University of Groningen

Summary of Internship

Numerical Quantum-chemistry studies of transition metal impurities in SiC

Author:
Mikel Martínez Garrido
(S4752295)

Supervisor:
Prof. Caspar van der Wal
Second supervisor:
Prof. Remco Havenith
Daily supervisor:
Rick Beltman MSc.

Zernike Institute for Advanced Materials

Physics of Nanodevices

May 20, 2025

1 Internship Description

1.1 Introduction

This work is a continuation of my previous research undertaken during my Bachelor thesis project, titled *Theoretical Modelling of Tungsten Defects in SiC* [1]. It consisted of a group theory analysis of the crystal system, through which the electronic structure and optical transition rules were derived for three different charges states: W_{Si}, W_{Si}^{+1} and W_{Si}^{-1}. It was followed by preliminary *ab-initio* simulations and an attempt to obtain an effective Hamiltonian of the system analytically.

At the end of the project, an interesting result was noted. The experimental data on the tungsten defects in SiC [2] showed a discrepancy with the rest of the experimental data on the transition metal defects in SiC. The results for vanadium [3] [4], molybdenum [5], chromium [6] [7], tantalum [8], and niobium defects [9] indicated that, for heavier defects, the energy difference between the ground and first excited states increases. Indeed, large energy separations in these systems are crucial for robust, efficient, and high-fidelity quantum telecom devices. As shown for vanadium and molybdenum in [10], such systems support clean optical transitions, enhanced coherence times, and improved control over quantum states.

However, this trend does not persist in the case of heavier defects such as tungsten. My research internship focused on addressing this anomaly and seeking an explanation for this physical phenomenon. This question has been addressed through numerical simulations and computational quantum chemistry software packages. A deeper understanding of the behaviour of tungsten within SiC crystals would contribute to the design and future development of advanced quantum telecom devices.

1.2 Research Activities and Findings

During the initial months of the internship, the open-source OpenMolcas software package was used. Initially, a simplified model (the point charge model) system was used to investigate the electronic structure of several transition metal defects: vanadium, chromium, niobium, molybdenum, tantalum, tungsten, and rhenium. A set of basic point charges was placed around the defects to simulate the crystal field effect produced by SiC. The resulting energy-level splittings and degeneracies were found to be consistent with the preliminary group theory analysis.

Subsequently, the positions of the point charges around the defects were systematically varied to examine how their electronic structures responded. Although the distances between the defects and point charges were not optimised to accurately replicate the SiC crystal field, the objective was to identify relative inconsistencies among the defects. It was observed that as the point charges approached the defects, orbital mixing occurred earlier in the heavier defects than in the lighter ones. Specifically, when the initial distance was reduced by a given percentage, the d-orbitals remained as the ground state for defects such as vanadium and chromium, whereas in the cases of tungsten, tantalum, and rhenium, the d-orbitals exchanged with the s-orbitals, resulting in the s-orbitals becoming the new ground state. Although the SiC structure is distorted around the defects, this deformation was sufficiently minor not to affect the aforementioned observations. Based on these results, the following hypothesis was proposed: for lighter atoms, the d-orbitals constitute the ground state, whereas for heavier atoms, the electronic structure within SiC becomes increasingly hybridised or restructured, with the s-orbitals forming the ground state instead of the d-orbitals. This phenomenon is attributed to the more complex electronic structure of the heavier defects, whose free-atom configurations become significantly perturbed when interacting with neighbouring

atoms in the SiC lattice.

In the final stage of this internship, the initial hypothesis was tested through more accurate and computationally intensive simulations. For this purpose, the BAND software package—an advanced periodic density functional theory (DFT) code developed as part of the Amsterdam Modelling Suite—was employed. Two supercells, 3×3×3 and 5×5×2, were constructed for the 4H-SiC polytype. A defect was introduced at the origin of each supercell, and following geometry optimisation, single-point energy calculations were carried out. Spin–orbit coupling was included in these final simulations, resulting in the splitting of energy levels into Kramers doublets.

As expected, the volume of the optimised structures did not vary by more than 0.4% across the different defects introduced. Nevertheless, the single-point calculations revealed a rich electronic structure, with the orbitals corresponding to each energy level post-processed and visualised. The results were subsequently compared to those obtained from the point charge model. This comparison, along with the broader analysis, will be compiled in a comprehensive report to be submitted to the *Physics of Nanodevices* research group.

