08

Nature of stable and metastable states of the electronic structure of vacancy threads on the surface of silicon carbide

© S.A. Kukushkin, A.V. Osipov

Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences, St. Petersburg, Russia
E-mail: andrey.v.osipov@gmail.com

Received October 20, 2025
Revised November 14, 2025
Accepted November 15, 2025

A system containing silicon vacancies on the surface of SiC-3*C* silicon carbide has been studied by the density functional theory. It is shown that the initial state of a system with a zero magnetic moment is metastable. The Si atom on the vacancy thread is a strong centre of attraction for electrons, despite their Coulomb repulsion. Therefore, it is advantageous for an electron from a weakened carbon atom in the C−C bond to tunnel to a silicon atom in the Si−C bond and thereby reduce its length from 1.96 Åto 1.92 Å. Relaxation of the elastic energy of the Si−C bond provides a decrease in the total energy by 0.29 eV. During tunnelling, the electron reverses its spin, doubling the total magnetic moment. Thus, the negative Hubbard correlation energy of electrons (negative-U) is realized in the system. In the presence of an external magnetic field, electrons can tunnel through any closed loop of vacancy threads, ensuring the diamagnetism of this material.

Keywords: silicon carbide, silicon vacancies, negative correlation energy, magnetic moment, negative-U, diamagnetism.

DOI: 10.61011/TPL.2026.03.63060.20538

Unique physical, mechanical, and electrical properties make silicon carbide (SiC) one of the most promising wide-gap semiconductors [1,2]. Since both silicon and carbon are group IV elements, SiC has certain features that A^2B^6 and A^3B^5 crystals are lacking. Specifically, silicon vacancies V_{Si} in SiC have a magnetic moment, which in itself distinguishes this semiconductor from others [1]. In addition, the SiC surface also differs greatly in its properties both from the surfaces of A^2B^6 and A^3B^5 crystals and from the surfaces of Si and C crystals. For example, the surfaces of silicon Si(111) and diamond C(111) with the (1×1) reconstruction are antiferromagnetic [3], while the surfaces of 3*C*-SiC(111) and 3*C*-SiC($11\bar{1}$) with the (1×1) reconstruction are, on the contrary, ferromagnetic. Presumably, it is the silicon vacancies in SiC that are responsible for the anomalous magnetic susceptibility, diamagnetic properties, and terahertz emission of SiC containing V_{Si} [4–6], since ideal SiC without V_{Si} does not have these properties.

It is very hard to create V_{Si} in SiC, since the approximate formation energy of uncharged V_{Si} is 8 eV [7], while the formation energy of carbon vacancies V_C is approximately 2 times lower. Only V_C are formed if one tries to produce vacancies in SiC thermally. Therefore, V_{Si} in SiC are obtained through irradiation with high-energy particles: both electrons [8] and neutrons or protons [9]. A large number of unwanted defects form in this case, and the concentration of V_{Si} still remains very low [8]. A fundamentally new approach to SiC production was proposed in [10]: cubic SiC is formed through a chemical reaction of a Si crystal with carbon monoxide gas (CO). When 3*C*-SiC is synthesized by this method, silicon vacancies are one of the intermediate reaction products that are essential to the growth of a SiC film. The method was developed to a significant extent in [11,12] with the aim of obtaining an even greater concentration of silicon vacancies and increasing the 3*C*-SiC layer thickness. Since the approximate formation energy of silicon vacancies in a Si crystal is 3.3 eV [13], a large number of vacancies form near the surface when a Si crystal is heated in vacuum to a temperature on the order of 1300 °C within several minutes. If a thin layer of silicon on its surface is converted at this point into 3*C*-SiC in a chemical reaction with CO gas

$$2\mathrm{Si}(crystal) + \mathrm{CO}(gas) = 3C\text{-}\mathrm{SiC}(crystal) + \mathrm{SiO}(gas)\uparrow, \quad (1)$$

a certain fraction of vacancies in silicon are transformed into V_{Si} in 3*C*-SiC [11,12]. Following the completion of Si–CO reaction, a certain fraction of formed vacancies are „sealed“ in the SiC layer, but most of them merge into pores in silicon under the SiC film. Since the diffusion of CO gases into the reaction zone and SiO from the reaction zone proceeds largely through vacancies, the diffusion coefficients increase by approximately two orders of magnitude. This, in turn, leads to an approximately order-of-magnitude increase in resulting thickness of the SiC layer (compared to the thickness obtained using the method [11]). However, regardless of whether SiC samples were obtained by the method [10] or synthesized by the method [11,12], they all contain a certain concentration of silicon vacancies V_{Si}, which leads to the emergence of a number of unusual phenomena: anomalous magnetic susceptibility, diamagnetic properties, and Aharonov–Bohm and de Haas–van Alphen quantum effects manifested at room temperature. In addition, they emit electromagnetic waves in the terahertz

