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An Atomic Scale Study of Structural and Electronic Properties for α -Zirconium with Single Vacancies and Vacancy Clusters

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We study structural, electronic, and energy properties of pure zirconium with isolated vacancies and their clusters. We discuss the lattice constant change in pure zirconium with different concentrations of isolated vacancy and different configurations of di- and trivacancy. We analyse the stability of small vacancy clusters containing divacancy characterized by different distances between two vacancies and trivacancy of different configuration. As shown, the lattice constant decreases with an increase in the concentration of isolated vacancies, whereas single vacancy formation energy increases indicating that isolated vacancies will tend to form clusters. By studying stability of small vacancy clusters containing di- and trivacancies, it is shown that, if the distance between vacancies in a cluster does not exceed the first-neighbours' distance, the corresponding vacancy cluster will be stable. In the opposite case, the interaction between vacancies in divacancy promotes formation of isolated vacancies, whereas the trivacancy will decompose into divacancy and isolated vacancy or three isolated vacancies, depending on distances between vacancies in trivacancy. Distributions of electronic density and density of states for pure zirconium with single vacancy as well as the most stable configurations of di- and trivacancies are studied in detail.

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Key words: *ab initio* calculations, linearized augmented plane wave method, vacancy, binding energy, electronic properties.

У даній роботі проведено дослідження структурних, електронних та енергетичних властивостей чистого цирконію з ізольованими вакансіями та вакансійними кластерами. Визначено значення параметра ґратниці чистого цирконію з різною концентрацією ізольованих вакансій та з бі- й тривакансіями різної конфігурації. Проаналізовано стабільність малих кластерів вакансій, що містять бивакансії, які характеризуються різними віддалями між двома вакансіями, та тривакансії різної конфігурації. Показано, що зі збільшенням концентрації ізольованих вакансій параметр ґратниці зменшується, в той час як значення енергії формування одиначної вакансії збільшується. Останнє вказує на те, що ізольовані вакансії при збільшенні концентрації їх будуть, як правило, утворювати кластери. При вивченні стійкості малих кластерів вакансій, що містять бі- та тривакансії, показано, що у випадку, якщо віддаль між вакансіями в кластері не перевищує значення радіуса першої координаційної сфери, відповідний вакансійний кластер буде стійким. В іншому випадку взаємодія між вакансіями у бивакансії сприяє формуванню ізольованих вакансій, в той час як тривакансії розпадаються на бивакансію та ізольовану вакансію або три ізольовані вакансії, залежно від віддалі між вакансіями у тривакансії. Проведено детальне дослідження розподілу електронної густини та густини станів для чистого цирконію з однією вакансією та найбільш стабільними конфігураціями бі- та тривакансій.

Ключові слова: розрахунки з перших принципів, метод лінеаризованих приєднаних пласких хвиль, вакансія, енергія зв'язку, електронні властивості.

В данной работе проведено исследование структурных, электронных и энергетических свойств чистого циркония с изолированными вакансиями и вакансионными кластерами. Установлены значения параметра решётки чистого циркония с различной концентрацией изолированных вакансий и с би- и тривакансиями различной конфигурации. Проанализирована устойчивость малых вакансионных кластеров, содержащих бивакансии, которые характеризуются различными расстояниями между двумя вакансиями, и тривакансии различной конфигурации. Показано, что с увеличением концентрации изолированных вакансий параметр решетки уменьшается, в то время как значение энергии формирования одиначной вакансии увеличивается. Последнее указывает на то, что изолированные вакансии при увеличении их концентрации будут, как правило, образовывать кластеры. При изучении устойчивости малых кластеров вакансий, которые содержат би- и тривакансии, показано, что в случае, когда расстояние между вакансиями в кластере не превышает значение радиуса первой координационной сферы, соответствующий вакансионный кластер будет устойчивым. В противоположном случае взаимодействие между вакансиями в бивакансии приведет к формированию изолированных вакансий, в то время как тривакансии распадаются на бивакансию и изолированную вакансию либо три изолированных вакансии в зависимости от расстояния между вакансиями в тривакансии. Проведено

детальное изучение распределения электронной плотности и плотности состояний для чистого циркония с одной вакансией и наиболее устойчивыми конфигурациями би- и тривакансий.

Ключевые слова: расчёты из первых принципов, метод линеаризованных присоединённых плоских волн, вакансия, энергия связи, электронные свойства.

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1. INTRODUCTION

The reliability of modern nuclear power plants is determined by the behaviour of structural materials under simultaneous influence of irradiated particle fluxes, high temperatures, static and dynamic loads [1]. Increasing requirements for safety of nuclear reactors, along with the creation of new concepts provide a focused search of radiation resistant materials and develop physically reasonable models of their behaviour in such non-equilibrium conditions. The successful solution of these problems requires a deep understanding of the processes of microstructure transformations in materials subjected to irradiation influence.

