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Properties of Zr-12,5% Nb and Zr-25% Nb Alloys with hcp and bcc Lattices: *ab-initio* Modeling

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Ab-initio calculations of the electronic structure for Zr – 12,5 % Nb and Zr – 25 % Nb alloys are done using density functional theory, method of linearized augmented plane-wave approximation and generalized gradient approximation. The structural and energetic properties, such as the electron densities, densities of states, energetically and X-ray spectra in the case of the hcp and bcc lattices are calculated. Optimal values for the lattice constants are found. The most favorable structure for each studied alloy is defined.

Keywords: Ab-initio calculations, Hcp and bcc structures, Zirconium-niobium alloys.

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1. INTRODUCTION

The question of modernization of existing structural materials for the active zone of atomic reactors and creation of new materials is one of the paramount problems in modern nuclear physics and energetics. Zirconium is one of the main elements for materials of reactor engineering. This is connected, first of all, with the fact that zirconium is characterized by small thermal-neutron capture cross-section [1]. Therefore, metallic zirconium which does not contain hafnium is used for the production of fuel elements for nuclear reactors. Zirconium-niobium alloys are used as the most usable materials for the production of structural elements of the active zone of atomic reactors [2]. Zr-Nb alloys with low percentage of niobium are characterized by a good combination of the nuclear, mechanical, and corrosion properties. They are not inclined to the decrease in the corrosion resistance under radiation and possess high strength, in particular, higher creep resistance [1, 2].

Increase in the niobium percentage in Zr-Nb alloy leads to the deterioration of alloy properties that makes impossible their usage in reactor engineering. In particular, this is connected with the fact that Zr-Nb alloys with increased content of niobium have a large tendency to the flood. During exploitation of the alloy in reactor, hydrogen diffuses inside the alloy because of corrosion processes. When concentration of hydrogen in the alloy exceeds the solubility limit, it precipitates in the form of the brittle hydride phase. In connection with this, study of zirconium-niobium alloys with increased content of niobium is also an actual problem.

Corrosion behavior of Zr-Nb alloy with Nb content of 0,02-20% was investigated in the work [3], where it was established that decrease in the volume part of the bcc phase and niobium concentration in the hcp phase decreases the corrosion rate of the alloy. The problem of investigation of the hydride phase formation processes in Zr-Nb alloys which contain 20% and 40% of niobium was solved in the works [4-6]. For the theoretical investigation and description of the hydride phase formation processes in Zr-Nb alloy with increased content of niobium, the plastic theory was used in [7].

The authors of [8] have studied the diffusion coefficients of Zr and Nb atoms in Zr-Nb alloys with decreased and increased content of niobium. It was revealed that mechanism of Zr and Nb diffusion is defined by the specific character of the lattice dynamics and is the monovacancy one. Investigation of the coarse-grain bcc Zr-Nb alloy with 19% of niobium in order to establish the diffusion coefficients of hafnium and niobium was performed in the work [9], where it is discovered that hafnium diffuses faster than niobium does. Theoretical investigation of the influence of niobium atom as the substitution atom and vacancy in the hcp zirconium crystal at zero temperature was carried out in the work [10]. It was established that zirconium + vacancy structure will be energetically less favorable then zirconium + niobium structure.

Radiation effect on the formation processes of the bcc phase in Zr-Nb alloy with 20-88% of niobium was experimentally studied in works [11-15]. Results of the experimental investigations at temperatures of ~ 700 K concerning structural properties of the hcp and the bcc phases in Zr-Nb alloy varying the percentage composition are represented in [16-18].

In the present work we will perform calculations in order to determine structural and electronic properties of Zr-12,5% Nb and Zr-25% Nb alloys in the cases of the bcc and hcp structures. All calculations will be carried out using the density functional theory (DFT) [19, 20], full-potential linearized augmented plane-wave (FLAPW) method, and generalized gradient approximation (GGA) which are realized in the WIEN2k software package [21]. For each investigated structure we will perform the optimization procedure which will allow to determine the optimal values of the lattice parameters. We will establish the energetically more favorable lattice type for each studied structure. We will calculate the dependences of the electron density, density of states, energy and X-ray absorption spectra.

