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Computational Study of the Silicon Vacancy in 3C-SiC and Perspectives for Quantum Technologies

Tommaso Fazio[1,2,a*], Giuseppe Fisicaro[1,b], Ioannis Deretzis[1,c], Elisabetta Paladino[2,1,d] and Antonino La Magna[1,e]

[1]Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e Microsistemi (CNR-IMM), Z.I. VIII Strada 5, I-95121 Catania, Italy

[2]Dipartimento di Fisica e Astronomia "Ettore Majorana", Università di Catania, Via S. Sofia 64, I-95129 Catania, Italy

[a*]tommaso.fazio@dfa.unict.it, [b]giuseppe.fisicaro@imm.cnr.it, [c]ioannis.deretzis@imm.cnr.it, [d]elisabetta.paladino@dfa.unict.it, [e]antonino.lamagna@imm.cnr.it,

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Abstract. We theoretically study point defects in 3C-SiC for applications in Quantum Technologies, focusing on the neutral silicon vacancy, with an electron spin of 1, magnetically interacting with the SiC nuclear spin bath containing Si-29 and C-13 nuclei. Initially, the system's energetics are explored with *ab-initio* methods based on the Density Functional Theory. Thereon, we apply a Hahn-echo sequence on the electron spin and study the effects of the bath dynamics on the electron spin's coherence. The Electron Spin Echo Envelope Modulation (ESEEM) phenomenon, due to single nuclear spin flipping processes, and the overall decay, or decoherence, due to the electron spin's entanglement with the bath, are examined. We exploit the Cluster Correlation Expansion (CCE) theory to calculate an approximate version of the coherence function and study its behavior.

1. Introduction

Silicon carbide (SiC) is a well-known material of interest for different technological applications, ranging from shields in accelerators [1] to power devices in electronics [2] and quantum sensors of magnetic field and temperature gradients [3]. For Quantum Technology (QT) applications, the color centers generated by point-like defective configurations constitute the active states. Out of the many SiC polytypes, the most studied ones in the literature are the hexagonal 4H- and 6H-SiC [4], due to the availability of high-quality samples. Recently though, the fabrication techniques and the defectivity control of cubic 3C-SiC during the growth process have been greatly enhanced (see e.g. Ref. [5]). Consequently, QT driven investigations dedicated to 3C-SiC based systems could raise an increasing interest in the near future.

Due to the relative lack of dedicated studies, our research deals with point defects in 3C-SiC. In particular, we considered the neutral silicon vacancy (V_{Si}) magnetically interacting with a bath of naturally occurring Si-29 and C-13 paramagnetic nuclei, i.e., a composite system of interest for QTs because of its optical and coherent control properties [3]. The V_{Si} center, in its neutral charge configuration, can be modeled as a spin-1 defect that evolves in the magnetic environment constituted by the spin-1/2 nuclear spin bath around it. Various control techniques can be applied to the electron spin, such as the use of microwave control pulses that are highly transition-selective [4], effectively reducing the three electron spin's eigenstates to two in the resulting dynamics, so that it can be considered as a qubit. Here we study the effect of the Hahn-echo sequence, an established control technique allowing to refocus the spin coherence resulting from the effect of static magnetic field inhomogeneity and applied in ref. [6] to investigate the residual decoherence of divacancy defects in 4H-SiC. To theoretically model such sequence of control pulses, we have employed the Cluster Correlation Expansion (CCE) theory [7]. Such theory consists in breaking up the bath in uncorrelated clusters containing different numbers of interacting nuclear spins, and thereby expressing the qubit coherence as a product of all the contributions coming from the different clusters.

The rest of the paper is organized as follows: section 2 deals with the *ab-initio* methods used to calculate the energetics of a neutral silicon vacancy in 3C-SiC. In section 3, based on the system's parameters derived via the *ab-initio* methods, we numerically calculate the spin coherence evolution under the Hahn-echo sequence, at the first and second order of the CCE expansion, and derive estimates of the decoherence time. Finally, in section 4 our conclusions and ideas for further work are discussed.