In the most of the important from practical viewpoint situations such as irradiation by neutrons and high-energy heavy ions, material damage is realized due to cascades of atomic collisions. This leads to formation of microscopic areas of damage (from 1 to 10 nm) with high local concentration of point defects (vacancies and interstitial atoms). Because of both the emergence and the relaxation of cascade damage zones, one can observe following phenomena: amorphization, annealing of defects, nucleation of a new phase and vacancy clusters, formation of vacancy and interstitial loops, defects packaging, *etc.* [2–4]. As a result, microstructure transformations affecting physical and mechanical properties of the irradiated material occur.

The process of formation and relaxation of cascade damage areas defies analytical description, because it requires solving the problem of many bodies collision with the influence of a large number of interacting factors. Nowadays, to provide a theoretical description of a point defects rearrangement in materials, one can effectively use numerical simulations in the framework of a multiscale modelling scheme [5]. This method allows one to study physical mechanisms of microstructure transformations in wide range of space and time scales. By using such multiscale modelling scheme, it is possible to predict and examine behaviour of already used structural materials and design novel materials exploited in extreme non-equilibrium conditions by reducing time and costs comparing to corresponding experimental studies. This approach is based on consistent application of various modelling tech-

niques at various hierarchical levels. Thus, methods of quantum-mechanical (*ab initio*) calculations give the possibility to consider structural and electronic properties of the material [6–9]. The obtained results regard to lattice and energy constants allowing one to construct interatomic interaction potential and explore restructuring processes of atomic structure at atomic displacement cascades realization in the framework of molecular dynamics methods [9–11]. Combined results of *ab initio* calculations and molecular dynamics simulations give the possibility to construct the evolution equations for point defects densities and their loops, in the framework of the continuum rate theory, and modelling the system evolution according to Monte Carlo methods [12–16]. A realization of such multiscale modelling procedure is very ambitious problem needing to its solution a huge database of structural element parameters, development of corresponding computation codes cross-linked with different hierarchical levels of description, and huge computational resources. There are hybrid methods that include several hierarchical levels. Among them, one can distinguish a phase field crystal method, which is widely used to study crystalline systems. This method allows one to describe a formation of structural disorder, motion of point and linear defects (dislocations), and transformations on micro- and mesoscopic scales [17–20]. Considering some narrow problems related to a study of special aspects of above phenomena in most of cases, one could use a combination of few approaches of this scheme.

The materials used in nuclear power industry and reactor technology should have a certain set of properties. Among them, the most important property is a small section of thermal neutron capture. This characteristic defines the ability of a material to detain and absorb neutrons and, thus, prevent the spread of chain reaction of displacement cascade. The most common material for reactor instrumentation is Zirconium. The pure Zirconium is characterized by the low value of thermal neutron capture cross section, which is around 0.18 barn [21]. Thus, Zirconium is used as based material for membrane fuel cells (rods). As far as tremendous amount of point defects appears during irradiation, the problem to study the behaviour of defects in Zirconium is actual for nuclear science and energetics. In this regard, it is important to study comprehensively the properties of Zirconium with vacancies.

In this paper, we perform an atomic scale study of pure Zirconium with different concentration of isolated vacancies, Zirconium with di- and trivacancies within the framework of *ab initio* calculations. These defects are produced by irradiation in atomic collisions. The main aim of the current research is to define the change in lattice constants with increase in concentration of isolated vacancies in pure Zirconium, define the formation energy of single vacancy, di- and trivacancies with

different configurations. According to the optimization procedure allowing one to obtain the optimal lattice constants and minimal total energy of Zirconium crystal with vacancies, we will define the energetically more favourable (stable) configuration of di- and trivacancy inside unit cell.

The work is organized in the following manner. In the next section, we present the main aspects of the density functional theory to calculate the electronic structure. In the Section 3, we present models of Zirconium with different vacancy clusters. In the Section 4, we perform optimization procedure for Zirconium structures with single vacancy and vacancy clusters, define optimal values of lattice constants, study stability of small vacancy clusters and discuss main electronic properties of Zirconium with one, di- and trivacancy. Main conclusions and prospects for the future are collected in the last section.

2. METHODS

In this section, we present brief description of main theories, methods and approximations used to perform quantum-mechanical calculation of electronic structure of crystals. All calculations made within this study were done in the framework of Density Functional Theory [22, 23], Linearized Augmented Plane Wave Method [24], and Generalized Gradient Approximation [25, 26] used in WIEN2k programs package [27].

According to the Born–Oppenheimer approximation, which is used in most calculations of the electronic structure, one supposes that nucleus being a part of the considered system, are considered as non-mobile (fixed) ones. The electrostatic potential V , created by these ‘fixed’ cores, is external to the electrons. The stationary state of the electrons is described by a wave-function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, as a solution of the Schrödinger equation:

$$\mathbf{H}\Psi \equiv [\mathbf{T} + \mathbf{V} + \mathbf{U}]\Psi = \left[\sum_i^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 \right) + \sum_i^N V(\mathbf{r}_i) + \sum_{i \neq j} U(\mathbf{r}_i, \mathbf{r}_j) \right] \Psi = E\Psi, \quad (1)$$

where \mathbf{H} is the Hamiltonian of electronic subsystem, N is the number of electrons; U defines electron–electron interaction. It follows that the main difference of one-particle system from the many-body system lies in the presence of the term, describing electron–electron interactions. There is a large amount of methods for solving the many-body Schrödinger equation based on the expansion of the wave function using the Slater determinant, which is an expression that describes the wave-function of a multi-fermionic system that satisfies anti-symmetry requirements and consequently the Pauli principle by changing sign upon exchange of two electrons (or other fermions) [28,

29]. The most simple of them is the Hartree–Fock method known as the approximation method for determination of the wave function and the energy of a quantum many-body system in a stationary state [30, 31]. A common problem for all these methods lies in the large computing complexity, due to which the scope of the Hartree–Fock method and all methods based on it is limited by not too large systems.