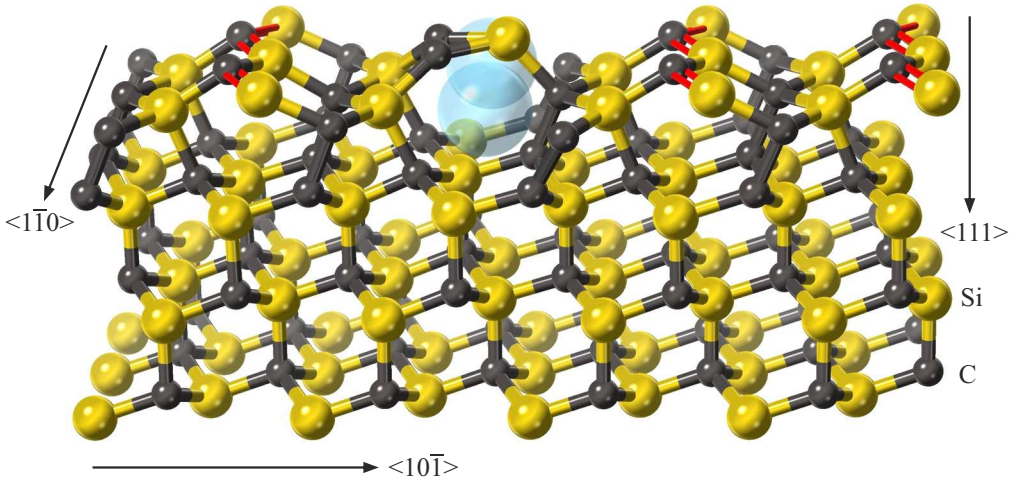

Figure 1. Metastable state of a vacancy thread in the $\langle 1\bar{1}0\rangle$ direction on the 3*C*-SiC$(11\bar{1})$ surface with the (2×1) reconstruction. Voids formed by silicon vacancy V_{Si} are represented as translucent spheres. Si−C bonds in Pandey chains are highlighted in red; the magnetic moment is zero. A color version of the figure is provided in the online version of the paper.

range [4–6]. The aim of the present study is to establish possible reasons for the emergence of these properties in 3*C*-SiC containing V_{Si} in density-functional-theory (DFT) calculations [14].

Let us note first that silicon vacancies V_{Si} in 3*C*-SiC interact with each other in a highly anisotropic manner. It can be shown using the DFT method [14] that they repel each other in all directions except $\langle 1\bar{1}0\rangle$ [15]. In direction $\langle 1\bar{1}0\rangle$ V_{Si} are attracted to each other even if they have the same charge [15]. This strong attraction is attributable to the formation of new C−C carbon bonds, which reduce greatly the elastic energy of a crystal. There are three equivalent $\langle 1\bar{1}0\rangle$ directions in 3*C*-SiC, and it is along these directions that Si atoms are positioned. The angle between these directions is 60°. Owing to this attraction, V_{Si} are arranged in threads in the $\langle 1\bar{1}0\rangle$ directions with alternating Si atoms and V_{Si}, namely $\ldots$−Si−V_{Si}−Si−V_{Si}−Si−$\ldots$. Moreover, the density functional method reveals that V_{Si} are attracted very strongly to the surface of a 3*C*-SiC crystal. Calculations in the present study were performed using the plane-wave Medea-VASP code with pseudopotentials based on the projector augmented waves (PAW) method [14]. The surface was characterized by a supercell $21.4 \times 6.16 \times 21.1$ Åin size containing an atomic SiC core (slab) with three layers of atoms (64 C atoms and 64 Si atoms) and a vacuum gap above with a thickness of 12 Å. Periodic boundary conditions were set in all three directions in the supercell. The vacuum gap is needed to isolate the surface from artificial interaction with the core through periodic boundary conditions along the z axis [14]. The removal of one of two Si atoms along the y axis (i.e., every second atom) is equivalent to the formation of a vacancy thread along the y axis, which corresponds to the $\langle 1\bar{1}0\rangle$ direction of a 3*C*-SiC crystal. Thus, the approximate distance between vacancy threads in directions x and z is 22 Å, which is a fine model for non-interacting threads. Minimization of the energy of this system provides an opportunity to study the properties of a vacancy thread on the 3*C*-SiC. surface. The PBE functional in the spin-polarized approximation was used to calculate the system energy [14]. A Monkhorst–Pack [14] k-point grid was used for integration over the Brillouin zone. The distance between points was less than 0.2 Å^{-1}, which ensured high accuracy of calculations of the magnetic properties of the system. In the present study, V_{Si} are considered to be uncharged, which corresponds to high-resistance (undoped) Si from which 3*C*-SiC was grown.