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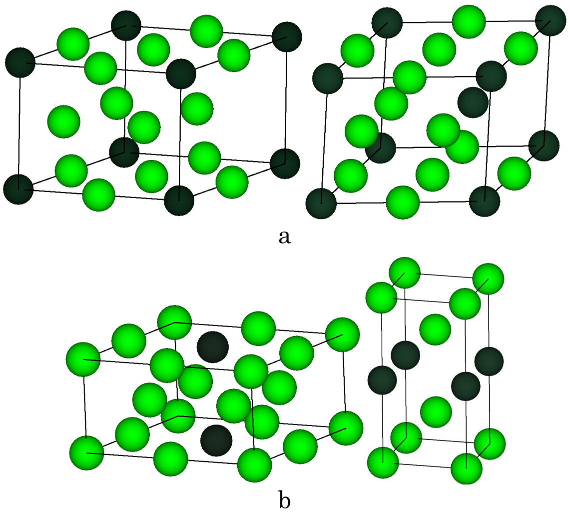
2. MODELS OF Zr-Nb ALLOYS

Investigation of Zr-12,5% Nb and Zr-25% Nb alloys is the aim of the present work. Since β-phase which is characterized by the hcp structure is stable for zirconium at temperatures to 863 K and niobium has the bcc structure, it is obvious that Zr-x% Nb alloys will have either the hcp or the bcc structure. One can expect that the hcp structure will be stable at small concentrations of niobium x for Zr-x% Nb alloy, and the bcc structure – at large concentrations. Moreover, at high temperatures $T > 863$ °C Zr-x% Nb alloys with sufficient concentration of niobium x will have the bcc structure, since at such temperatures both niobium and zirconium are characterized by the bcc structure.

Since zirconium and niobium differ by one electron and the hcp and the bcc structures are characterized by the dense packing, then for models of Zr-x% Nb alloys it is logically to use the assumption that niobium atoms in the hcp structure of zirconium or zirconium atoms in the bcc structure of niobium will be the substitutional atoms. Investigation of a supercell with 48 atoms for the hcp structure of zirconium, which contains vacancy and niobium atom in the internode position near vacancy, have shown that niobium atom takes this vacancy position during the relaxation process [22]. The latter confirms that in Zr-Nb alloy niobium/zirconium atoms will be the substitutional ones. The models of the studied Zr-12,5% Nb and Zr-25% Nb structures with the hcp (a) and the bcc (b) structures are shown in Fig. 1. The hcp and bcc structures for the model of Zr-12,5% Nb alloy are illustrated here on the left; and of Zr-25% Nb alloy – on the right.



a

b

Fig. 1 – Models of the investigated Zr-12,5% Nb (on the left) and Zr-25% Nb (on the right) structures in the case of the hcp (a) and the bcc (b) structures. Zirconium atoms are denoted by the light balls, niobium atoms – by the dark ones

Now we consider in detail the models of the hcp structures which have the *ABA* configuration (Fig. 1a). In the case of 12,5% Nb, the hcp crystal of zirconium has Nb substitutional atom in the plane *A* in the position (0, 0, 0). The hcp structure with 25% Nb additionally contains niobium atom in the plane *B* in the position (1/3, 2/3, 1/2). The data of the hcp structure belongs to the space group 187*P*6*m*2 and has four non-equivalent atoms each which specify a number of symmetry operations. Zr-12,5% Nb alloy is characterized by one atom of niobium and three non-equivalent atoms of zirconium: Zr$_1$, Zr$_2$, and Zr$_3$. Thus, there are Zr$_1$ atoms (which have two bounds r_1 each with Nb atoms) in the plane *A* that contains niobium atoms. Zr$_2$ atoms are located in the plane *B* and also have two bounds r_2 each with niobium atoms, but correlation $r_2 > r_1$ takes place. Zr$_3$ atoms are also located in the plane *B*, but they do not have Nb atoms as the closest neighbors. Zr-25% Nb hcp structure is characterized by two non-equivalent Nb atoms and two non-equivalent Zr atoms (one in each plane).