Among the most popular and versatile methods available to solve the problem of the calculation of systems involving the large number of particles (electrons), one can distinguish the Density Functional Theory (DFT). DFT is a computational quantum-mechanical modelling method widely used in physics, chemistry and materials science to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With the use of DFT, one can reduce the problem of the many-body system with the potential of electron–electron interaction U to the one-particle problem where the term U is absent. By using this theory, the properties of a many-electron system can be determined by using functionals, *i.e.* functions of another function, which, in this case, is the spatially dependent electron density. The electron density $n(\mathbf{r})$ used to construct the formalism of density functional theory is given by:

$$n(\mathbf{r}) = N \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 \dots \int d^3\mathbf{r}_N \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N). \quad (2)$$

Hohenberg and Kohn in 1964 have shown [32] that this expression can be drawn: for a given electron density in the ground state $n_0(\mathbf{r})$ the corresponding wave function of the ground state $\Psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N)$ can be found. By the other words, Ψ_0 is the unique functional on $n_0(\mathbf{r})$ that is $\Psi_0 = \Psi_0[n_0]$, and, therefore, all other physically observed values O are also functional on n_0 :

$$\langle O \rangle [n_0] = \langle \Psi_0 [n_0] | O | \Psi_0 [n_0] \rangle. \quad (3)$$

Particularly, the ground state energy can be written in the form:

$$E_0 = E [n_0] = \langle \Psi_0 [n_0] | \mathbf{T} + \mathbf{V} + \mathbf{U} | \Psi_0 [n_0] \rangle, \quad (4)$$

where the contribution of the external potential $\langle \Psi_0 [n_0] | \mathbf{V} | \Psi_0 [n_0] \rangle$ can be rewritten through the electron density $n(\mathbf{r})$ in the form:

$$V [n] = \int V(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r}. \quad (5)$$

Functionals $T[n]$ and $U[n]$ are the same for all systems, whereas $V[n]$, obviously, depends on the type of the considerable system. For a given system, functional V is known, and one can minimize the energy functional

$$E[n] = T[n] + U[n] + \int V(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} \quad (6)$$

with respect to the electron density distribution $n(\mathbf{r})$, if expressions for $T[n]$ and $U[n]$ are known. A result of the minimizing one gets the electron density in the ground state n_0 , and all observed quantities in the ground state.

The variational problem of minimizing the energy functional $E[n]$ can be solved by using the Lagrange multipliers method, as it was done by Kohn and Sham in 1965 [33]. Thus, the energy functional in the above expression can be written as an effective functional of electron density in the one-particle system:

$$E_s[n] = \langle \Psi_s[n] | T_s + V_s | \Psi_s[n] \rangle, \quad (7)$$

where T_s is responsible for the kinetic energy of the free particle, whereas V_s is the effective external potential for the electron subsystem. It is clear that $n_s(\mathbf{r}) = n(\mathbf{r})$, if one takes V_s in the form

$$V_s = V + U + (T - T_s). \quad (8)$$

One-particle system can be solved by using Kohn–Sham equations [33] for the auxiliary system, without electron–electron interaction:

$$\left[-\frac{1}{2} \nabla^2 + V_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad (9)$$

The solution of Eq. (9) gives orbitals ϕ_i , which are used to reconstruct the electron density $n(\mathbf{r})$ of the initial many-body system:

$$n(\mathbf{r}) \stackrel{\text{def}}{=} n_s(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2. \quad (10)$$

An effective one-particle potential V_s has the form

$$V_s = V + \int \frac{e^2 n_s(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + V_{XC}[n_s(\mathbf{r})], \quad (11)$$

where the second term, corresponding to the Hartree (or Coulomb) energy, describes electron–electron Coulomb repulsion, whereas the last term V_{XC} is the exchange–correlation potential, which includes all many-body interactions. As far as both the Hartree term and the term V_{XC} depend on electron density $n(\mathbf{r})$ defined by ϕ_i relating to V_s , the solution of self-consistent Kohn–Sham equations (9) can be obtained by using an iterating procedure of continuity approximations: (i) starting from the initial approximation for $n(\mathbf{r})$ one calculates the corresponding term V_s ; (ii) with given V_s one solves the Kohn–Sham equations and

defines φ_i ; (iii) by using obtained φ_i one can get the next approximation for the electron density $n(\mathbf{r})$.

