39] and $3.6 \text{ nm}^2/\text{s}$ in our simulations. The difference between the two values might be explained by the assumed Gaussian line shape in the simulations, leading to too large linewidths for low ^{29}Si abundances (see above). Qualitatively, the dependence of D_{NN} in the nearest-neighbor model [Eq. (4)] with ^{29}Si abundance shows a maximum for less than 1% and a moderate decrease for high abundances. This is in contrast to experiments [39] and previous simulations on a different lattice [60] with both predicting a moderate monotonic increase. The discrepancy might result from an overestimation of the linewidth for low and an underestimation for high abundances (see above).

Estimating the nuclear spin diffusion based on a lattice approach given by Eq. (6) yields $D_{\text{lat}} \approx 136 \text{ nm}^2/\text{s}$ for 4.7% natural abundance. Considering the rather slow convergence

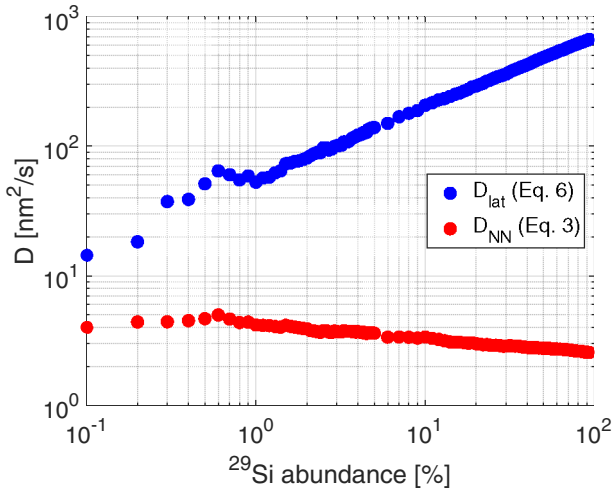


FIG. 5. Spin-diffusion coefficient D extracted from the nearest-neighbor approximation as given in Eq. (4) showing nearly identical values to Ref. [39]. Extracting the spin-diffusion coefficient with a lattice calculation of Eq. (6) gives much larger spin-diffusion values. The difference between the two approaches might result from the contributions of more distant nuclear spins (cf. main text and Fig. 3). The small bumps at 2% ^{29}Si abundance are from the change in cutoff distance (cf. Sec. II and Fig. 4).

of the summed (cumulative) coupling to the central spin (cf. Fig. 3), the estimated spin diffusion is an order of magnitude larger than for the nearest-neighbor model [cf. Eq. (4)] as shown in Fig. 5.

To support the results of the lattice approach, which give an order of magnitude larger natural abundance spin-diffusion coefficient compared to the more commonly used nearest-neighbor approach, we discuss the relaxation experiments by Lee *et al.* [35]. The relaxation experiments in Ref. [35] assumed smaller particles in the simulations than experimentally used to match experiment and theory; i.e., the particles had a diameter of 5 μm , while in the simulations a diameter of 700 nm was used. If spin diffusion would be faster than assumed in the relaxation simulations, this could explain the need for reduced particle sizes in the simulations, possibly supporting the validity of the larger spin-diffusion coefficient of the lattice approach [Eq. (6)]. This might suggest that spin diffusion is faster than estimated in the nearest-neighbor model for silicon [34,39]. Buildup and decay finite-difference simulations shown below cannot discriminate between the two spin-diffusion coefficients as both lead to reasonable results. Therefore, further studies are required to understand how to accurately simulate the spin-diffusion coefficient from first principles.

4. Finite-difference nanoparticle simulations

Spin-diffusion times of spherical 20 nm particles ($D \approx 3.6$ or $136 \text{ nm}^2/\text{s}$) are shorter than 1 min, which is much shorter than the hours-long buildup times. To better understand this slow hyperpolarization buildup, we adopt spatiotemporal finite-difference simulations as introduced in Refs. [40,41]. In these, an outer part of the sample containing the unpaired electrons is considered to be hyperpolarized to the steady-state

polarization continuously with spin diffusion transporting this hyperpolarization toward the core of the particles with relaxation affecting each element at all times. With D from the above simulations, all parameters except the relaxation times $T_{1,\text{in}}$ and $T_{1,\text{out}}$ in the inner (core) and outer (shell) parts of the particles are fixed. Simulated buildups and the best-fit parameters are given in Fig. 6(a). For completeness, both D from the nearest-neighbor approach [Eq. (4), $D = 3.6 \text{ nm}^2/\text{s}$] and the lattice model [Eq. (6), $D = 136 \text{ nm}^2/\text{s}$] were used in the finite-difference simulations providing similar relaxation times at 7 T. For the 3.4 T simulations, the fewer and lower signal-to-noise ratio (SNR) data points complicate the simulations as evident by the weaker variation of the calculated residues with variation of the relaxation times shown in Fig. S14 of the Supplemental Material [33]. Nevertheless, at both magnetic fields the general trend of $T_{1,\text{out}}$ similar to the buildup time and much longer $T_{1,\text{in}}$ persists.