Now we consider the models of the bcc structures Zr-12,5% Nb and Zr-25% Nb represented in Fig. 1b on the left and on the right, respectively. In the case of 12,5% Nb, for the effective lattice parameters we have: (2*a*, 2*a*, *a*), and then Nb atom takes the effective position (1/2, 1/2, 0). For the bcc structure which has 25% Nb, effective lattice parameters are the following: (*a*, *a*, 2*a*) and niobium atom is located in the position (0, 0, 1/2). Both structures belong to 123*P*4*mmm* symmetry group and are characterized by one non-equivalent Nb atom. Zr-12,5% Nb alloy consists of three non-equivalent atoms of zirconium: Zr$_1$, Zr$_2$, and Zr$_3$ which are located on the distances $a\sqrt{3}/2$, a, and $a\sqrt{2}$, respectively, far from niobium atom; while alloy with 2%Nb has only two non-equivalent atoms of zirconium Zr$_1$ and Zr$_2$.

3. CALCULATION TECHNIQUE

According to the Born-Oppenheimer approximation which is applied in the majority of calculations of the electron structure, nuclei which enter into composition of the studied system are considered to be stationary. Then, electrostatic potential V formed by nuclei is the external one for electrons. Stationary state of electrons is given by the wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ which is the solution of Schrödinger equation $H\Psi \equiv \left[\hat{T} + \hat{V} + \hat{U}\right]\Psi = E\Psi$. Here H is the Hamiltonian of the electron subsystem; N is the number of electrons; U determines the electron interaction. Presence of the term U is the main difference between the single-particle and many-body problems. At present, there is a large quantity of the solution techniques of the many-body Schrödinger equation based on the expansion of the wave function using the Slater determinant [23]. The Hartree-Fock method is the simplest one based on which a number of modern methods are developed [24]. Considerable computational laboriousness is their common problem. Because of this fact, application of the Hartree-Fock method and its derivatives are limited by not very large systems. The DFT method significantly solves the calculation problem of many-body systems by the reduction of the many-body problem with the electron interaction potential U to the single-particle problem where term U is absent.

Formalism of the DFT is based on the introduction of particle density by the equation

$$n(\mathbf{r}) = N\int d^3\mathbf{r}_2 \ldots \int d^3\mathbf{r}_N \Psi^*(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N).$$

Hohenberg and Kohn have shown that this expression can be reversible [19]: using the known particle density in the ground state $n_0(\mathbf{r})$, one can find the corresponding wave function of the ground state $\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Thus, Ψ_0 is a unique functional from $n_0(\mathbf{r})$, and, so, all observed physical values are also the functionals of n_0.

It is known that functionals $T[n]$ and $U[n]$ are the same for all systems, and $V[n]$, obviously, depends on a certain studied system. For the specified system, the view of V is known, and, so, one can minimize the functional

$$E[n]=T[n]+U[n]+\int V(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} \qquad (1)$$

relative to the particle density distribution $n(\mathbf{r})$ under the condition that expressions for $T[n]$, $U[n]$ are known. Result of minimization of functional (1) is the particle density in the ground state n_0 and all values observed in the ground state as well. Variational problem of finding the minimum of the energy functional $E[n]$ was firstly solved by Kohn and Sham [25] using the method of the Lagrange multipliers. Solution of the Kohn-Sham equations for the accessory system without electron-electron interaction gives the orbitals, using which the electron density of initial many-particle system is reproduced.

Calculations of the structural and electron properties of the studied Zr-12,5% Nb and Zr-25% Nb alloys were carried out within DFT [19] using the linearized augmented plane-wave (LAPW) method, GGA with parameterization [20] which are realized in the Wien2k software package [21]. The given method self-consistently includes main and valence electrons and is widely used in calculations of the band structure of solids [21]. In calculations, the muffin-tin (MT) sphere radiuses were taken as 2,1 at units for both zirconium and niobium atoms. A number of basic functions $R_{MT}\,k_{max} = 7$, where R_{MT} is the minimum radius of MT sphere; k_{max} is the maximum value of the modulus of the reciprocal lattice vector. Propagation by spherical harmonics inside atomic spheres was performed up to $l_{max} = 10$. Integration over the Brillouin zone was carried out using 1000 k-points. Convergence of calculations to 0,0001 Ryd and 0,001 e^{-1} for the total crystal energy and crystal charge, respectively, was taken as the criterion of termination of the iteration procedure.