To define the form of the exchange–correlation potential V_{XC} in Refs. [34, 35], authors obtained an interpolation formula:

$$V_{XC}(n) \approx -\frac{1.222}{r_s(n)} - 0.066 \ln\left(1 + \frac{11.4}{r_s(n)}\right), \text{ where } r_s(n) = \left(\frac{3}{4\pi n}\right)^{1/3}. \quad (12)$$

This was tested by Monte Carlo simulations and is fair for any density. The corresponding exchange–correlation energy can be found in the framework of local-density approximation (LDA) in the form:

$$E_{XC}^{\text{LDA}} = \int n(\mathbf{r})V_{XC}(n(\mathbf{r})) d\mathbf{r}.$$

One of the generalizations and improvements of the local-density approximation is known as Generalized Gradient Approximation that takes into account the inhomogeneous distribution of electron density, or so-called generalized gradient expansion. In this approach, the expression for the exchange–correlation energy expanded in powers of the gradient density. An expression for expansion has the form [25, 26]:

$$E_{XC}^{\text{GGA}}[n] = E_{XC}^{\text{LDA}}[n] + \int n(\mathbf{r})\varepsilon_{XC}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r},$$

where, for $\varepsilon_{XC}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$, the approximated expression was obtained [25, 26].

3. MODELS OF ZIRCONIUM WITH SMALL VACANCY CLUSTERS

It is known that pure α -Zirconium is characterized by h.c.p. (hexagonal close packed) lattice with two lattice constants: a in x and y directions and c in z direction, with structural ration $c/a > 1$. Moreover, Zirconium crystal is characterized by shifted one against another one two planes A and B , and in z direction, the Zirconium crystal has a structure $ABABAB\dots$. In h.c.p. Zirconium crystal, there are two groups of atoms, which are inside the first coordination sphere: six atoms are located in the same plane (let say A) on a distance $d_2 = a$, and six atoms are located in another plane (B) on a distance $d_1 = \sqrt{a^2/3 + c^2/4}$. The structural relation for the pure Zirconium is $c/a \cong 1.5925$ that gives $d_1 < d_2$. The main aim of this article is to study the main structural and electronic properties of Zirconium with small concentration of isolated vacancies and small vacancy clusters (di- and trivacancies). We perform *ab initio* calculations of Zirconium with different concentrations

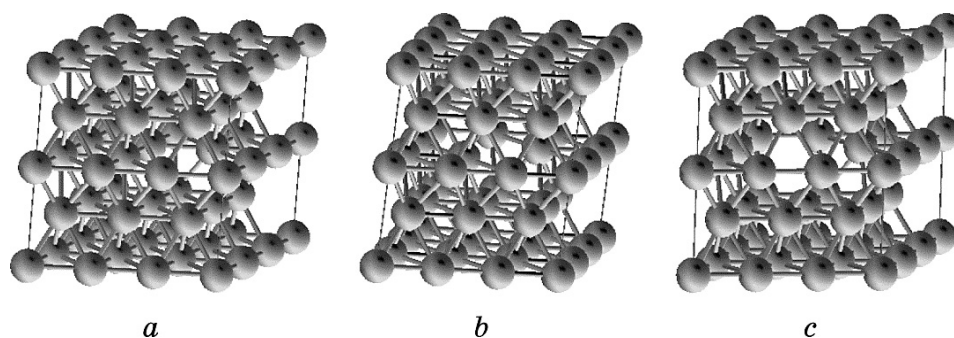


Fig. 1. Structures of α -Zirconium with single vacancy (*a*), divacancy (*b*) and trivacancy (*c*) in basal plane of unit cell containing 35, 34 and 33 Zirconium atoms, respectively.

of isolated vacancies in a periodic supercell containing one vacancy and different number of Zirconium atoms inside h.c.p. unit cell. To study properties of Zirconium with small vacancy clusters, we use 36 Zirconium atoms inside unit cell. In Figure 1, we present structures of Zirconium with single vacancy, divacancy and trivacancy in basal plane of unit cell containing 35, 34 and 33 Zirconium atoms, respectively.

In the next section, we present results of lattice constants change in Zirconium with different concentration of isolated vacancies, and two vacancies separated by distance, discuss formation energy of single, di- and trivacancies of different type and main electronic and energetic properties of Zirconium crystal with different number of vacancies in a cluster.

4. RESULTS AND DISCUSSION

We start our study with determination the optimal values of lattice constants for pure α -Zirconium with different concentration of isolated vacancies and with two vacancies separated by different distances in the framework of optimization procedure.

4.1. Lattice Constants Change

In our study, we assume that the structural relation c/a for h.c.p. Zirconium with small concentration of vacancies will not be changed crucially and consider the case for the constant value of c/a for pure Zirconium. In such a case, the optimization procedure to define the optimal values of lattice constants in Zirconium with different vacancy concentration lies in the minimization of the total energy of the studied crystal by varying the unit cell volume. Results for the lattice con-

