International Scientific Conference 20 UNITECH 26

INTERNATIONAL SCIENTIFIC CONFERENCE
19-21 November 2026
GABROVO

FIRST PRINCIPLES INVESTIGATION OF THE LOCAL COORDINATION DEPENDENT ELECTRONIC PROPERTIES OF Ga INTERSTITIAL DEFECTS IN GaP NANOWIRES

Sena Guler Ozkapi

Vocational School of Technical Sciences, Trakya University, Edirne, 22030, Turkey

**Corresponding author: senaguler@trakya.edu.tr*

Abstract

In this study, the effects of Ga interstitial defects on the structural stability and electronic properties of a hydrogen-passivated GaP nanowire are investigated using first-principles calculations based on density functional theory. Two different defect configurations are considered in which the Ga atom placed at an interstitial site is surrounded by four Ga atoms or four P atoms. Electronic band structure calculations reveal that the pure GaP nanowire exhibits semiconductor character with a band gap of approximately 2.47 eV. The introduction of Ga interstitial defect into the pure GaP nanowire induces the formation of defect-related electronic states within the forbidden energy band. It has been observed that the band gap narrows significantly in the configuration with four neighbouring Ga atoms, while in the configuration with four neighbouring P atoms, an electronic band intersects the Fermi energy level. Results reveal that the electronic properties of the GaP nanowire depend significantly not only on the presence of the Ga interstitial defect but also on the local atomic environment where the defect is located. The results demonstrate that the local coordination of interstitial defects in GaP nanowires plays an important role in determining the electronic structure.

Keywords: GaP nanowire; interstitial defect; density functional theory; electronic structure.

INTRODUCTION

Due to its good optical and electrical performance, Gallium phosphide (GaP) is commonly found in semiconductor devices. GaP is a III–V semiconductor with a wide bandgap and a high refractive index, possessing remarkable electronic and optical properties and an important material for optical devices, light emitting diodes, and photoelectrochemical applications [1-3].

Reducing GaP to the nanoscale enables the emergence of quantum confinement effects and size-dependent electronic properties. While bulk GaP has indirect bandgap at room temperature, reducing the material to the nanoscale can lead to significant changes in its electronic structure [4]. These properties make GaP-based nanostructures attractive for various applications, such as integrated photonics, nonlinear optics, photodetectors, and quantum technologies [5].

Owing to the high surface-to-volume ratio in nanowires, dangling bonds can influence the nanowire's electronic properties by giving rise to surface-induced electronic states near the band gap. Therefore, surface passivation with hydrogen largely suppresses surface-induced electronic states by saturating dangling bonds, thereby enabling a more reliable investigation of the nanowire's intrinsic electronic properties and defect-induced states [6-12].

Point defects can significantly affect the electronic structure of semiconductors, leading to the formation of new electronic levels within the band gap, alterations in charge carrier behaviour, and changes in the material's electrical and optical properties

This is an open access article licensed under Creative Commons Attribution 4.0 International
Print ISSN: 1313-230X, Online ISSN: 3033-1404

[13-15]. In particular, interstitial defects, local structural disruptions caused by atoms located outside their normal atomic positions in the crystal lattice, can lead to significant changes in electronic properties due to bond interactions with neighbouring atoms [16-22].

Although there have been various theoretical studies on the electronic properties and intrinsic point defects of GaP, research on the effects of interstitial defects on the electronic structure of GaP nanowires appears to be relatively limited. In particular, a comparative investigation of how the presence of an interstitial atom in different local atomic environments affects structural stability and electronic properties is important for understanding the defect–local coordination relationship. Accordingly, in this study, the effect of a Ga interstitial defect on the structural and electronic properties of a hydrogen-passivated GaP nanowire was investigated using first-principles calculations based on density functional theory. Two different local coordinations were considered, in which the Ga interstitial atom is surrounded by four Ga atoms and four P atoms; the relative stabilities of the configurations were compared, and the effects of local coordination on the electronic structure were examined through band structure and total and partial density of states (DOS/PDOS) calculations.

EXPOSITION

GaP nanowires were investigated using first-principles calculations based on density functional theory (DFT) [23,24]. The calculations were performed using the Quantum ESPRESSO software package [25]. Electron exchange-correlation interactions were described using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA) [26]. A cut off energy of 40 Ry was used for the plane waves. The k points in the first Brillouin zone were set to 1x1x6 in the band structure calculations, and 1x1x30 in the DOS calculations to ensure high accuracy at certain computational costs.