Table 1: Formation energies of a neutral silicon vacancy in 3C-SiC and total magnetization for different fcc supercells and k-point sets. Different calculation schemes for the defect's spin are examined, such as the non-polarized (np), non-collinear (nc) and spin-orbit coupling (soc) schemes.

fcc supercell	number of atoms	k points	Form.Ener.(eV)	Tot.Mag.(Bohr mag/cell)
3x3x3 np	53	4 4 4	7.30	not defined
3x3x3 nc	53	4 4 4	7.30	(0.00 0.00 0.09)
3x3x3 soc	53	4 4 4	7.30	(0.00 −0.00 0.09)
4x4x4 np	127	4 4 4	7.72	not defined
4x4x4 nc	127	4 4 4	7.61	(0.00 0.00 2.00)
4x4x4 soc	127	4 4 4	7.61	(0.00 −0.00 2.00)
5x5x5 np	249	4 4 4	7.89	not defined
5x5x5 nc	249	4 4 4	7.65	(0.00 −0.00 2.00)
5x5x5 soc	249	4 4 4	7.64	(0.00 0.00 2.00)
5x5x5 np	249	L	7.89	not defined
5x5x5 nc	249	L	7.65	(0.00 −0.00 2.00)
5x5x5 soc	249	L	7.65	(0.00 0.00 2.00)
6x6x6 np	431	4 4 4	7.93	not defined
6x6x6 np	431	L	7.93	not defined
6x6x6 nc	431	L	7.66	(0.00 0.00 2.00)
6x6x6 soc	431	L	7.65	(0.00 −0.00 2.00)
7x7x7 np	685	3 3 3	7.94	not defined
7x7x7 np	685	L	7.94	not defined
7x7x7 nc	685	L	7.66	(−0.00 0.00 2.00)
7x7x7 soc	685	L	7.65	(0.00 −0.00 2.00)

2. *Ab-Initio* Defect Formation Energy

Ab-initio methods based on Density Functional Theory (DFT) are important to calculate, among others, energetic and electronic structure properties of molecules and solids [8]. They can also be used to calibrate magnetic Hamiltonians associated to electron spins interacting with nuclear spin baths, allowing to calculate, for instance, the hyperfine tensor components. The Hamiltonian can be written as

$$\mathcal{H} = \mathcal{H}_e + \sum_i \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}_i - \sum_i \mu_N \mathbf{B}\cdot\mathbf{g}_N\cdot\mathbf{I}_i + \sum_{i\neq j}\mathbf{I}_i\cdot\mathbf{P}\cdot\mathbf{I}_j \quad (1)$$

$$\mathcal{H}_e = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E\left(S_x^2 - S_y^2\right) - \mu_B\mathbf{B}\cdot\mathbf{g}_e\cdot\mathbf{S} \quad (2)$$

The first term in Eq. (1) is the electron spin Hamiltonian, which is composed by the Zero-Field Splitting (ZFS) terms (first and second term of Eq. (2)), describing the electron spin's self-interaction, and the Zeeman interaction with an external applied magnetic field (last term of Eq. (2)). The last three terms of Eq. (1) are the magnetic hyperfine interactions between the electron and the nuclear spins, the Zeeman terms for each nuclear spin and the dipolar interactions between nuclear spins, respectively. In this context, *ab-initio* methods are used to capture physical effects due to the 3D

distribution of the spin density in the vicinity of the qubit, which extends significantly until the third neighbor shell in 3C-SiC crystal structure. These effects are not included by the semiclassical approximation, where the electron and nuclear spins are viewed as interacting point magnetic dipoles.

For our computational study we have used the free and open-source Quantum Espresso (QE) code [9] for the energetics. Thus, we have started from the energetics of the defect, by calculating the formation energy of a neutral silicon vacancy within a 3C-SiC supercell with variable size (see Table 1 above). We have used a 4×4×4 k-point grid for the smaller supercells and an L point sampling for the larger ones, to obtain a good balance between the accuracy of the calculation and its computational cost. Note that from a 4×4×4 supercell onward the system's magnetization reaches a stable value, which is the one we expect for an electron spin-1. Furthermore, an interesting thing to note is the importance of correctly modeling the system's spin properties, as this can greatly enhance the convergence of the calculation (see Fig. 1 below). Then we studied other charge states for the V_{Si} and calculated the corresponding formation energies as functions of the electrochemical potential within the bandgap of a 7×7×7 3C-SiC supercell (see Fig. 2 below). We have observed that both the neutral and charged states can be stable in a given range of the electrochemical potential, which can be varied with doping. For instance, the neutral V_{Si} we are interested in is the most stable defect for a p-doped 3C-SiC sample. These calculations have been performed with ultrasoft pseudopotentials.

