

Electronic Structures of the Zr–He, Zr–H, and Zr–He–H Systems

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Abstract—Ab initio calculations of the electronic structures of the Zr–He, Zr–H, and Zr–He–H systems have been carried out. The effect of impurities of hydrogen and helium on the electronic structure of hpc Zr has been considered. It has been found that the 1s states form a narrow band below the conduction band bottom of Zr. Unlike helium, hydrogen dissolving in zirconium does not form an additional band but it chips off a band of hybridized metal–hydrogen states from the conduction band bottom of Zr, forming a chemical bond. It has been revealed that helium forms a weak chemical bond with Zr atom as a result of hybridization of its 2s states with valence states of Zr. Helium also increases the covalent component of the bond between Zr atoms in the first coordination sphere.

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1. INTRODUCTION

The behavior of light gas impurities in metals are extensively studied for several recent decades [1–3]. Of specific interest are the studies of the effect of hydrogen and helium atoms on the properties of structural materials of nuclear reactors. These impurities form as a result of (n, p) and (n, α) nuclear reactions during neutron bombardment of metals. Additional atomic hydrogen is accumulated in the structural materials during radiolysis of water used as coolant in water-moderated water-cooled power reactors (WWER). As for helium, it can penetrate to materials also as a result of filling of gas gaps of fuel elements.

Accumulation of atoms of hydrogen and helium in near-surface regions of a metal brings about the formation of solid solution with high impurity concentration and, as a result, causes the hydrogen and helium embrittlement and also gas swelling of the material. All these factors significantly deteriorate operating properties of metals and alloys [4–7]. In this connection, it is necessary to study in detail the influence of impurities of hydrogen and helium on the electronic structure of a metals and alloys based on them.

The purpose of this work is a theoretical ab initio investigation of the effect of H and He impurities in combination and separately on the electronic structure and the properties of zirconium whose alloys are widely used as structural materials of fuel elements for the fuel core of WWER.

2. CALCULATION PROCEDURE

The self-consistent calculations of the electronic structures of the Zr–He, Zr–H, and Zr–He–H systems with impurity concentration of ~6 at % were performed in terms of the electron density functional theory using a generalized gradient approximation [8] that was linearized by the augmented plane-wave method [9, 10] that was realized in the FLEUR program package. The muffin-tin (MT) sphere radii were chosen to be 2.3 atomic units (a.u.) for Zr atoms and 1.0 a.u. for He and H atoms. The parameter of cutting-off of the basis from plane waves $k_{\max} = 4.0$ a.u.⁻¹ corresponds to ~170 basis functions per atom. The eigenvalues of the Hamiltonian were calculated in 14 k -points of the Brillouin hexagonal close-packed structure at each of iterations of self-consistency. The procedure of self-consistency of the electron density was performed to the convergence of the total energy not worse than 0.001 meV, which corresponded to the convergence of the charge density not worse than 1×10^{-7} e/a.u.³, where e is the electron charge. The calculated cells of the Zr–He and Zr–H systems contained 16 atoms of the metal and one helium impurity atom in the octahedral interstitial site and one hydrogen impurity atom in the tetrahedral interstitial site. The calculated cell of the Zr–He–H system contained 16 atoms of the metal and one helium atom and one hydrogen atom in corresponding interstitial sites.

The densities of electron states (DES) were calculated by the linear method of tetrahedrons on the network from 54 k -points in the Brillouin zone. The