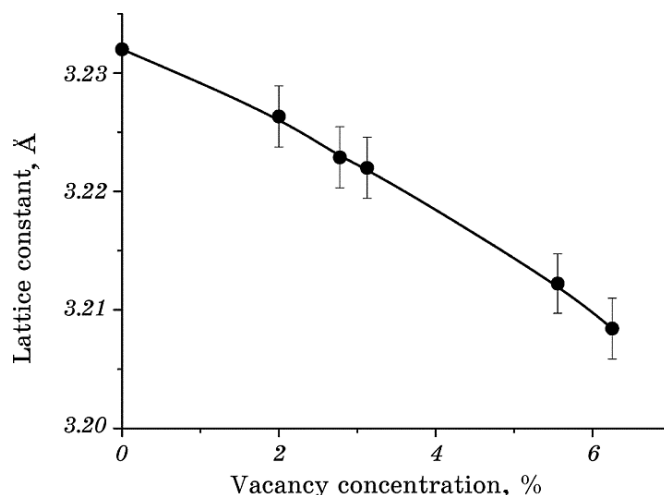


Fig. 2. Optimal values of lattice constant a in pure α -Zirconium with different concentrations of single vacancy.

stant change with increase in the concentration of isolated vacancies in pure Zirconium are shown in Fig. 2. Here, point that corresponds to zero concentration of vacancies relates to the lattice constant for the pure Zirconium. It is seen that an increase in the concentration of isolated vacancies leads to decrease in the optimal value of the lattice constant a . As far as we have assumed a constant value for the structural ratio c/a , in the graph, we indicate error bars.

Next, let us analyse a change in the optimal values of lattice constant in Zirconium unit cell with the same number of atoms and two vacancies separated by different distances. To that end, we have used the unit cell with 66 atomic lattice sites. Corresponding results are shown in Fig. 3. Here, with the use of insertion, we have shown the schematic presentation of the corresponding configuration of two separated vacancies on the h.c.p. lattice, where v_0 denotes the position of the first vacancy and v_1, \dots, v_5 denotes positions of the nearest positions of vacancies. The minimal distance between two vacancies v_0 and v_1 is $d_1 = \sqrt{a^2/3 + c^2/4}$. A distance between v_0 and v_2 is $d_2 = a$; between v_0 and v_3 , distance is $d_3 = \sqrt{4a^2/3 + c^2/4}$; between v_0 and v_4 , distance is $d_4 = c$; and between v_0 and v_5 , distance is $d_5 = a\sqrt{3}$. Hence, the relation $d_1 < d_2 < d_3 < d_4 < d_5$ holds.

From Figure 3, it follows that an increase in the distance d between two vacancies affects slightly the optimal lattice constant value a_{opt} . At the same time, the dependence of optimal lattice constant versus distance has non-monotonic character: if two vacancies lie in the first co-

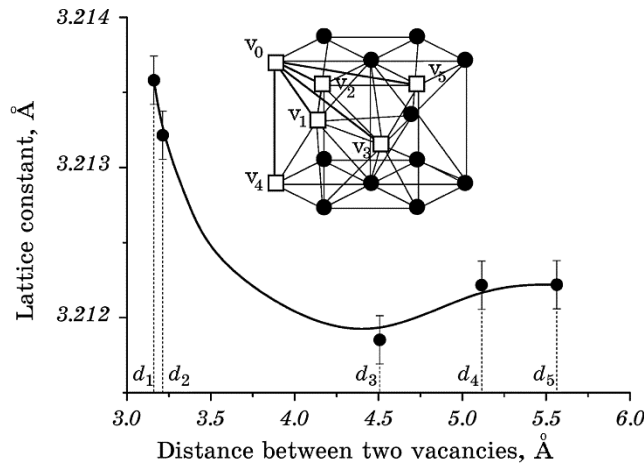


Fig. 3. Optimal values of lattice constant a in pure α -Zirconium with two vacancies, separated by different distances. The corresponding configurations of two vacancies are sketched on the h.c.p. lattice in the insertion, where v_0 denotes the position of the first vacancy and v_1, \dots, v_5 denotes the positions of the nearest vacancies.

ordination sphere, then a_{opt} decreases with growth in d . The minimal value of a_{opt} corresponds to the distance d_3 , and in case when two vacancies are separated by d_4 , one gets $a_{\text{opt}}(d_4) > a_{\text{opt}}(d_3)$. Such effect arises due to h.c.p. structure of Zirconium. Further increase in the distance between two vacancies does not affect a_{opt} . This effect means that these two vacancies do not interact due to large distance between them.

In the next subsection, we will discuss the stability of small vacancy clusters, containing two vacancies (divacancy) separated by a different distance and three vacancies (trivacancy) constructed in different way, by computing formation energy of each vacancy cluster.

4.2. Stability of Small Vacancy Clusters

Before doing calculations of vacancy clustering, it is worth to compute the formation energy of single vacancy in pure Zirconium and compare results with corresponding known ones obtained by other authors, using different methods. We have calculated formation energy E_f of one vacancy in Zirconium crystal, which contains different number of atoms inside unit cell. It corresponds to formation energy of isolated vacancies with different concentration. Obtained results show that an increase in isolated vacancy concentration leads to an increase in the value of the formation energy E_f . It means that the structure of Zirconium with large concentration of separated isolated vacancies will be unstable and these separated vacancies will tend to form clusters. This

effect was checked and approved by molecular dynamics simulations for pure Zirconium with large concentration of separated vacancies [9], where it was shown that heating of the studied sample results in the movement of isolated vacancies, formation of vacancy clusters and their restructuring in dislocations.