4. RESULTS AND DISCUSSION

To perform calculations of the properties of model Zr-12,5% Nb and Zr-25% Nb alloys, the optimization procedure was carried out in order to determine the lattice parameters and, in the case of the hcp structures, the structural ratio c/a measured experimentally. In the case of the bcc alloys, optimization procedure was performed in a usual way: the unit cell volume was varied and the minimum of the dependence of the total crystal energy on the volume (which corresponds to the optimal value of the lattice parameter) was found. The results of the optimization procedure as the dependence of the total crystal energy (counted from the minimum value) on the unit cell volume are represented in Fig. 2.

In the case of the hcp structures, optimization is complicated because it is necessary to find the absolute minimum of the total energy as a function of two values, namely, the unit cell volume and the structural ratio c/a. The given problem was solved as follows. The value of the structural ratio was fixed for each crystal and using this value, the total energy minimum on the unit cell volume (as well as for the bcc alloys) was found. Changing the value of the structural ratio, dependence of the total energy on the structural ratio, whose minimum determines the optimal ratio c/a for each structure, was obtained. The results are shown in Fig. 3.

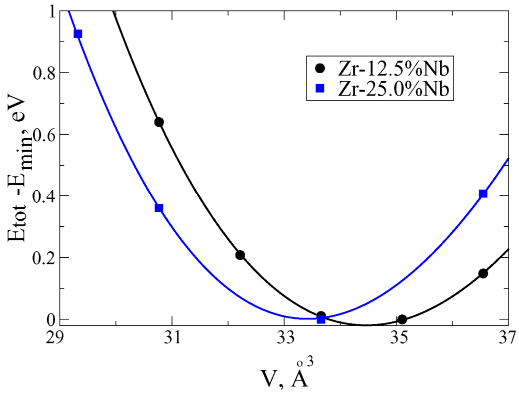


Fig. 2 – Dependence of the total energy (counted from the minimum value) on the unit cell volume for the bcc alloys

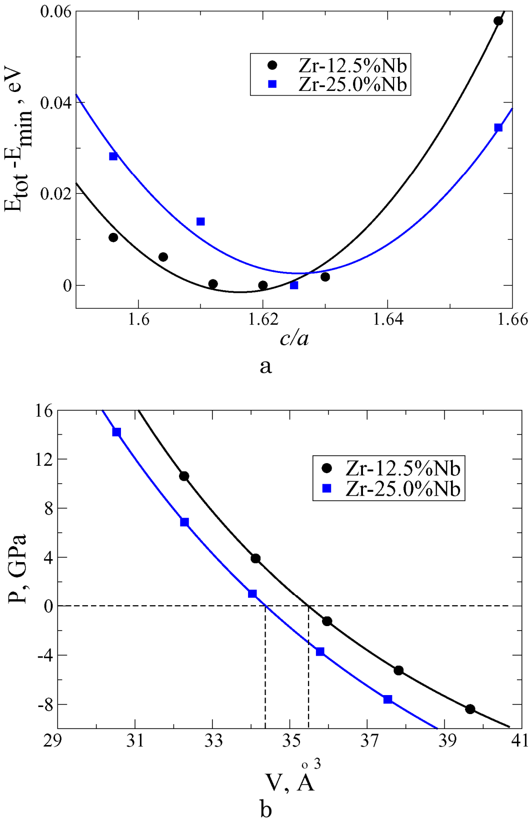


Fig. 3 – Dependence of the total energy (counted from the minimum value) on the structural ratio *c/a* (a) and dependence of the pressure inside the crystal on the unit cell volume (b) for the hcp alloys

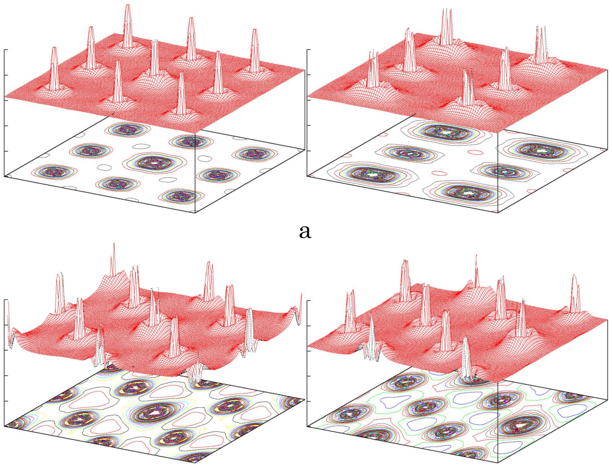
Table 1 – Optimal values of the lattice parameter (angstroms) and, in the case of the hcp structures, structural ratio for the studied structures. Experimental data a_{exp} (angstroms)

