Temperature dependent study of Na_xSi_{136} type II Si clathrate spin dynamics

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We report the temperature dependence of relaxation time (T_1) and phase memory (T_M) of Na dopants in type II Si clathrate films utilizing electron paramagnetic resonance (EPR). There is a rich history directed at understanding defect properties in conventional diamond Si motivated by its dominant position in the microelectronics industry. Type II Si clathrates represent an alternative crystal structure to diamond Si. This cage-like inclusion compound is made up of a Si lattice with interstitial "guests" situated inside the cages. Our recent advances have allowed the synthesis of Na guest, type II Si clathrate films with low enough Na concentration for the Na to be considered a dopant and the spin dynamics of isolated Na donors to be investigated.[1]

EPR gives insight into the electron spin dynamics of the Na donors and their placement and interactions within the Si cages. The naturally occurring Na isotope, ^{23}Na, has nuclear spin 3/2 with the EPR spectrum exhibiting four hyperfine lines associated with the interaction of the electron and nuclear spins. Hyperfine features associated with Na atoms in neighboring cages, clustered Na, and interactions with ^{29}Si isotopes on the cage, are also observed.[2] Pulsed-EPR spectra exhibit clear spin echo signals with T_1 times in the hundreds of microseconds at temperatures near 7 K, and T_M times above a microsecond. The effects of various parameters (i.e. temperature, magnetic field center, Na concentration) on the relaxation time and phase memory are reported. The relaxation time exhibits thermally activated behavior from 6-14K suggesting an Orbach relaxation pathway. Strong similarities and important differences between the spin dynamics of Na in clathrate and P in diamond Si will be discussed along with Na's potential to function as a qubit in quantum applications. This work was supported by National Science Foundation award #2114569.
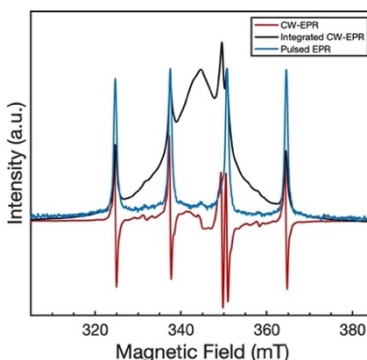
[1] Y. Liu et al., Appl. Phys. Rev., **8**, 4(2021).
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Figure 1 EPR spectra of Na doped type II Si clathrate.
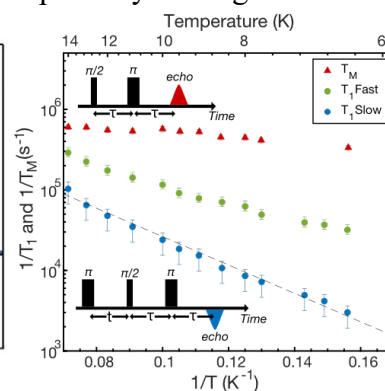
Figure 2 Na_xSi_{136} type II clathrate T_1 and T_M times.

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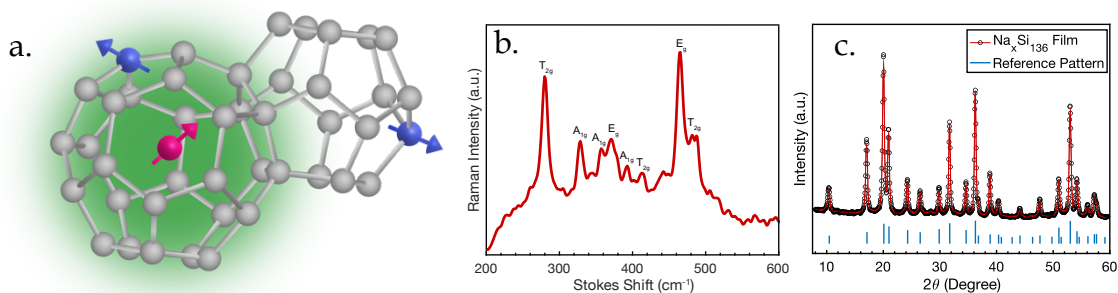
Supplementary Information

Figure 3 (a) Type II Si clathrate with spin 3/2 Na donor nucleus (pink) and donor electron (green) inside large Si cage (grey) with spin 1/2 ^{29}Si (blue). (b) Raman spectrum of Na_xSi_{136} film (c) XRD of Na film Na_xSi_{136} with reference pattern