To define the formation energy E_f of one vacancy in pure Zirconium, we have calculated the difference between the total energy of Zirconium crystal with $N - 1$ atoms and one vacancy in the unit cell with 66 atomic lattice sites and the total energy of N atoms in the same unit cell. The calculated within this work value of formation energy of one vacancy in pure Zirconium using WIEN2k package [36] is $E_f = 2.11$ eV. We compare our result with obtained previously *ab initio* ones calculated by Quantum Espresso package [37] and Siesta package [38] and known results from molecular dynamics simulation using Embedded Atom Method [39]. Results for energy formation of one vacancy in Zirconium crystal are shown in the Table in insertion in Fig. 4. It follows that our result is in good correspondence with known results of theoretical and numerical study.

Next, we will calculate the formation energy of divacancy in pure Zirconium. It should be noted that in h.c.p. Zirconium there are four types of divacancies, which are characterized by different distances between two vacancies, but not larger than the larger lattice constant c . Hence, to study stability of divacancies, we will perform calculations for two vacancies in the unit cell with 66 atomic lattice sites with distances d_1, d_2, d_3 and d_4 . After building configurations corresponding to the chosen divacancies, we define the formation energy of each divacancy E_f^{di} in a way presented above. Next, to characterize the stability

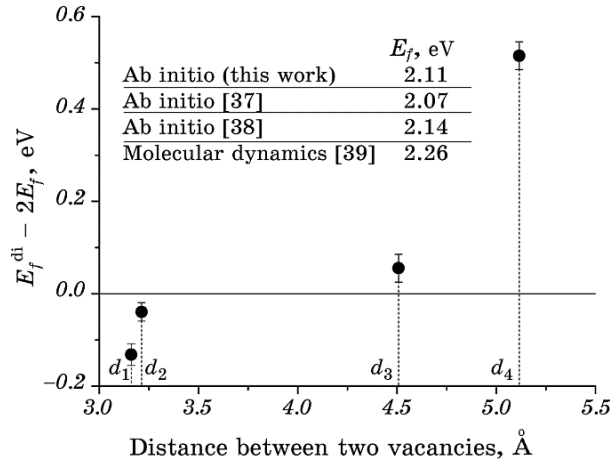


Fig. 4. Binding energies of four possible divacancies. In the insertion, we present results for formation energy of single vacancy in pure α -Zirconium.

of each divacancy, we have found the binding energy as a difference between obtained value of E_f^{di} and double formation energy of single vacancy E_f for the same unit cell. In such a case, the negative value of this difference for fixed d_i means that two vacancies attract each other and the corresponding divacancy is stable: it is energetically more favourable than two isolated vacancies. In the opposite case, two vacancies will repel and the related divacancy will be unstable. Obtained results of binding energy for each divacancy are shown in Fig. 4. *Ab initio* calculations show that with an increase in the distance between two vacancies in unit cell of pure Zirconium the formation energy of divacancy increases. From Figure 4, it follows that if the distance between two vacancies in a divacancy is not larger than the smallest lattice constant a , *i.e.* vacancies are the first-nearest neighbours lying in the first coordination sphere only, then the binding energy takes negative value meaning that these divacancies are stable (see symbols for $d = d_1$ and $d = d_2$). Moreover, the divacancy, lying in prismatic plane (the distance between vacancies is d_1) is around three times stable than the divacancy in a basal plane (d_2). Other two configurations of divacancy corresponding to vacancies separated by more than one nearest-neighbour distance are characterized by positive values of binding energy. These divacancies are unstable (see symbols for $d = d_3$ and $d = d_4$).

To define the most stable configuration of trivacancy in pure Zirconium, we have studied four configurations of trivacancy, namely, C1, C2, C3 and C4, when three vacancies are separated by different distances, d_{12} , d_{23} , d_{13} . First configuration C1 corresponds to three vacancies lying in a basal plane with $d_{12} = d_{23} = a$, $d_{13} = a\sqrt{3}$. The second configuration C2 corresponds to the case when the trivacancy lies in prismatic plane with $d_{12} = a$, $d_{23} = \sqrt{a^2/3 + c^2/4}$, $d_{13} = \sqrt{4a^2/3 + c^2/4}$. The third configuration C3 corresponds to the trivacancy in a basal plane with $d_{12} = d_{23} = d_{13} = a$. The last configuration C4 is characterized by three vacancies in prismatic plane with $d_{12} = a$, $d_{23} = d_{13} = \sqrt{a^2/3 + c^2/4}$. These four types of trivacancies are shown in Fig. 5 in the left hand side, whereas results of *ab initio* calculations for binding energies of the corresponding trivacancies calculated in the same way as for divacancies are shown in Fig. 5 in the right hand side. From obtained results, it follows that configurations C1 and C2 are characterized by positive values of binding energy and, hence, they are unstable, whereas configurations C3 and C4 are stable ones due to negative values of the corresponding binding energy. This result can be explained in the same way as for divacancies: if vacancies, which form the trivacancy, are first-nearest neighbours, then the corresponding vacancy cluster will be stable. All other configurations of trivacancy corresponding to vacancies separated by more than one nearest-neighbour distance are