	12,5% | bcc	25% | bcc	12,5% | hcp	25% | hcp
a	3,534	3,186	3,498	3,145
c/a	–	1,617	–	1,626
a_{exp}	3,553	–	3,515	–

Using the optimal structural ratio, the standard optimization procedure was carried out, namely, we have defined the optimal unit cell volume which corresponds to the value of the lattice parameter in accordance with the volume determination $V_{opt} = (c/a)a^3\sin(2\pi/3)$. Here, instead of the total energy, the change in the pressure inside the crystal at the change in the unit cell volume was studied: unit cell has the optimal volume at zero pressure. Results are shown in Fig. 3b. Optimal values of the lattice parameter and, in the case of the hcp structures, structural ratio are represented in Table 1. The known experimental values for the lattice parameter of the bcc Zr-Nb alloys at the temperatures of the order of 700 K [16] are given in the last row of the Table. It is seen that the values of the lattice parameter of the bcc alloys obtained theoretically are slightly less than the experimental ones. This looks natural since all calculations were performed at zero temperature, and increase in the crystal temperature leads to the extension of the unit cell and, correspondingly, to the increase in the value of the lattice parameter.

Comparing the values of the total energies per the unit cell and the optimal values of the lattice parameters, we find from the performed calculations that at niobium concentration of 12,5%, Zr-Nb alloy will have the hcp structure with higher probability, and at niobium concentration of 25% – the bcc structure will be energetically more favorable.

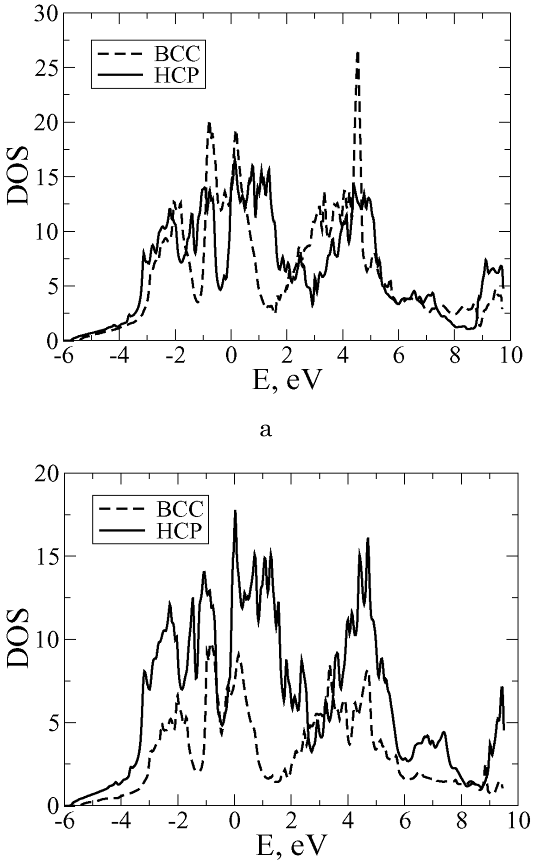
Using the obtained optimal values of the lattice parameters, calculations of the electron density for four studied structures were carried out; results are in Fig. 4.


a

b

Fig. 4 – Electron densities for structures Zr-12,5% Nb (on the left) and Zr-25% Nb (on the right) in the case of the bcc (a) and the hcp (b) structures in the planes of existence of Nb atoms: plane (0, 0, 0) for Zr-12,5% Nb structures (on the left); plane (1, 0, 0) for Zr-25% Nb bcc structure (a, on the right); plane (0, 0, 2) for Zr-25% Nb hcp structure (b, on the right). Electron density in the plane (0, 0, 0) is topologically the same as the density for Zr-12,5% Nb hcp structure (b, on the left)

Calculations of the total density of states (DOS) for the studied Zr-12,5% Nb and Zr-25% Nb alloys which have energetically more favorable hcp and bcc structures, respectively, using the optimal values of the lattice parameters, are given in Fig. 5. In Fig. 5a, b solid lines correspond to the alloys with the hcp structure, dashed lines – to the alloys with the bcc structure.