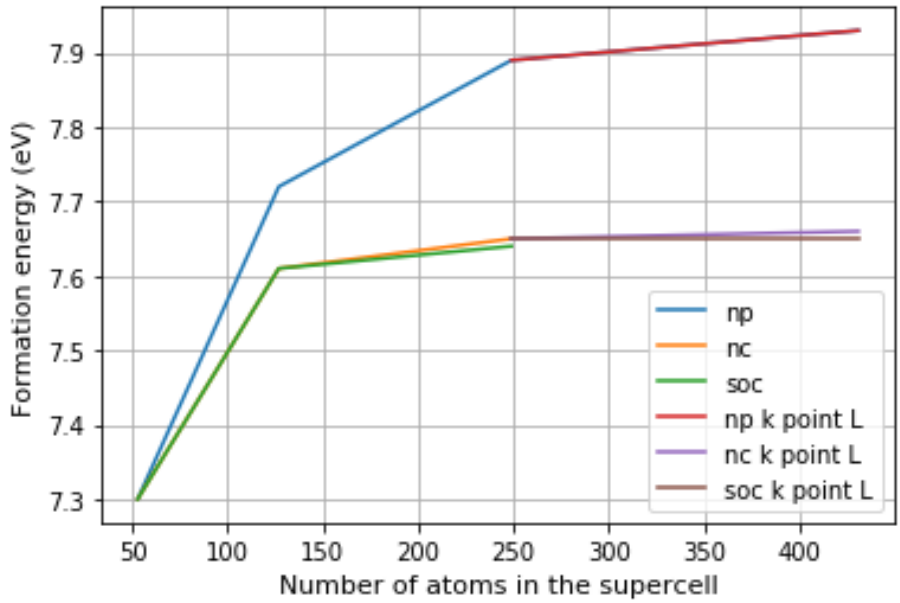

Fig. 1: Finite scaling analysis of the formation energy for different calculation schemes. Note the faster approach to convergence with a non-collinear (nc) scheme, and adding the spin-orbit coupling (soc), as opposed to the non-polarized (np) scheme.

3. Application of CCE Theory

In order to tackle the electron-nuclear spin bath problem, we applied the CCE theory [7]. Such theory allows to calculate the off-diagonal component of a solid-state spin quantum system's density matrix, or coherence. In particular, a Python 3 code developed and benchmarked by us, implementing the CCE theory found in literature [10], has been used to calculate the coherence under a Hahn-echo sequence. The CCE equations are the following:

$$U_C^{HE} = e^{-i\mathcal{H}_C\tau} e^{-i\pi S_x} e^{-i\mathcal{H}_C\tau} \tag{3}$$

$$\rho_C(t) = U_C \rho_C(0) U_C^{\dagger} \tag{4}$$

$$\tilde{\rho}_{ab}^{\{C\}} = \frac{\langle a|\rho_C(t)|b\rangle}{\prod_{C'} \tilde{\rho}_{ab}^{\{C'\subset C\}}} \quad (5)$$

$$\rho_{ab} = \tilde{\rho}_{ab}^{\{0\}} \prod_i \tilde{\rho}_{ab}^{\{i\}} \prod_{i,j} \tilde{\rho}_{ab}^{\{ij\}} \cdots \quad (6)$$

Eq. (3) is the Hahn-echo unitary operator describing the dynamics of the density operator associated to the electron spin interacting with a generic cluster C in Eq. (4), while the Hamiltonian in the exponentials is given by Eqs. (1) and (2), where the only nuclear spins within cluster C are present. Eq. (4) is then substituted in Eq. (5), which is the definition of the contribution to the coherence coming from cluster C. Finally, the coherence in Eq. (6) is calculated as the product of all the contributions coming from the different *uncorrelated* clusters. Therefore, since the expansion of Eq. (6) can be cut from a given cluster dimension onward, the order of approximation of the theory is defined as the number of nuclear spins inside the biggest clusters we include in Eq. (6). The benchmark was done against Seo et al. [6], whose study is focused on a divacancy in 4H-SiC.

Our results, obtained with the customized code, confirm the ones found in the literature [6], and extend them to a neutral V_{Si} in 3C-SiC. In particular, the decay of the coherence is obtained already at the second order of approximation of the CCE theory, or CCE2 level, as shown in Fig. 3 below, left panel. The figure shows the coherence of the qubit under the Hahn-echo sequence, for an external applied magnetic field of 65 G. The blue curve is the coherence calculated at the first order of approximation of the theory, or CCE1 level, where the only contributions considered are from non-interacting nuclear spins. The rapid oscillations of the curve are known as the ESEEM phenomenon in the literature, and are expected to be reproduced at the CCE1 level. At the CCE2 level (orange curve), where also contributions from clusters containing pairs of nuclei are considered, the decay appears. Therefore, pairwise interactions within the bath are responsible for a coherence decay that is not cancelled by the echo [6]. We observe from the right panel of Fig. 3 that, under the approximations performed, the predicted coherence decay is in the milliseconds range. The figure shows the CCE2 coherence and a stretched exponential function fitting its decaying envelope, as well as the optimal values, obtained via a curve-fitting algorithm, for the Hahn-echo coherence time T_2 and the stretching factor n of the exponential. These values are 1.124 and 2.448 ms, respectively, for the 150 G curve.