The nanowire model was constructed along the [111] crystallographic direction of GaP with a zinc-blende crystal structure. Based on the distance between the outermost atomic centers of the Ga and P atoms, the diameter of the GaP nanowire core was determined to be approximately 1.4 nm. The unsaturated bonds on the nanowire surface were passivated with hydrogen atoms. The modelled GaP nanowire is shown in Figure 1.

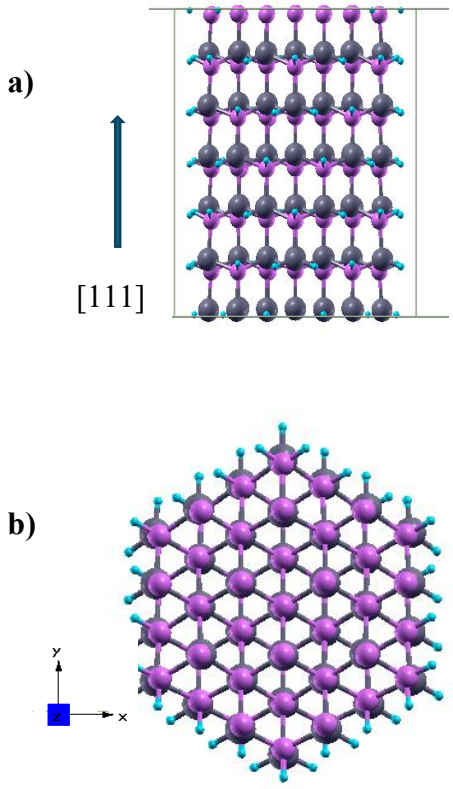


Fig. 1. *Atomic structure of hydrogen-passivated zinc-blende GaP nanowire modelled along the [111] crystallographic direction: a) side view and b) top view along the nanowire axis. (Grey atoms: Ga, Purple atoms: P, Blue atoms:H)*

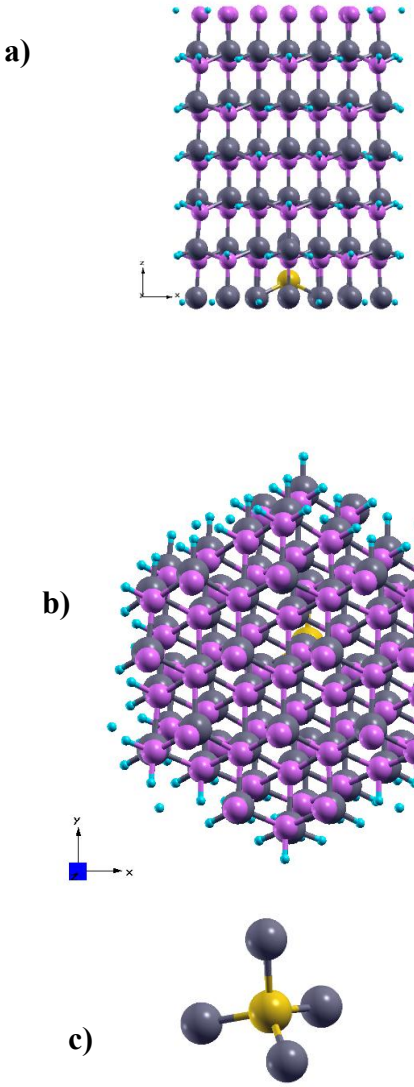


Fig. 2. *The atomic structure of the GaP nanowire containing an interstitial Ga defect surrounded by four Ga atoms, following geometric optimization: a) side view, b) top view at a slight angle, and c) the local coordination environment consisting of the interstitial Ga atom and its four nearest-neighbour Ga atoms. The interstitial Ga atom is shown in a different colour (yellow) to distinguish it from the other Ga atoms*