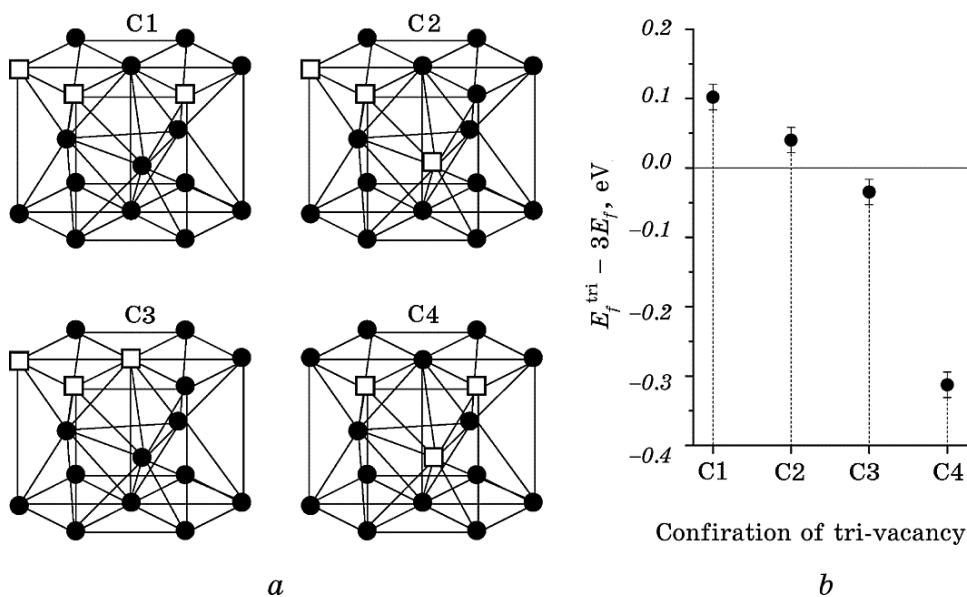


Fig. 5. Configuration of different types of trivacancy in unit cell of pure α -Zirconium and binding energies of corresponding trivacancies.

unstable. Both configurations C3 and C4 are characterized by two nearest-neighbour vacancies for each vacancy, whereas in configurations C1 and C2 only one vacancy has two nearest-neighbours. In such a case, one has the symmetry breaking of the problem.

To analyse the stability of these two configurations, one needs to make addition calculations. Let us initially discuss the stability of configuration C1 in detail. This configuration is characterized by two distances between vacancies, namely d_2 and d_5 with $d_2 < d_5$. As was shown before, the divacancy with a distance between two vacancies d_5 is unstable, comparing to two isolated vacancies. Hence, the cluster C1 will decompose to energetically more favourable configuration, characterized by a stable divacancy with a distance d_2 and one isolated vacancy. The configuration C2 is characterized by three distances between vacancies, d_1 , d_2 and d_3 with $d_1 < d_2 < d_3$ and d_3 is larger than the first nearest-neighbour distance. As far as the divacancy with a distance d_1 is more stable than the divacancy with distance d_2 (see Fig. 4), hence, one can expect that the cluster C2 will decompose to the configuration characterized by divacancy with distance d_1 and an isolated vacancy.

4.3. Main Properties of Zirconium with Vacancies

In this section, we will discuss main properties of the pure Zirconium

with isolated vacancy, divacancy and trivacancy. We will make calculations of the electronic density, density of states and X-ray spectra for Zirconium unit cell containing 66 atomic sites and one vacancy and the most stable configurations of divacancy (in prismatic plane) and trivacancy (configuration C4) by using obtained corresponding optimal values of lattice constants.

Initially let us consider distribution of electron density of these three structures. To demonstrate the change in electronic density around vacancies, we have used the plane containing single vacancy and the corresponding vacancy cluster. Results for electron density distribution for structure with single vacancy, bi- and trivacancy are shown in Figs. 6, *a-c*, respectively. It follows that electronic density of atoms, which have vacancies as first-nearest neighbours is deformed: it becomes stretched in the direction of neighbouring atoms. The electronic density of those atoms, which have Zirconium atoms, as first-nearest neighbours, remains symmetric.

Now, let us discuss dependences of densities of states (DOS) for Zirconium crystal containing single vacancy, di- and trivacancy. The calculated total densities of states for these three structures are shown in Fig. 7. Here, for each case, energy is counted from the corresponding Fermi energy E_F . From Figure 7, it follows that an increase in the number of vacancies leads to decrease of main peaks of DOS but does not change crucially the topology of DOS. According to obtained DOS, one can calculate energetic spectrum (band structure). It is known that DOS and band structure are related in the following way: main peaks in DOS correspond to energy values, when two or more energy curves in band structure are characterized by the same energy value.

The corresponding values of the Fermi energy for these three structures are shown in insertion in Fig. 7. It is seen that the larger vacancies cluster has the smaller number of electrons and the smaller value of the Fermi energy. This result is in good correspondence with well.