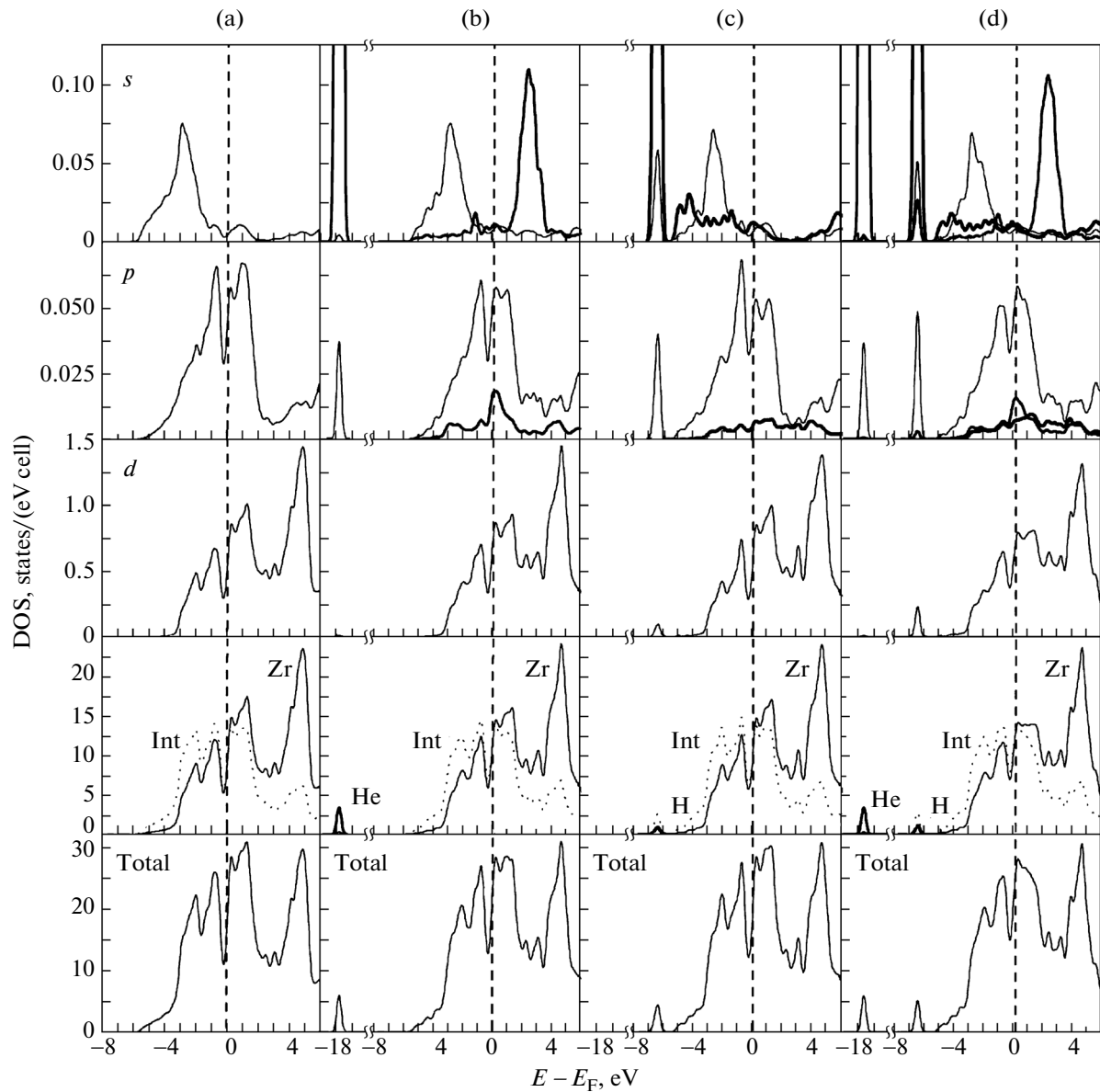


Fig. 1. Densities of states (DOS) of (a) pure Zr and (b) the Zr–He, (c) Zr–H, and (d) Zr–He–H systems. The plots show the total density of states (Total), local density of states in the interatomic region (Int) and MT-spheres of zirconium, helium, and hydrogen atoms, and also local partial densities of the s , p , and d states.

DESs were smoothed using Gaussians with the root-mean-squared width of 0.13 eV.

3. RESULTS AND DISCUSSION

The calculations of the total energy of the Zr–He, Zr–H, and Zr–He–H systems for the hexagonal close-packed (hcp), the face-centered cubic, and volume-centered cubic structures of zirconium performed in [11–13] show that, as the content of the impurity of helium and/or hydrogen is ~6 at %, the hcp structure of zirconium is the most stable of all the structures under consideration. In this case, the preferred position of helium atom is the octahedral inter-

stitial site and that of hydrogen atom is the tetrahedral interstitial site. In this work, the electronic structures of the Zr–He, Zr–H, and Zr–He–H systems is exactly considered for these impurity positions.

3.1. Density of States

Figure 1 depicts the DES curves of pure Zr and the Zr–He, Zr–H, and Zr–He–H systems calculated in this work for the cases when helium atoms are in the octahedral interstitial site and hydrogen atoms are in the tetrahedral interstitial site of the hcp lattice of zirconium. The total density of states is shown in the lower row. The second row at the bottom shows the

local densities of states in the interatomic region and MT spheres of atoms of zirconium, helium, and hydrogen. Three upper rows show the local partial densities of states of the *s*-, *p*-, and *d*-types in the MT spheres of He and H atoms, and also Zr atoms of the first coordination sphere of the impurity for the Zr–He, Zr–H, and Zr–He–H systems.

Panels of the bottom row show that DES of zirconium is not significantly changed at the hydrogen and helium concentrations under consideration. The four-peak structure of DES characteristic of Group IV transition hcp metals is distorted slightly. The second row panels show that almost half of the valence charge density of zirconium is in the interatomic region, and another its part is in the MT-spheres of its atoms.