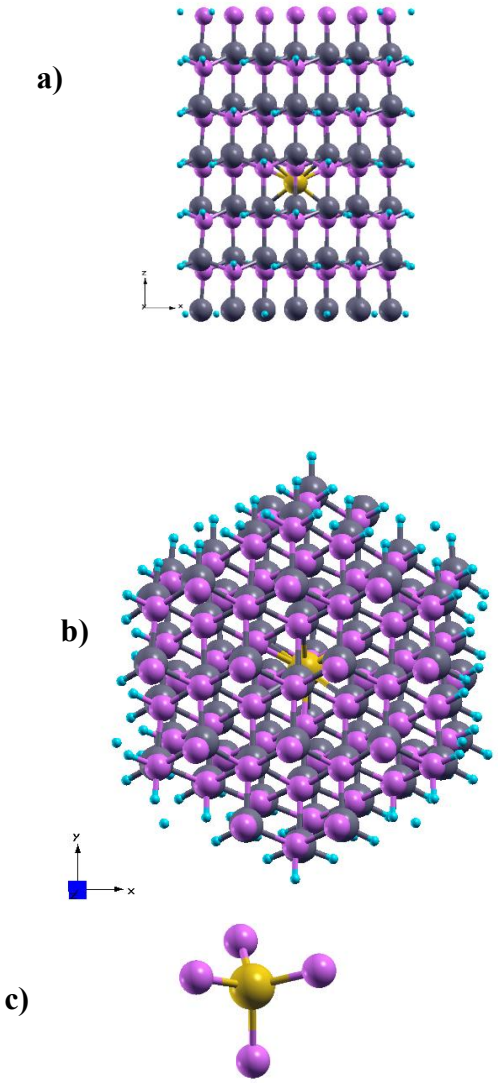


Fig. 3. *The atomic structure of the GaP nanowire containing an interstitial Ga defect surrounded by four P atoms, following geometric optimization: a) side view, b) top view at a slight angle, and c) the local coordination environment consisting of the interstitial Ga atom and its four nearest-neighbour P atoms. The interstitial Ga atom is shown in a different colour (yellow) to distinguish it from the other Ga atoms*

To investigate the effects of the interstitial Ga atom on its local atomic environment, two different tetrahedral interstitial sites were considered. In the first configuration, the interstitial Ga atom was placed in a local environment formed by four Ga atoms (Fig.2), while in the second configuration, it was placed in a local environment formed by four P atoms (Fig.3). Geometric optimization was performed for both defect structures, and the relative energetic stability of the configurations was evaluated by comparing the total energies of the optimized structures. The calculation results showed that the structure in which the Ga atom is placed in a tetrahedral interstitial position, surrounded by four Ga atoms, has a lower total energy and is therefore more energetically stable.

To determine the effect of the Ga interstitial defect on the electronic properties of GaP nanowires, the electronic band structures and density of states for pure nanowire and nanowires containing Ga interstitial defects surrounded by four Ga and four P atoms were investigated.

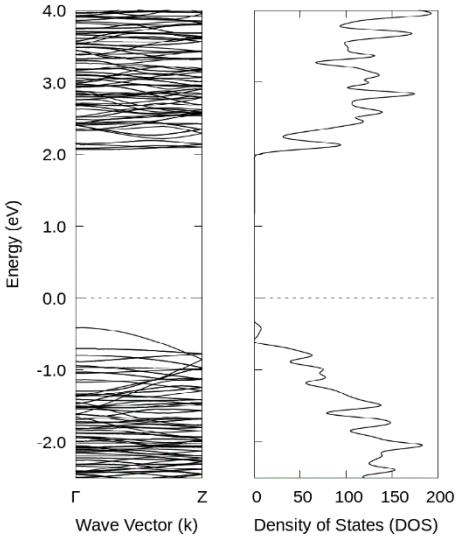


Fig.4. *Electronic band structure (left) and total electronic density of states (DOS) (right) of the pure GaP nanowire. The Fermi energy level is set to 0 eV.*

The electronic band structure and total density of states (DOS) of the pure GaP nanowire are shown in Figure 4. Upon examination of the electronic band structure, it can be seen that there are no electronic states around the Fermi energy level (0 eV) and that a distinct bandgap exists between the valence band and the conduction band. The calculated bandgap is approximately 2.47 eV, a result that demonstrates that the pure GaP nanowire exhibits semiconducting behavior. The total density of states (DOS) results also support the band structure findings, as the density of states is zero around the Fermi level. Furthermore, electronic states are observed to be concentrated at different energy levels in the valence and conduction bands.