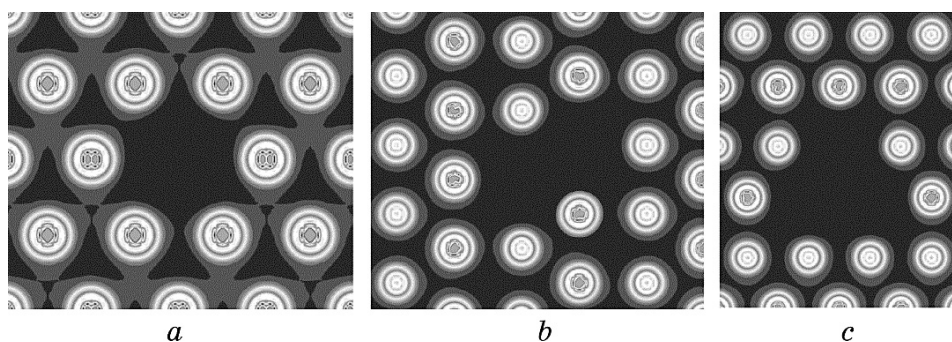


Fig. 6. Electron densities for pure Zirconium with (a) single vacancy, (b) divacancy in prismatic plane, (c) trivacancy in prismatic plane.

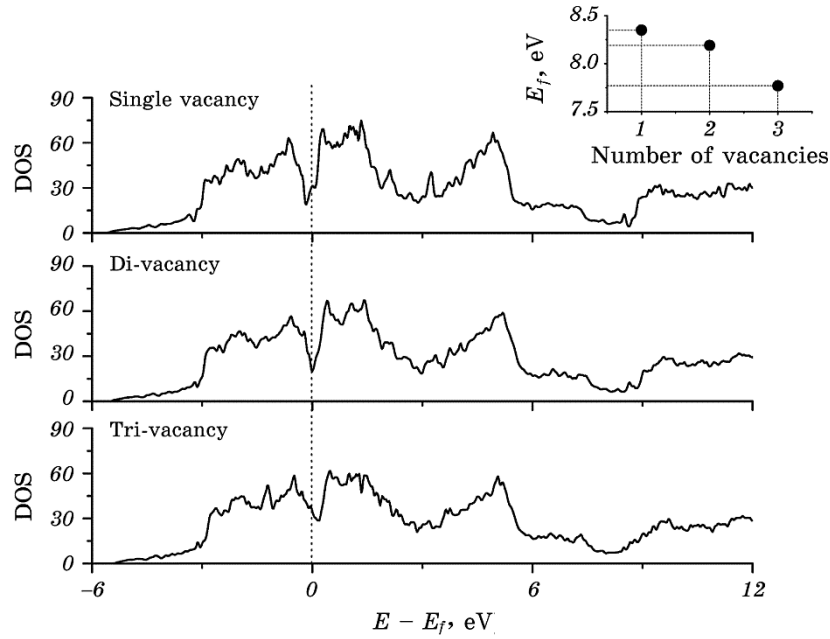


Fig. 7. Total density of states for pure Zirconium with single vacancy, divacancy and trivacancy, counted from the corresponding Fermi energy level.

known theoretical relation between number of electrons and the Fermi energy: $N = 16\sqrt{2\pi}m^{3/2}E_F^{3/2}/\hbar^3$, where m is the mass of an electron, \hbar is the Planck constant. According to this relation, with a decrease in the number of electrons (increase in number of vacancies in the actual case), the Fermi energy decreases. The Fermi surface is defined by those energy curves in band structure, which are cross the Fermi energy level.

5. CONCLUSIONS

In this article, we have studied structural, electronic, and energy properties of pure hexagonal close packed Zirconium with vacancies. We have analyzed structures of Zirconium with different concentration of isolated vacancies, structures of Zirconium with two vacancies separated by different distances and structures with trivacancy of different configuration.

By performing optimization procedure, we have found that an increase in concentration of isolated vacancies in pure Zirconium leads to decrease in optimal values of lattice constants. It is found that an increase in a distance between two vacancies leads to non-monotonic dependence of lattice constant on distance: it initially decreases, takes

minimal value, and slightly increases. If the distance between vacancies is larger than the larger lattice constant value, then, the lattice constant does not change, meaning that vacancies can fill each other on distances less than the larger lattice constant.

We have computed the energy of one vacancy formation in pure Zirconium, which is in a good correspondence with known theoretical results coming from *ab initio* calculations and molecular dynamics simulations. By considering stability of small vacancy clusters, we have shown that divacancy is stable only if the distance between two vacancies does not exceed the first-nearest neighbour distance. By studying trivacancies, we have found that these clusters are stable if all three vacancies are first-nearest neighbors. It is shown that a decrease in a distance between vacancies in clusters leads to stabilization of the corresponding small vacancy cluster.

We have discussed main properties of Zirconium crystal with single vacancy, di- and trivacancy and shown that the electronic density of an atom, which has a vacancy as a first-nearest neighbour becomes stretched in the direction of neighbouring atoms, whereas electron density of those atoms, which have Zirconium atoms as first-nearest neighbours, remains symmetric. It is found that the Fermi energy decreases with an increase in number of vacancies in a cluster, which corresponds well to known theoretical estimation. We have computed the total density of states of these three structures and shown that with an increase in the number of vacancies in a cluster the height of main peaks of total density of states decreases.

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