It follows from an analysis of the total DES that introduction of helium into a Zr octapore (the bottom row of column *b*) leads to the formation of a narrow (~0.8 eV) band of He *s* states, which is 12 eV lower than the bottom of the Zr valence band and to a decrease in the width of a valence band by approximately by ~0.2 eV. As a result, DES of the metal in the filled part of the spectrum increases, and its increase at the Fermi level is 5.5 states/(eV cell). As hydrogen dissolves in a tetrapore of the Zr lattice (column *c*), a narrow peak ~1.0 eV wide forms below the valence band bottom of Zr; the peak corresponds to hybridized metal–hydrogen states that are preferably formed by the *s*-orbitals of hydrogen (~66%), which decreases the valence band width of zirconium almost by 0.4 eV. In addition, the existence of hydrogen in the Zr lattice increases DES at the Fermi level by 2 states/(eV cell) with respect to the value for pure zirconium. Thus, the increase in the degree of metallicity of zirconium should be expected at both the hydrogen dissolution and the introduction of helium.

Simultaneous introduction of hydrogen and helium (column *d* in Fig. 1) decreases the conduction band width of Zr by almost 0.6 eV. This value corresponds to the summary decrease in the conduction band of Zr provided by each impurity individually. In the Zr–He–H system, DES of zirconium at the Fermi level also increases (6.5 states/eV cell), and this value is higher than corresponding values for the Zr–He and Zr–H systems but is lower than their summary value. The DES peaks formed by 1*s* states of H and He are shifted with respect to their positions in the Zr–H and Zr–He systems by –0.12 and 0.14 eV, respectively. The latter circumstance seems to show that hydrogen and helium interact in Zr. Columns *b* and *c* in Fig. 1 clearly show that impurities of hydrogen and helium variously influence the electronic structure of zirconium. In particular, the overlapping of DES of hydrogen and zirconium in the filled part of the spectrum indicates the hybridization of H 1*s* states with valence states of zirconium, while He 1*s* states form a slightly dispersing deep-lying band that does not overlapped with the zirconium states. Moreover, the unoc-

cupied 2*s* states of atomic He form a fairly wide band above the Fermi level (at approximately 3 eV) of the Zr–He system and penetrate to the region of occupied zirconium states and hybridize with them. However, because of low density of the occupied 2*s* states of helium, the degree of hybridization is low. Because of this, the Zr–He bond is weak. The interaction of zirconium with helium is substantially different than that of zirconium with hydrogen.

Column *d* in Fig. 1 shows the combined influence of impurities of helium and hydrogen on the electronic properties of zirconium. So, we can see that the presence of hydrogen does not almost influence the densities of the *s* and *p* states of He in the energy range under consideration, exception for the energy range of preferred localization of H 1*s* states (~6.5 eV). On the other side, helium noticeably changes DES of hydrogen, decreases it in the range from –6 to –1 eV and increases it in the unoccupied part of the spectrum (from 2 to 4 eV). This decreases the binding energy of hydrogen with Zr and can favor the release of hydrogen from the metal at lower temperatures. Lastly, the overlapping of DES of hydrogen and helium in the occupied part of the spectrum demonstrates the existence of the H–He bond.

An analysis of local partial DES of the *s*-, *p*-, and *d*-types in the MT spheres of Zr atoms of the second coordination sphere for the Zr–He–H system allows one to state that helium and hydrogen atoms interact only with the nearest zirconium atoms. This is confirmed by the fact that DES peaks of zirconium clearly observed for zirconium atoms of the first coordination sphere in columns *b*, *c*, and *d* are absent in the range of the 1*s* states of hydrogen and helium.

3.2. Charge Density

Important information on the influence of hydrogen and helium on the electronic structure of Zr can be obtained from an analysis of the distribution of the valence charge density of pure zirconium and the Zr–He, Zr–H, and Zr–He–H systems. Figures 2–4 show the distributions of the valence charge density of pure zirconium and also above-mentioned systems containing ~6 at % helium and hydrogen. Figure 2 demonstrates the charge density in the $(11 - \frac{1}{2} 0)$ plane

perpendicular to the basal crystallographic plane (0001) of the hcp lattice and passing through atoms of zirconium, helium, and hydrogen. In the top, the charge density profiles calculated along the directions marked by bright lines. Figures 3 and 4 show the valence charge density in two planes parallel to basal plane (0001) of the hcp structure, passing through a helium atom in an octahedral interstitial site and a

hydrogen atom in a tetrahedral interstitial site, respectively. An analysis of Figs. 2b–4b shows that helium introduced to the octahedral interstitial site of