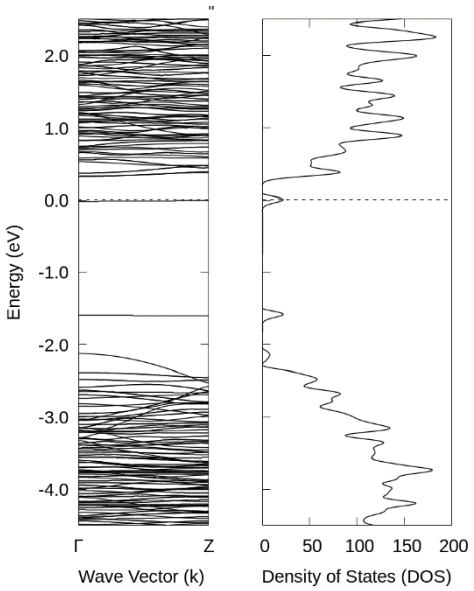


Fig.5. *Electronic band structure (left) and total electronic density of states (DOS) (right) of the GaP nanowire containing a Ga interstitial defect surrounded by four Ga atoms. The Fermi energy level is set to 0 eV.*

The electronic band structure and total density of states (DOS) of the GaP nanowire containing a Ga interstitial defect surrounded by four Ga atoms are shown in Figure 5. Compared to the pure GaP nanowire, it is evident that the Ga interstitial defect induces significant changes in the electronic band structure. Specifically, new electronic states emerge within the band gap, and a band with low dispersion forms near

the Fermi energy level. Furthermore, a relatively flat band is observed at approximately −1.6 eV. The contributions observed within narrow energy ranges corresponding to these bands in the total density of states further support the changes identified in the band structure.

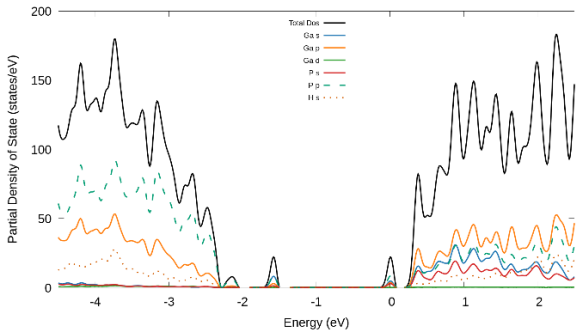


Fig.6. *Total density of states (DOS) of the GaP nanowire containing a Ga interstitial defect surrounded by four Ga atoms and the partial density of states (PDOS) showing the orbital contributions of Ga, P, and H atoms.*

The partial density of states (PDOS) results for the GaP nanowire containing a Ga interstitial defect surrounded by four Ga atoms are presented in Figure 6. In the low-energy region of the valence band, specifically between −4.5 and −2.3 eV, the P-p orbitals provide the dominant contribution, with Ga-p orbitals also making significant contributions in this range. A narrow electronic state observed at approximately −1.6 eV below the Fermi level is found to possess primarily Ga-s orbital character. Near the Fermi level, the electronic states receive contributions from the s and p orbitals of both Ga and P atoms in varying proportions. In the conduction band region, contributions arise from Ga-s and Ga-p orbitals, as well as P-s and P-p orbitals, whereas the contribution from Ga-d orbitals within the examined energy range is quite limited.

The electronic band structure and total density of states (DOS) of the GaP nanowire containing a Ga interstitial defect surrounded by four P atoms are shown in Figure 7. Compared to the pure GaP nanowire, the Ga interstitial defect leads to the formation of new electronic states within the band gap. Notably, one of the bands near the Fermi energy level crosses this level.

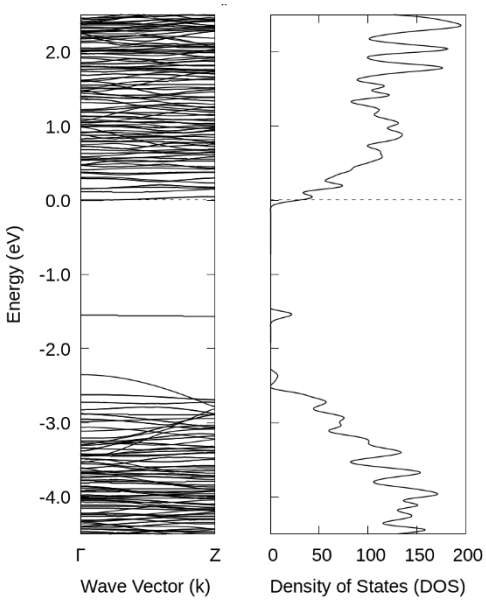


Fig.7. *Electronic band structure (left) and total electronic density of states (DOS) (right) of the GaP nanowire containing a Ga interstitial defect surrounded by four P atoms. The Fermi energy level is set to 0 eV.*

This assessment is further supported by the presence of electronic states near the Fermi level in the total density of states. Furthermore, a low-dispersion band observed at approximately −1.6 eV may point to the existence of localized electronic states. When compared to the structure with an interstitial defect surrounded by four Ga atoms, it becomes evident that the local atomic environment influences the energy distribution of the electronic states generated by the Ga interstitial defect. These results demonstrate that the impact of a Ga interstitial defect on the electronic properties of the GaP nanowire can vary depending on the local atomic neighbourhood.