Figure 1 shows the studied system with a vacancy thread on the 3*C*-SiC surface, which is obtained by minimizing the total energy. For definiteness, only the C-surface of 3*C*-SiC (i.e., 3*C*-SiC$(11\bar{1})$) was investigated in the present study. The results for the silicon surface are very close. As the energy is minimized, the (2×1) surface reconstruction, which corresponds to the energy minimum for numerous crystals with a diamond-like structure [16], is established. This approach provides an opportunity to examine energy V_{Si} as a function of distance to the SiC C-surface, but this requires the use of larger supercells. Figure 2 shows the dependence of energy of a system with one vacancy V_{Si} (vacancy thread in the $\langle 1\bar{1}0\rangle$ direction) on the distance between the vacancy and the C-surface of 3*C*-SiC. The points in this figure corresponding to distances 0, h_0, and $2h_0$ ($h_0 = 2.52$ Å is the SiC layer height) were calculated directly with the use of supercells, and point $10h_0$ was estimated using a similar model with an infinite distance from V_{Si} to the surface. It is evident that vacancy threads are attracted very strongly to the crystal surface. Therefore, a large number of vacancies are likely to assemble into threads on the 3*C*-SiC surface at a SiC growth temperature on the order of 1200 °C. Let us emphasize that the initial state of the vacancy thread on the 3*C*-SiC surface has zero magnetic moment, since additional π bonds form between Si and C atoms with dangling bonds on the (2×1) surface.

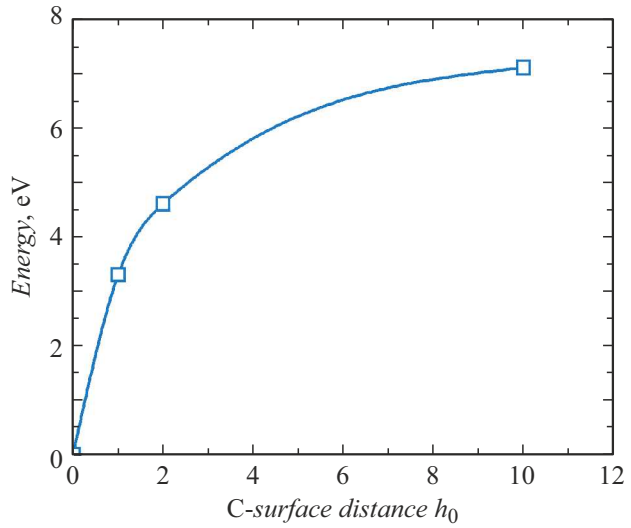

Figure 2. Dependence of the energy of a system with one vacancy V_{Si} (vacancy thread in direction $\langle 1\bar{1}0\rangle$, Fig. 1) on the distance from V_{Si} to the 3*C*-SiC$(11\bar{1})$ surface; $h_0 = 2.52$ Å is the SiC primitive cell size. The system with V_{Si} on the 3*C*-SiC$(11\bar{1})$ surface corresponding to Fig. 1 was taken as the zero point.

These π bonds form zigzag lines called Pandey chains [17], which eliminate the very possibility of forming a magnetic moment. The bonds in these chains are shown in red in Fig. 1.