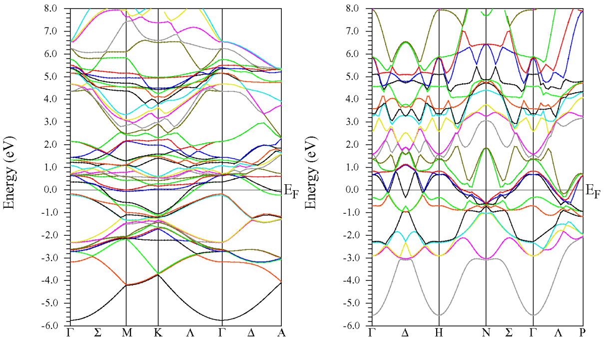


a

b

Fig. 5 – Dependence of the density of states (DOS) on the energy counted from the Fermi energy for a) Zr-12,5% Nb alloy; b) Zr-25% Nb alloy under the condition of the hcp (solid line) and the bcc (dashed line) structures

It is seen that for Zr-12,5% Nb alloy amplitude of the fundamental peaks on the dependence of the density of states is larger for the bcc structure (Fig. 5a), while for Zr-25% Nb alloy situation is opposite: density of states for the hcp structure takes larger values than for the bcc structure (Fig. 5b). The given result confirms the fact that Zr-12,5% Nb alloy is characterized by the hcp lattice and Zr-25% Nb alloy has the bcc structure.



a

b

Fig. 6 – Energy spectra for the structures: a) hcp Zr-12,5% Nb and b) bcc Zr-25% Nb

Obtained dependences allow to calculate the energy spectra which for hcp Zr-2,5% Nb and bcc Zr-25% Nb alloys are represented in Fig. 6a and Fig. 6b, respectively. It follows from the comparison of the behavior of the density of states in Fig. 5 and spectra in Fig. 6 that intersection of "webs" in *k*-points in Fig. 6 corresponds to the peaks of the total density of states on the given energy levels counted from the Fermi energy.

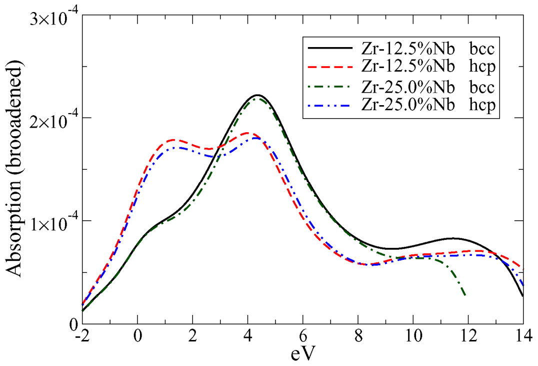


Fig. 7 – Dependences of the X-ray absorption spectra on the edge of the absorption line

Dependences of the X-ray absorption spectra for Zr-12,5% Nb and Zr-25% Nb alloys with the bcc and hcp lattices are illustrated in Fig. 7. As seen from the figure, in the case of the bcc structures irrespective of the percentage of niobium, dependences of the X-ray absorption spectra are characterized by two peaks: one on small energies and one on large energies. The hcp structures are characterized by two peaks on small energies and one peak on large energies. The latter can be explicitly used for the validity of the obtained results.

5. CONCLUSIONS

We have performed ab-initio modeling of the electron structure of Zr-12,5% Nb and Zr-25% Nb alloys formed by incorporation of niobium atom as the substitutional atom into zirconium crystal (or of a large amount of Zr atoms into niobium crystal) at zero temperature using the DFT, FLAPW method, and GGA. We have carried out optimization procedures in order to determine the optimal values of the lattice parameters of the mentioned structures and, in the case of the hcp alloys structural ratio *c*/*a*. It is revealed that the hcp structure will be more probable at 12,5% Nb, while the bcc structure will be more favorable at 25% Nb. Structural and energy properties of Zr-12,5% Nb and Zr-25% Nb alloys in the case of the hcp and the bcc lattices are investigated. The electron densities, densities of states, energy spectra, and X-ray absorption spectra for each structure with the hcp and the bcc lattices are calculated. Obtained results agree well with the experimental data by the numerical simulation.

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