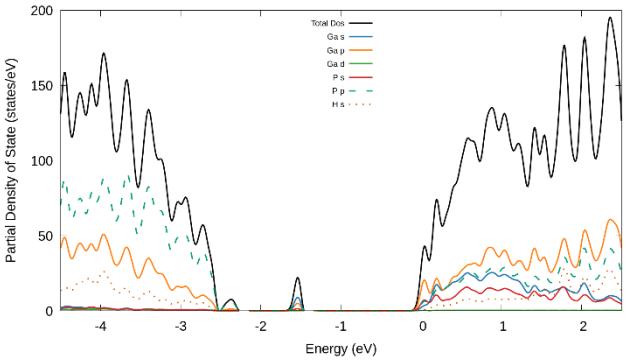


Fig.8. *Total density of states (DOS) of the GaP nanowire containing a Ga interstitial defect surrounded by four P atoms and the partial density of states (PDOS) showing the orbital contributions of Ga, P, and H atoms.*

The partial density of states (PDOS) results for the GaP nanowire containing a Ga interstitial defect surrounded by four P atoms are presented in Figure 8. In the energy range of approximately −4.5 to −2.5 eV within the valence band, the P-p orbitals provide the dominant contribution, while the Ga-p orbitals also make a significant contribution in this region. A narrow electronic state observed at approximately −1.6 eV is found to possess primarily Ga-s orbital character. Electronic states near the Fermi energy level are contributed to by Ga-s, Ga-p, and P-p orbitals. In the conduction band region, in addition to the notable contributions from Ga-p and P-p orbitals, there are also contributions from Ga-s and P-s orbitals, whereas the contribution of Ga-d orbitals within the examined energy range is quite limited.

CONCLUSION

In this study, the effects of a Ga interstitial defect in a hydrogen-passivated GaP nanowire on its structural and electronic properties, depending on the local atomic neighbourhood, were investigated within the framework of density functional theory. For this purpose, two different structures were considered, in which the Ga interstitial atom was surrounded by four Ga and four P atoms, and the results were compared with those of the pure GaP nanowire.

Geometric optimization revealed that the structure with four Ga atoms in its neighbourhood has a lower total energy than the structure with four P atoms in its neighbourhood. Electronic band structure calculations showed that the pure GaP nanowire exhibits semiconducting behaviour with a bandgap of approximately 2.47 eV. The Ga interstitial defect in the four Ga atom neighbouring structure reduced the bandgap. In contrast, the band crossing is observed near the Fermi energy level in the four P-atom-neighbouring structure.

Partial density of states analyses have shown that P-p orbitals dominate in the low-energy region of the valence band in both defective structures, while Ga-s orbitals primarily contribute to the narrow electronic states at approximately −1.6 eV. As a result, it was determined that the local atomic neighbourhood of the Ga interstitial defect significantly affects the electronic band structure of the GaP nanowire and the electronic states around the Fermi level.

ACKNOWLEDGMENTS: *The numerical calculations reported in this paper were fully performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA resources).*

REFERENCE

[1] Liu, B. Y., Wei, L. W., Ding, Q. M. & Yao, J. L. Synthesis and optical study of GaP nanowires. Nanotechnology 15, 1745–1748 (2004).

[2] Ohashi, K., McCann, J. & Bockris, J. O. M. Stable photoelectrochemical cells for the splitting of water. Nature 266, 610–611 (1977).

[3] Standing, A. et al. Efficient water reduction with gallium phosphide nanowires. Nat Commun 6, 7824 (2015).

[4] G. Liao, N. Luo, K.-Q. Chen, H. Q. Xu, "Electronic Structures of Free-Standing Nanowires made from Indirect Bandgap Semiconductor Gallium Phosphide," *Scientific Reports*, **6**, 28240 (2016).