The results of DFT calculations in the present study demonstrate that this state of the electron subsystem without a magnetic moment is metastable. A stretched Si−C bond located directly in a vacancy thread may become shorter if an additional electron is localized on it. This leads to partial relaxation of the elastic Si−C bond energy, and the energy gain may be greater than the Coulomb repulsion energy of electrons. Calculations reveal that this is exactly what happens in SiC containing vacancy threads of uncharged V_{Si}. The solution with magnetic moment $\mu = 0$ is not the only one; there is also a solution with magnetic moment $\mu = 2\mu_B$, where μ_B is the Bohr magneton. The energy of the latter solution, which is found by choosing a suitable initial approximation of the electron wave function, is $\Delta E = 0.29$ eV lower than the energy of the metastable solution. Calculations of the electron localization function (ELF) [18] in this system demonstrate that an electron tunneled from a C atom involved in the formation of the C−C bond to a Si atom in a vacancy thread (Fig. 3):

$$Si^0 + C^0 \rightarrow Si^- + C^+ + \Delta E. \qquad (2)$$

In the initial metastable state without a magnetic moment, the length of this bond was $l_{Si-C,0} = 1.96$ Å; in the final stable state with $\mu = 2\mu_B$, it is $l_{Si-C,1} = 1.92$ Å (for comparison, the Si−C bond length in unstressed SiC is $l_{Si-C} = 1.89$ Å). Since the lengths of other bonds change to a much smaller extent, the main change in elastic energy is associated with this Si−C bond. It should be emphasized that when an electron tunnels from C to Si, its spin is reversed, doubling the magnetic moment value. The tunneling distance of an electron is 3.75 Å, which is approximately 2−3 times shorter than its characteristic de Broglie wavelength. The magnetic moment density in the stable state is shown in Fig. 3; the shortened Si−C bond is highlighted in green. The magnetic moment regions correspond fully to a p electron of both Si and C atoms, which indicates clearly that it is the p electron involved in hybridization that is tunneling.

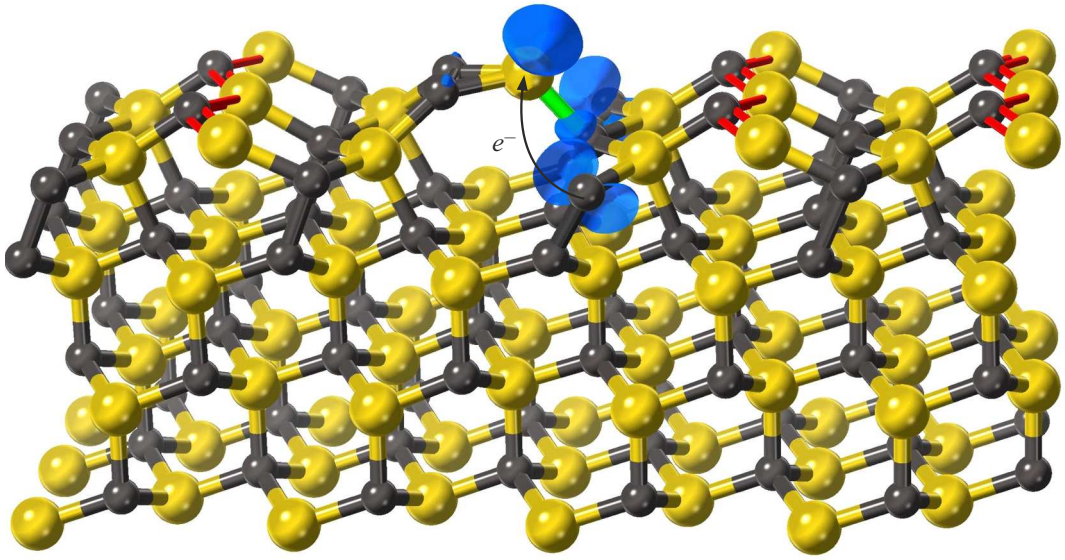

Figure 3. Region of localization of the magnetic moment in a vacancy thread in a stable state with $\mu = 2\mu_B$. The regions with a magnetic moment density of $0.15\, e/Å^3$ are highlighted in blue. The arrow indicates the direction of electron tunneling $Si^0 + C^0 \rightarrow Si^- + C^+$ over a distance of 3.75 Å with a simultaneous spin reversal. The relaxed Si−C bond is highlighted in green, and Si−C bonds in Pandey chains are highlighted in red. A color version of the figure is provided in the online version of the paper.