Silicon clathrates represent an alternative crystalline form of silicon with a direct or nearly direct bandgap. The material has a much higher absorption coefficient, a larger bandgap, and more efficient light emission properties than diamond silicon.[1] As a result it is being actively explored for potential applications in solar energy conversion and optoelectronics. Typical synthesis pathways, however, introduce Na guests into the clathrate cages. Na contributes electrons and the materials have metallic properties. We have focused on reducing the Na concentration to the point where the Na can be viewed as a donor atom and the clathrate as a semiconductor.[1] This creates a situation where Na in the clathrate plays a role analogous to P in diamond Si (Si:P). Much like Si:P, the spin properties of Na in Si clathrate could have interesting application as qubits but in an optically active, larger bandgap material.[2] This is the first study to explore spin relaxation time and phase memory in the type II silicon clathrate system. The paramters examined in this study are key initial indicators for a materials potential for application in quantum systems. While the spins decay more rapidly than Si:P, doping levels are much higher and the material is much more defective. This suggests decay times can be increased and during this talk we will discuss approaches for acheiving this.

To synthesize sodium doped type II Si clathrate films, a two-step procedure adapted from powder synthesis has been developed.[1] First, bulk sodium metal is evaporated from a Ta crucible and diffused into a silicon wafer under an inert argon atmosphere to form NaSi. The wafer is then annealed under vacuum to thermally decompose the film into clathrate. The clathrate films are then characterized through a variety of techniques including Raman spectroscopy, x-ray diffraction (XRD), and scanning electron microscopy. Inversion recovery measurements of Na_xSi_{136} (0<x<24) type II clathrate films were performed from 6.4-25K. Each inversion recovery experiment was performed with the field centered around the highest field hyperfine line around 364 mT at 9.81 GHz,which is the right most peak in *Fig. 1*. The inversion recovery transients from 6.4-14K can be seen in *Fig. 2* before (inset with linear intensity scale) and after (main panel with log scale) inverting and subtracting the ground state magnetization taken from the end of the transient where the electrons have returned to the ground state and the signal plateaus. The time for this to occur increases with decreasing temperature indicating that temperature in this region play affect the relaxation times of type II Si clathrates. This is consistent with other silicon materials.[3]
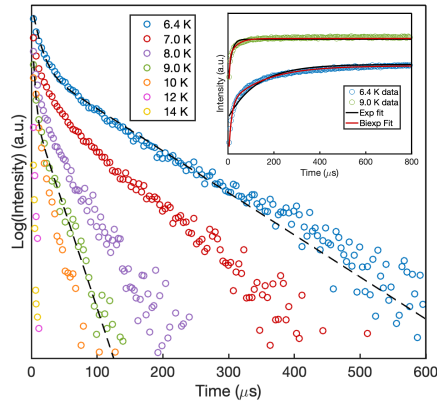
Figure 4 Semi-log plot of the inversion recovery experiments from 6.4-14K with black dashed lines showing the biexponential fit.

A simple exponential did not produce a good fit to the inversion recovery transients. A biexponential fit described the relaxation times more accurately. The slow decaying term in the biexponential is more commonly attributed to the relaxation time with the fast decaying term attributed to spectral diffusion or other effects.[4] The biexponential fit still does not completely describe the system and this could be indication of multiple relaxation times at work due to inhomogeneity in the samples. More work would need to be done to fully understand this process. However, these current biexponential fits provide an indication of the trends the relaxation times follow. Measurements were taken from 6.4 K (the lowest temperature achieved by the equipment) up to 25 K. The inverted echo from the three-pulse inversion recovery experiment became difficult to locate and measure above about 14 K so only those temperatures below this were used to extract the temperature dependence. A similar method was used to extract T_M from the echo decay experiments. Less of a deviation from exponential behavior was observed especially at higher temperatures and trends were established utilizing a single exponential.

The mechanism behind the spin relaxation was also examined. The Arrhenius plot of $\log(1/T_1)$ in Fig. 1b shows a linear dependence over the temperatures of 6.4-14 K. This dependence suggests the two-phonon Orbach mechanism may be dominating at these temperatures.[5] The slope of this fit gives an activation energy to the excited state of ΔE=40.6 K consistent with previous reports of clathrate binding energy.[2] The T_M curve seems to have more spin diffusion contributions than just T_1, which is not being the limiting factor in T_M over this temperature range. In comparison, for Si:P, T_M saturates at low temperature but is largely bounded by T_1 and the curves almost match up at higher temperatures.[6] The behavior we are seeing can potentially be explained by the phase memory experiencing this saturation at even higher temperatures. Differences in Na concentration of Na_xSi_{136} films with carrier densitys of roughly 10^{18} cm^{-1} and 10^{20} cm^{-1} were also explored.

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