The long $T_{1,\text{in}}$ can be explained by the (assumed) relative absence of paramagnetic defects in the core [cf. Sec. S3 of the Supplemental Material [33], for a basic electron paramagnetic resonance (EPR) characterization of the sample]. With paramagnetic relaxation nearly absent, a rigid crystalline lattice with a Debye temperature of 645 K and liquid-helium temperatures, the relaxation in the core would be vanishing as found in the simulations. The relaxation in the outer (shell) part of the sample is attributed to the naturally forming paramagnetic defects (often called P_b centers) between the silicon core and the oxide shell [10,35]. We would like to note again that we model the relaxation in the outer shell homogeneously, while in reality this will depend on the distance to the nearest paramagnetic center.

The buildup simulations can be adjusted to simulate the measured room-temperature decays [cf. Fig. 2(b)] and are shown for the 20 and 50 nm particles in Figs. 6(b) and 6(c). The relaxation time in the inner (core) part of the particles is between 1 and 2 h, while at the outer (shell) part between 0.2 and 0.5 h for both particles and both choices of spin-diffusion coefficients (3.6 and $136 \text{ nm}^2/\text{s}$). For the faster spin diffusion, the simulation model shows a weaker sensitivity to $T_{1,\text{in}}$ compared to slower spin diffusion (cf. Fig. S15 of the Supplemental Material [33]). The similar results for vastly different spin-diffusion coefficients provide a posterior justification for the simplifying assumption in the finite-difference simulations of including only spin diffusion between neighboring radial segments. While this assumption likely leads to an underestimation of the time to hyperpolarize nuclear spins at the very center of the particle (it requires steps through all radial segments), this is practically not of relevance as the spin diffusion is faster compared to other processes as discussed in the following.

Both the buildup and the decay simulations estimate the relaxation time in the core ($T_{1,\text{in}}$) to be longer than the measured experimental timescale (buildup or decay time), while the relaxation time in the shell ($T_{1,\text{out}}$) is similar to the experimental timescale. Furthermore, the effect of faster spin diffusion reduces the model's sensitivity to $T_{1,\text{in}}$. With the relaxation in the shell determining the buildup or decay time, this results in a monoexponential behavior as only one parameter is rate limiting [31]. Thus, the problem of understanding the polarization dynamics in silicon nanoparticles is mostly