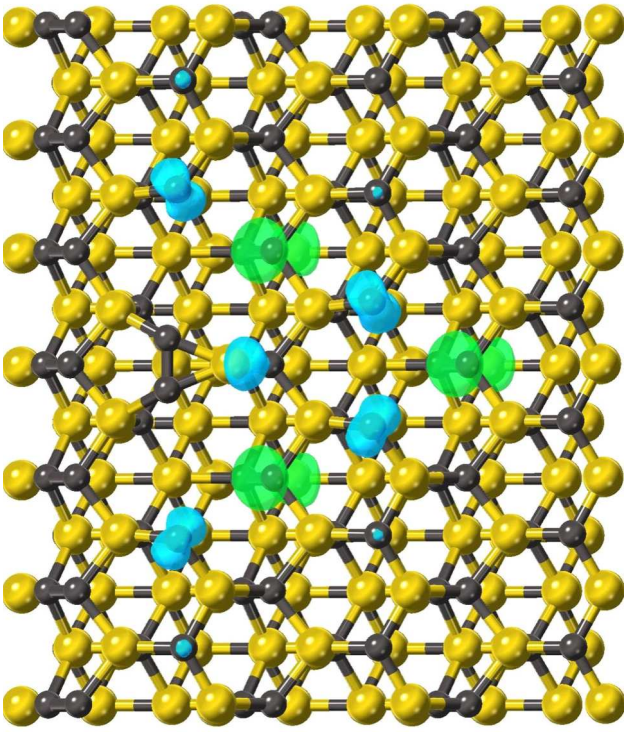

Figure 4. Closed loop on the SiC surface in the form of an equilateral triangle with a side of 6.16 Åand silicon vacancies at the vertices. In the stable state, the total magnetic moment is $3.9\,\mu_B$ (spin up). The regions with spin up and a magnetic moment density of $0.2\,e/Å^3$ are highlighted in blue, and the regions with spin down and a magnetic moment density of $0.1\,e/Å^3$ are shown in green. One Si atom and seven C atoms with their p electrons having a magnetic moment are involved in tunneling of an electron (or electrons) along the V_{Si} triangle. A color version of the figure is provided in the online version of the paper.

The tunneling time interval may be estimated using the formula

$$\Delta t \sim \frac{\hbar}{\Delta E} \sim \frac{6.6 \cdot 10^{-16}\,\text{eV} \cdot \text{s}}{0.29\,\text{eV}} \sim 2.3 \cdot 10^{-15}\,\text{s}. \qquad (3)$$

The obtained value is approximately two orders of magnitude smaller than the elastic oscillation time of a Si−C bond. Therefore, it may be assumed that the energy exchange between an electron and a Si−C bond proceeds without dissipation. It should be noted that the possibility of a dissipationless energy exchange between an electron and elastic bonds in a crystal has been discussed by Bagraev as early as in 1989 [19].

Since three identical $\langle 1\bar{1}0\rangle$ directions form a grid of straight lines intersecting at an angle of 60° on the SiC$(11\bar{1})$ surface, V_{Si} may form closed loops on the surface, such as triangles, hexagons, quadrangles, trapezoids, etc. Figure 4 shows the simplest case with three V_{Si} corresponding to an equilateral triangle with a side of 6.16 Å. Calculations reveal that this case is the one corresponding to the minimum energy for three vacancies. One Si atom and seven C atoms are involved in a complex manner in electron tunneling; the approximate magnetic moment is $3.9\,\mu_B$, and the total energy gain is 0.81 eV. If an external magnetic field is present, electrons may start to tunnel through these eight atoms (in a triangle), compensating for this field. To conclude, let us estimate magnetic susceptibility χ of the studied material. If we assume that electrons in an external magnetic field tunnel without dissipation along a closed loop on the surface, the magnetic susceptibility of this layer with a thickness of 0.25 nm and a density of $3.2\,\text{g/cm}^3$ will correspond to that of an ideal diamagnetic material (i.e. $-1/(4\pi)$). Accordingly, the susceptibility of a 25-nm-thick SiC film with its surface containing 10 % of regions with closed loops of vacancies is $\chi \sim -10^{-3}(3.2 \cdot 4\pi)^{-1}\,\text{cm}^3/\text{g} \approx -2.5 \cdot 10^{-5}\,\text{cm}^3/\text{g}$, which is very close to the experimental data [5] converted to a film thickness of 25 nm; i.e., the diamagnetism of SiC with vacancy threads on the surface is approximately 100 times stronger than the diamagnetism of pure SiC $(-2.7 \cdot 10^{-7}\,\text{cm}^3/\text{g})$.