Although this final phase of the project was time-consuming and computationally demanding, it yielded several significant results. The most significant part of the input code and the data post-processing and analysis is in a repository on GitHub: GitHub Link. The essential part and larger output files are included on the Y-drive system of RUG-FSE, in the directory of the Quantum Devices team. These results are intended to support the group's ongoing research. The report will serve as a foundation for future researchers, whether to build upon this work directly or to incorporate its insights into their own investigations.

References

[1] M. M. Garrido, "Theoretical modelling of tungsten defects in sic," University of Groningen, 2024. [Online]. Available: https://fse.studenttheses.ub.rug.nl/33256/.

[2] F. C. B. Andreas Gällström Björn Magnusson, "Optical identification and electronic configuration of tungsten in 4h- and 6h-sic," *Physica B: Condensed Matter*, vol. 407, pp. 1462–1466, 10 May 2012. DOI: 10.1016/j.physb.2011.09.062. [Online]. Available: https://www.sciencedirect.com/science/article/pii/S0921452611009537.

[3] C. M. Gilardoni, "Optically addressable spins in silicon carbide and 2d materials: The role of symmetry and spin-orbit coupling," Ph.D. dissertation, University of Groningen, 2021, p. 146. DOI: 10.33612/diss.192999111. [Online]. Available: https://pure.rug.nl/ws/portalfiles/portal/192999113/Complete_thesis.pdf.

[4] G. Wolfowicz, C. P. Anderson, B. Diler, O. G. Poluektov, F. J. Heremans, and D. D. Awschalom, "Vanadium spin qubits as telecom quantum emitters in silicon carbide," *Science Advances*, vol. 6, no. 18, eaaz1192, 2020. DOI: 10.1126/sciadv.aaz1192. [Online]. Available: https://www.science.org/doi/abs/10.1126/sciadv.aaz1192.

[5] C. M. Gilardoni, "Optically addressable spins in silicon carbide and 2d materials: The role of symmetry and spin-orbit coupling," Ph.D. dissertation, University of Groningen, 2021, p. 56. DOI: 10.33612/diss.192999111. [Online]. Available: https://pure.rug.nl/ws/portalfiles/portal/192999113/Complete_thesis.pdf.

[6] B. Diler, S. J. Whiteley, C. P. Anderson, *et al.*, "Coherent control and high-fidelity readout of chromium ions in commercial silicon carbide," *npj Quantum Information*, vol. 6, no. 11, pp. 1–6, 2020. DOI: 10.1038/s41534-020-0247-7. [Online]. Available: https://www.nature.com/articles/s41534-020-0247-7.

[7] N. T. Son, A. Ellison, B. Magnusson, *et al.*, "Photoluminescence and zeeman effect in chromium-doped 4h and 6h sic," *Journal of Applied Physics*, vol. 86, no. 8, pp. 4348–4353, 1999. DOI: 10.1063/1.371368. [Online]. Available: https://pubs.aip.org/aip/jap/article-abstract/86/8/4348/488179/Photoluminescence-and-Zeeman-effect-in-chromium?redirectedFrom=fulltext.

[8] B. Magnusson, N. T. Son, A. Csóré, *et al.*, "Excitation properties of the divacancy in 4h-sic," *Physical Review B*, vol. 98, p. 195 202, 2018. DOI: 10.1103/PhysRevB.98.195202. [Online]. Available: https://journals.aps.org/prb/pdf/10.1103/PhysRevB.98.195202.

[9] A. Gällström, B. Magnusson, S. Leone, *et al.*, "Optical properties and zeeman spectroscopy of niobium in silicon carbide," *Physical Review B*, vol. 92, p. 075 207, 2015. DOI: 10.1103/PhysRevB.92.075207. [Online]. Available: https://journals.aps.org/prb/abstract/10.1103/PhysRevB.92.075207.

[10] C. M. Gilardoni, "Optically addressable spins in silicon carbide and 2d materials: The role of symmetry and spin-orbit coupling," Ph.D. dissertation, University of Groningen, 2021. DOI: 10.33612/diss.192999111. [Online]. Available: https://pure.rug.nl/ws/portalfiles/portal/192999113/Complete_thesis.pdf.