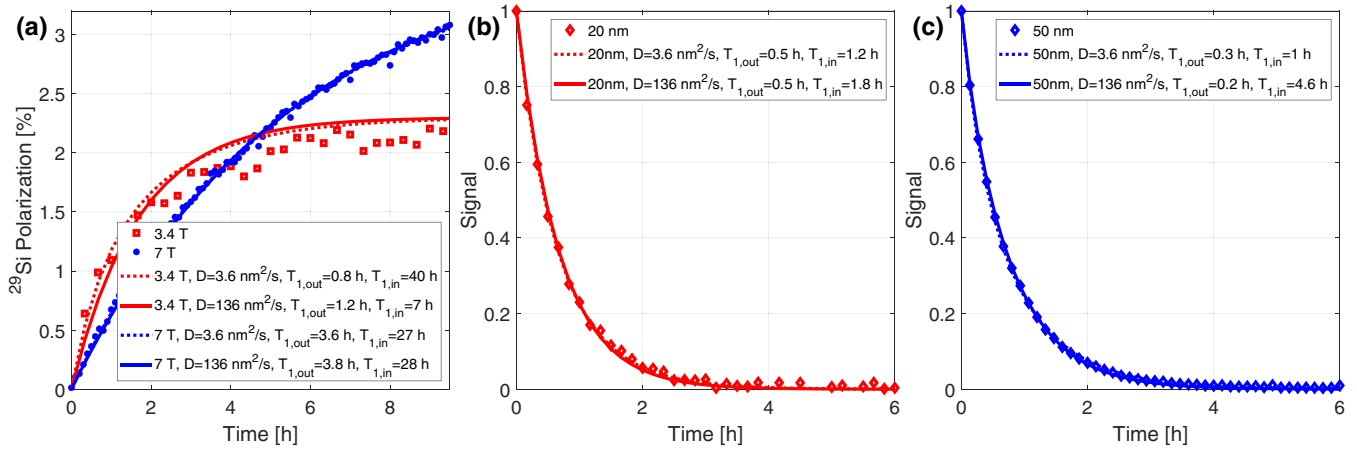


FIG. 6. (a) Experimental and simulated buildups at 3.4 and 7 T [cf. Fig. 2(a)] of the 20 nm particles. (b), (c) Experimental and simulated room-temperature decays of the 20 and 50 nm particles at 9.4 T [cf. Fig. 2(b)]. The simulated buildups and decays are characterized by a slow relaxation in the inner (core, $T_{1,\text{in}}$) part of the particle and faster relaxation in the outer (shell, $T_{1,\text{out}}$) part of the particle. The choice of the spin-diffusion coefficient D has little effect on the fits. The different T_1 values at 3.4 T are attributed to few, low SNR data points, resulting in an insensitive least-squares residue (cf. Fig. S13 of the Supplemental Material [33]).

reduced to understanding the processes in the shell. Below, we discuss the possible origin of the long relaxation times in silicon nanoparticles.

Owing to the low temperatures, the rigid silicon lattice, and the observed dependence of the hyperpolarization dynamics (buildup and decay times) on the thermal electron polarization (temperature and field) as shown in Fig. 2(a) and Fig. S7 of the Supplemental Material [33], as well as in Ref. [10], the nuclear relaxation is attributed to paramagnetic relaxation. The measured EPR spectra indicate a mixture of different P_b defects (cf. Sec. S3 of the Supplemental Material [33]). The P_b center is described as a dangling bond centered on a silicon atom with a 200–400 MHz hyperfine coupling to the central Si site, ~ 40 MHz for next-nearest Si atoms, and around 10 kHz for Si atoms two unit cells away [10]. With the paramagnetic relaxation rate and the DNP transfer rate depending on the square of the hyperfine coupling, the central Si atom of the P_b center will hyperpolarize and relax orders of magnitude faster than the other Si sites close to a P_b center if it is occupied with an NMR-active ^{29}Si atom. The fast hyperpolarization and decay of the central ^{29}Si of a P_b center suggests that these sites are the primary polarization pathway if the hyperpolarization could be transported to the bulk [10].

The strong frequency differences between nuclei near the P_b center due to different hyperfine couplings suppress spin diffusion by nuclear dipolar flip-flops. However, the electron itself modifies the nuclear spin diffusion in its vicinity, enabling non-energy-conserving nuclear flip-flops. Specifically, a term that describes an energy-conserving simultaneous electron flip-flop and nuclear flip-flop (electron-nuclear four-spin flip-flop) [61,62], which is proportional to the electron dipolar coupling D_{ee} (mediating electron flip-flops) and the nuclear dipolar coupling d_{nn} (nuclear flip-flops), could cause nuclear spin diffusion close to the electron. We remark that the electron-nuclear four-spin flip-flops do not depend on the linewidths but directly on the dipolar couplings of the involved spins. In addition, the energy difference between the nuclei involved in electron-nuclear four-spin flip-flops is dominated

by the hyperfine energy differences, possibly ranging into the megahertz range, compared to the nuclear dipolar energy differences on the order of hundreds of hertz giving rise to the nuclear linewidths. Isotope enrichment, i.e., the increase in ^{29}Si abundance, would increase the nuclear dipolar couplings by decreasing the average distance between ^{29}Si spins, eventually resulting in an increased electron-nuclear four-spin flip-flop rate.

In Ref. [9], silicon nanoparticles were synthesized with 4.7% (natural abundance), 10%, and 15% ^{29}Si abundance. After hyperpolarization, the room-temperature T_1 times of the different particles were measured with 20° monitoring RF pulses every 4 min. The measured T_1 times were 48, 35, and 17 min for 4.7%, 10%, and 15% ^{29}Si , respectively [9]. After correcting for the monitoring RF pulses [31], the relative ratio for relaxation rates ($1/T_1$) between the 4.7%, 10%, and 15% ^{29}Si particles is 1:2.5:8.2.