Thus, it was demonstrated via density-functional-theory calculations that SiC containing silicon vacancies supports tunneling of an electron from a C atom in a C−C bond to a Si atom involved in the formation of a stretched Si−C bond in a vacancy thread on the SiC surface. The reduction in elastic Si−C bond energy ensures electron–electron attraction despite the Coulomb repulsion (this effect is sometimes called the Hubbard attraction or negative Hubbard correlation energy, negative-U) [20]. Presumably, it is this suppression of electron repulsion through the elastic Si−C bond energy that induces the Aharonov–Bohm and de Haas–van Alphen quantum effects observed at room temperature in SiC containing V_{Si}.

Funding

This study was carried out under state assignment of the Ministry of Science and Higher Education of the Russian Federation at the Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences (contract No. FFNF-2021-0001, project registration No. 121112500383-9).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Y. Zhou, J. Tan, H.B. Hu, S. Hua, C. Jiang, B. Liang, T. Bao, X. Nie, S. Xiao, D. Lu, J. Wang, Q. Song, Appl. Phys. Rev., **12**, 031301 (2025). DOI: 10.1063/5.0262377

[2] E. Papanasam, B. Prashanth Kumar, B. Chanthini, E. Manikandan, L. Agarwal, Silicon, **14**, 12887 (2022). DOI: 10.1007/s12633-022-01998-9

[3] G. Allan, M. Lannoo, Phys. Rev. B, **29**, 1474 (1984). DOI: 10.1103/PhysRevB.26.5279

[4] N.T. Bagraev, S.A. Kukushkin, A.V. Osipov, V.V. Romanov, L.E. Klyachkin, A.M. Malyarenko, V.S. Khromov, Semiconductors, **55** (2), 137 (2021). DOI: 10.1134/S106378262102007X.
[5] S.A. Kukushkin, N.I. Rul', E.V. Ubyivovk, A.V. Osipov, V.V. Romanov, N.T. Bagraev, Phys. Solid State, **67** (4), 603 (2025). DOI: 10.61011/PSS.2025.04.61262.55-25.
[6] N.T. Bagraev, L.E. Klyachkin, A.M. Malyarenko, A.V. Osipov, S.A. Kukushkin, Phys. Solid State, **67** (8), 1376 (2025).
[7] F. Bruneval, G. Roma, Phys. Rev. B, **83**, 144116 (2011). DOI: 10.1103/PhysRevB.83.144116
[8] N. Iwamoto, B.G. Svensson, Semicond. Semimet., **91**, 369 (2015). DOI: 10.1016/bs.semsem. 2015.02.001
[9] T. Ohshima, T. Satoh, H. Kraus, G.V. Astakhov, V. Dyakonov, P.G. Baranov, J. Phys. D, **51**, 333002 (2018). DOI: 10.1088/1361-6463/aad0ec
[10] S.A. Kukushkin, A.V. Osipov, Appl. Phys., **113**, 49091 (2013). DOI: 10.1063/1.4773343
[11] S.A. Kukushkin, A.V. Osipov, Materials, **15**, 4653 (2022). DOI: 10.3390/ma15134653
[12] A.S. Grashchenko, S.A. Kukushkin, A.V. Osipov, A.V. Redkov, Catal. Today, **397-399**, 375 (2022). DOI: 10.1016/j.cattod.2021.08.012
[13] M.J. Puska, S. Poykko, M. Pesola, R.M. Nieminen, Phys. Rev. B, **58**, 1318 (1998). DOI: 10.1103/PhysRevB.58.1318
[14] J.G. Lee, *Computational materials science* (CRS Press, Boca Raton, 2017).
[15] S.A. Kukushkin, A.V. Osipov, Tech. Phys. Lett., **50** (11), 16 (2024). DOI: 10.61011/TPL.2024.11.59658.20027.
[16] Q. Zhu, L. Li, A.R. Oganov, P.B. Allen, Phys. Rev. B, **87**, 195317 (2013). DOI: 10.1103/PhysRevB.87.195317
[17] K.C. Pandey, Phys. Rev. Lett., **47**, 1913 (1981). DOI: 10.1103/PhysRevLett.47.1913
[18] A.D. Becke, K.E. Edgecombe, J. Phys. Chem., **92**, 5397 (1990). DOI: 10.1063/1.458517
[19] N.T. Bagraev, A.I. Gusarov, V.A. Mashkov, Sov. Phys. JETP, **68** (4), 816 (1989). DOI: 10.1134/1.2292376.
[20] J. Coutinho, A. Peaker, V. Markevich, J. Phys.: Condens. Matter, **32**, 323001(2020). DOI: 10.1088/1361-648X/ab8091

Translated by D.Safin