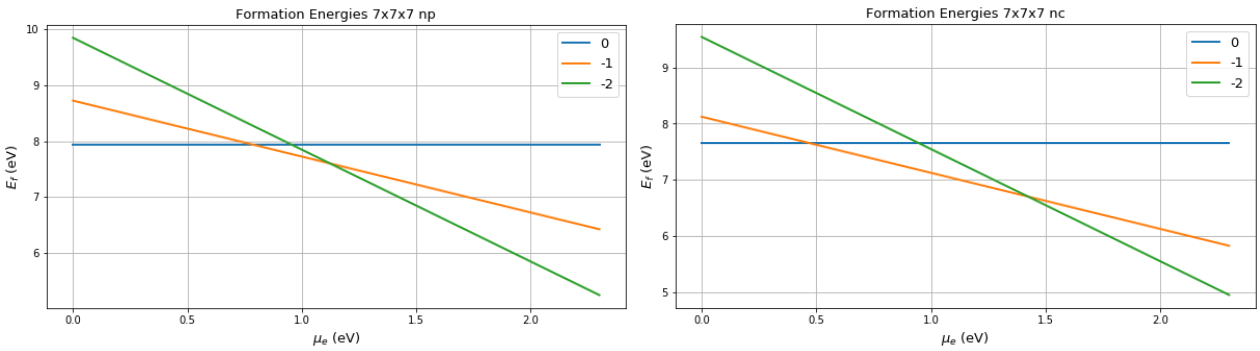

Fig. 2: Graph showing the formation energies of a V_{Si} with 0, -1 and -2 charge states as a function of the electrochemical potential within the bandgap for a 686-atom non-polarized (left) and non-collinear (right) 3C-SiC supercell, respectively.

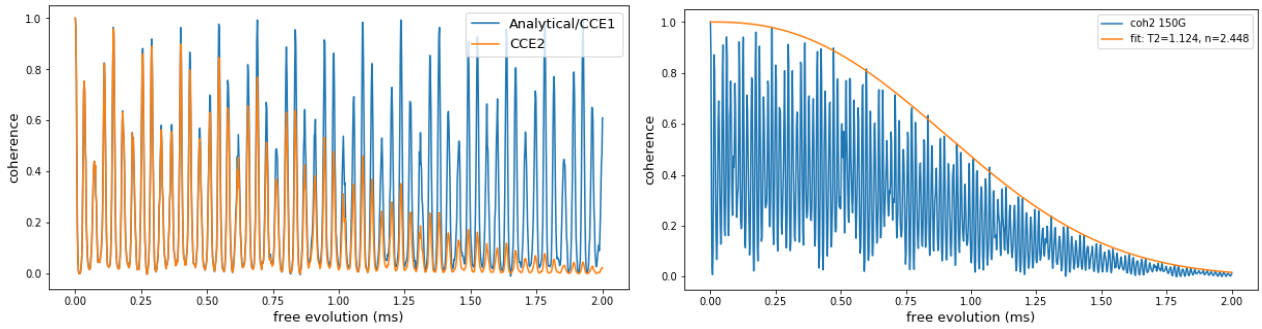

Fig. 3: Coherence of a neutral V_{Si} in 3C-SiC as a function of free evolution time, within a Hahn-echo sequence, for an external magnetic field of 65 and 150 G, respectively. The result is averaged over 50 different baths. Left: the blue curve is the analytical/CCE1 result and the orange one is the CCE2. Notice the coherence decay in the milliseconds range. Right: CCE2 coherence with a fitting exponential function $\exp(-(t/T_2)^n)$ and the optimal values for the parameters T_2 and n, in ms, in the inset.

4. Conclusions

In conclusion, we have used the density functional theory to study the formation energy of the silicon vacancy in 3C-SiC, analyzing its charge states and establishing their range of stability as a function of the Fermi level. Moreover, by applying the CCE theory by means of our in-house code, we have evaluated within reliable approximations the ESEEM phenomenon and the decoherence of the spin associated to the defect when Hanh spin-echo protocols with different magnetic field values are applied to the system. The estimated V_{Si} coherence time in 3C-SiC is in the milliseconds range.

We hope that our work can inspire new studies on the cubic polytype of SiC, which is gaining new attention within the scientific literature. As for our future perspectives, we are going to complete a magnetic calibration of the Hamiltonian and use the *ab-initio* calculated values of the hyperfine tensor in our code, to analyze the differences with the semiclassical ones. The preliminary results obtained with a module of QE called Quantum Espresso Gauge-Including Projector Augmented-Wave (QE-GIPAW) code [11, 12], show significant deviation with respect to the semiclassical estimates of the model parameters. Finally, we are going to extend such analysis to other defects in SiC and other technologically relevant materials like gallium nitride (GaN).

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