The nuclear dipolar couplings d_{nn} scale with the third inverse power of the average nuclear-nuclear distance ($d_{nn} \propto r_{n-n}^{-3}$). With r_{n-n}^{-3} inversely proportional to the isotope abundance f , the dipolar coupling is proportional to the isotope abundance ($d_{nn} \propto f$). Assuming a quadratic dependence on the electron-nuclear four-spin flip-flop effective Hamiltonian matrix element, the nuclear flip-flop rate (spin diffusion) close to the electron would scale with the dipolar coupling squared and, hence, with the isotope abundance squared. The relative ratio of the isotope abundances squared between the 4.7%, 10%, and 15% ^{29}Si particles is 1:4.5:10.2. Considering this simple estimation, the ratios between the isotope abundances are compatible with the RF corrected relaxation rates. Remaining discrepancies might in parts arise from effects not considered in the simple estimation above, e.g., reduced frequency differences between neighboring ^{29}Si atoms near the electrons due to their smaller distance and higher numbers of ^{29}Si atoms to couple to. For reduced frequency differences, the electron line shape might cause a further increase of the electron-nuclear four-spin flip-flop rate.

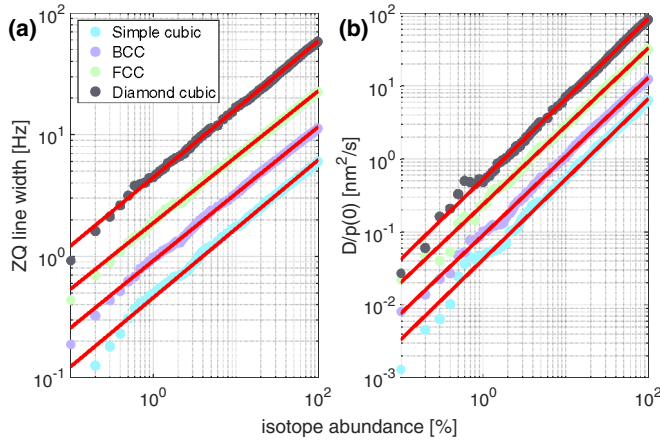


FIG. 7. (a) Simulated ZQ linewidth and (b) geometric contribution to the spin-diffusion coefficient $D/p(0)$ for generalized simple cubic, bcc, fcc, and diamond cubic lattices. The fit parameters are summarized in Table I and can be used to calculate the respective quantities with an analytic expression [cf. main text and Eqs. (7) and (8)].

We highlight that an increase in the ^{29}Si abundance leaves the total number of ^{29}Si nuclei per P_b center with a ^{29}Si atom at its strongly hyperfine-coupled central site constant. Thus, it appears unlikely that the long room-temperature relaxation times of silicon nanoparticles are simply due to inefficient paramagnetic relaxation by the P_b centers as in this case the T_1 relaxation times should be rather independent of the isotope abundance.

C. Generalization to other crystal structures

In the following, we will adopt the SQ and ZQ linewidth as well as the spin-diffusion simulations to simple cubic, body-centered cubic (bcc), face-centered cubic (fcc), and diamond cubic crystal structures. The gyromagnetic ratio is set to $10^6 \text{ rad}/(\text{s} \cdot \text{T})$ and the lattice constant to $1 \text{ \AA}$. An effective formula to estimate both the linewidth and spin diffusion is given based on the simulations. Therefore, adoption to other spin-1/2 crystals involves the change of gyromagnetic ratio, lattice constant, and isotope abundance as discussed below. We note that for crystals with a multiatomic basis the spin diffusion of one species can be described by the sublattice of the respective atomic species; e.g., in sodium fluoride (NaF), each of the two atomic species forms an fcc lattice, although heteronuclear dipolar couplings might influence the linewidths.

In Sec. S7 of the Supplemental Material [33], the dipolar cutoff distance similar to Fig. 3(b) and the SQ and ZQ linewidths similar to Fig. 4(a) are compared for all considered crystal structures. The results are very similar to the above-presented case of silicon. The ZQ lines of the different crystal structures are compared in Fig. 7(a) in a double logarithmic plot. The increasing number of atoms per conventional unit cell (1, 2, 4, and 8 for simple cubic, bcc, fcc, and diamond cubic) results in stronger dipolar couplings and with this larger linewidth.

TABLE I. Fit parameters (prefactor u and exponent m) from Fig. 7, fitted with Eqs. (7) and (8).