[5] Y. Wang, Z. Pan, Y. Yan, Y. Yang, W. Zhao, N. Ding, X. Tang, P. Wu, Q. Zhao, Y. Li, "A

review of gallium phosphide nanophotonics towards omnipotent nonlinear devices," *Nanophotonics*, **13**(18), 3207–3252 (2024).
[6] Schmidt, T. M. (2006). Hydrogen and oxygen on InP nanowire surfaces. *Applied Physics Letters, 89*, 123117.
[7] Zhang, Y., Shi, Y.-M., Bao, Y.-Z., Yu, X., Xie, Z.-X., & Ning, F. (2017). Effect of surface passivation on the electronic properties of GaAs nanowire : A first-principle study.
[8] Cuevas, J. L., De Santiago, F., Ramírez, J., Trejo, A., Miranda, Á., Pérez, L. A., & Cruz-Irisson, M. (2018). First principles band gap engineering of [1 1 0] oriented 3C-SiC nanowires. *Computational Materials Science, 142*, 268-276.
[9] Cahangirov, S., & Ciraci, S. (2009). First-principles study of GaAs nanowires. *Physical Review B, 79*, 165118.
[10] Huang, S.-P., Xu, H., Bello, I., & Zhang, R.-Q. Q. (2010). Tuning Electronic Structures of ZnO Nanowires by Surface Functionalization: A First-Principles Study. *Journal of Physical Chemistry C, 114*, 8861-8866.
[11] Vo, T., Williamson, A., & Galli, G. (2006). First principles simulations of the structural and electronic properties of silicon nanowires. *Physical Review B, 74*, 045116.
[12] Zhuo, K., & Chou, M. (2013). Surface passivation and orientation dependence in the electronic properties of silicon nanowires. *Journal of Physics: Condensed Matter, 25*.
[13] Gao, Y.-L., Sun, D., Jiang, X., & Zhao, J.-J. (2019). Point defects in group III nitrides: A comparative first-principles study. *Journal of Applied Physics*.
[14] Oba, F., Choi, M., Togo, A., & Tanaka, I. (2011). Point defects in ZnO: an approach from first principles. *Science and Technology of Advanced Materials, 12*.
[15] Janotti, A., & Van De Walle, C. (2007). Native point defects in ZnO. *Physical Review B, 76*, 165202.
[16] Freysoldt, C., Grabowski, B., Hickel, T., Neugebauer, J., Kresse, G., Janotti, A., & Van de Walle, C. G. "First-principles calculations for point defects in solids." *Reviews of Modern Physics*, **86**, 253–305 (2014).
[17] Cherati, N. G., Hashemi, A., & Gali, A. (2025). From mono- to hexa-interstitials: Computational insights into carbon defects in diamond. *Physical Review Research*.
[18] Zhang, Y., Jiang, S., Li, Y., Chen, C., Chen, Z., & Wang, X.-L. (2024). The influence of point defects on the electronic structures and optical properties of 3C-SiC. *AIP Advances*.
[19] Maji, R., Luppi, E., Degoli, E., & Contreras-García, J. (2022). Insight into the inclusion of heteroatom impurities in silicon structures.. *Physical chemistry chemical physics : PCCP*.
[20] Dhamotharan, K., Wang, S.-H., Hayes, S. P., Ramasse, Q., Phillips, L., Major, J. D., Zoppi, G., Clark, S. J., & Mendis, B. (2025). Electronic and vibrational properties of interstitial clusters in degenerately boron-doped silicon. *Journal of Physics: Condensed Matter, 37*.
[21] Ventura, C. I., & Fuhr, J. D. (2018). Effect of N interstitial complexes on the electronic properties of GaAs1−xNx alloys from first principles. *Physical Review Materials*.
[22] Kazakova, O., Varvarin, M. O., Galstian, I., Rud, M., & Len, E. (2025). Effect of oxygen vacancies and interstitial zinc and boron atoms on the electronic structure and properties of ZnO: DFT investigation. *Surface*.
[23] P.C. Hohenberg, w. Kohn, Inhomogeneous Electron Gas Phys. Rev. B 136 (1964) 864.
[24] W.Kohn, L.J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev A 140 (1965) 1133.
[25] P. Giannozzi et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys. Cond. Mat. 21 (2009) 39.
[26] Perdew, J.P., Burke, K. and Ernzerhof, M. (1996) Generalized Gradient Approximation Made Simple. Physical Review Letter, 77, 3865-3868.