	Simple cubic	BCC	FCC	Diamond cubic
u_{ZQ}	0.456(11)	0.918(12)	1.88(2)	4.44(5)
m_{ZQ}	0.568(8)	0.552(4)	0.544(3)	0.563(4)
u_{D}	0.042(2)	0.090(2)	0.237(6)	0.526(14)
m_{D}	1.103(14)	1.080(6)	1.075(8)	1.103(8)

Experimentally, the ZQ linewidth is difficult to measure. Fortunately, the SQ linewidth is a good approximation for the ZQ linewidth (cf. Fig. S12 of the Supplemental Material [33]) and this can be experimentally measured. The spectral density p of the fitted experimental line shape evaluated for zero frequency [$p(0)$] can be multiplied with prefactors described in Eq. (6). Figure 7(b) shows the spin-diffusion coefficient D divided by $p(0)$, which is a geometric quantity with some prefactors.

The fit parameters corresponding to Fig. 7 for the ZQ linewidths and $D/p(0)$ are summarized in Table I. Multiplication with the isotope abundance, gyromagnetic ratio, and lattice constant gives rise to the ZQ (and to some degree SQ) linewidth and spin-diffusion coefficient. Specifically,

$$\Delta\nu_{\text{ZQ}} = \frac{\tilde{\gamma}_n^2}{\tilde{a}_0^3} u_{\text{ZQ}}(f)^{m_{\text{ZQ}}}, \quad (7)$$

$$D = \frac{\tilde{\gamma}_n^4}{\tilde{a}_0^4} u_{\text{D}}(f)^{m_{\text{D}}} p_{\text{ZQ}}(0), \quad (8)$$

with $\tilde{\gamma}_n = \gamma_n/(10^6 \text{ rad}/(\text{s} \cdot \text{T}))$ and $\tilde{a} = a/(1 \text{ \AA})$ the rescaled nuclear gyromagnetic ratio and lattice constant. γ_n is the gyromagnetic ratio, e.g., $53.190 \times 10^6 \text{ rad}/(\text{s} \cdot \text{T})$ for ^{29}Si . f is the isotope abundance in %. The prefactor u and exponent m are summarized in Table I and describe the dependence of the spin diffusion on the underlying crystalline lattice and isotope abundance. To give an example of Eq. (7), for 4.7% ^{29}Si abundance, $\tilde{\gamma}_n = 53.190$, $\tilde{a} = 5.431$, $u_{\text{ZQ}} = 4.44$, and $m_{\text{ZQ}} = 0.563$, we find a ZQ linewidth of $53.190^2/5.431^3 \times 4.44 \times 4.7^{0.563} \approx 187 \text{ Hz}$ in good agreement with the simulated 191 Hz from Fig. 4 (cf. discussion of this value above).

The above approach to generate effective scalings for the ZQ/SQ linewidths and spin-diffusion coefficient could be used to derive similar expressions for other crystal structures. The used simulation files can be found online (cf. Data availability).

IV. CONCLUSIONS

Silicon nanoparticles with a natural core-shell geometry, i.e., paramagnetic defects on the outside of the particles (P_b centers) and a crystalline core with few defects, have room-temperature T_1 relaxation times $\geq 40 \text{ min}$ for particles with an average particle size of 20 nm. Lattice simulations of the SQ and ZQ lines can be used to simulate the buildup and decay dynamics of the particles, which reveal that the polarization dynamics is determined by the shell (outer) part of the particles containing the interface defects. Generalized, analytic expressions for the ZQ linewidth and spin-diffusion coefficient, considering the interaction with distant nuclei,

are derived from simulations for cubic crystal structures with further extension to other structures possible.

More generally, nanoparticles a few tens of nanometers in size can exhibit hyperpolarization enhancements and relaxation times similar to larger micrometer-sized particles if bulk and surface defects (dangling bonds) are inhibited from causing strong paramagnetic relaxation. The demonstrated and explained long room-temperature relaxation times in nanoparticles leave future increases in polarization levels as the main challenge to unlock the potential of hyperpolarized nanoparticle MRI.

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G.v.W., G.K., S.K., and M.E. conceptualized the research. G.v.W., K.T., N.Ş., A.H., V.G., and G.K. performed experiments and analyzed the data. G.v.W. and M.E. developed the simulation model. G.v.W. and N.Ş. implemented and performed the simulations. G.v.W. prepared the original draft. S.K. and M.E. acquired funding and provided supervision. J.O.M., V.P.L., S.K., and M.E. provided resources. All authors reviewed and edited the draft.

The authors declare that they have no competing interests.

DATA AVAILABILITY

Experimental and simulation data together with Matlab scripts are openly available from Ref. [66].

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