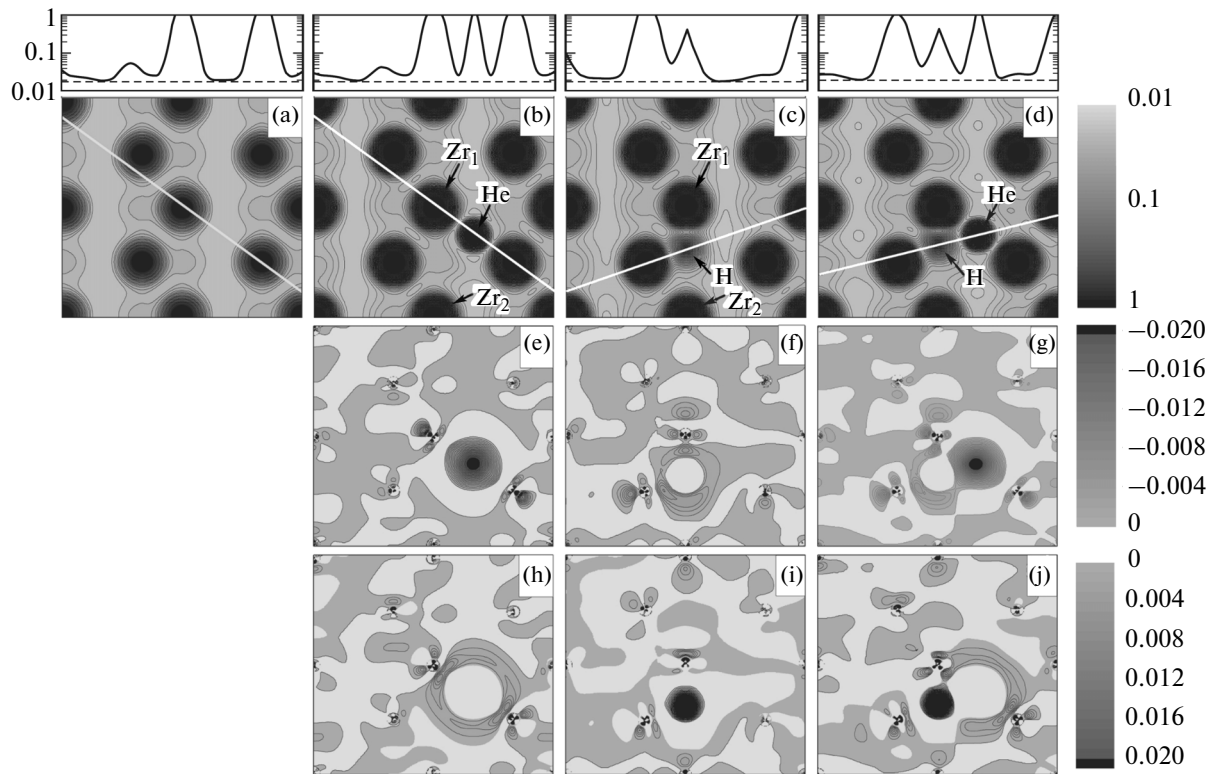


Fig. 2. Distribution of valence charge density $\rho(\mathbf{r})$ of (a) pure zirconium and (b) the Zr–He, (c) Zr–H, and (d) Zr–He–H systems in the $(11-\frac{1}{2}0)$ plane passing over atoms of zirconium and impurity. Panels (e–g) show negative and panels (h–j) show positive values of the difference of densities $\Delta\rho(\mathbf{r})$ for each of the systems. The arrows indicate the atomic positions or their projections to the plane under consideration. Digits 1 and 2 indicate Zr atoms of the first and second coordination spheres. In the top, the profiles of the distribution of the charge density along the directions shown by the bright line. The horizontal dashed line shows the level of the charge density in the interatomic region.

zirconium forms a bond with the nearest atoms of the metal, which is demonstrated by the existence of the common contour of isolines around them (Fig. 2b), and high density of the valence charge between them (as compared to that in an unoccupied interstitial site) (upper panel in Fig. 2b). We indicated the formation of this bond due to hybridization of He 2s states when discussing the density of states. In addition, helium increases the covalent component of the bond between Zr atoms of the first coordination sphere, which follows from the common contour of the isolines, enveloping these Zr atoms in Fig. 3b.

Figures 2c–4c clearly demonstrate the formation of a strong chemical bond between hydrogen and zirconium atoms, which is indicated by the large number of isolines enveloping Zr and H atoms (Figs. 2c and 4c) and a significant density of the valence charge between them that is higher than its value in unfilled interstitial site by a factor of almost four (the top panel in Fig. 2c).

The hydrogen and helium atoms, which are disposed in neighboring interstitial sites of the zirconium lattice, form chemical bond not only with the metal

atoms but also to each other. This is indicated by the existence of the common contour of isolines around these atoms in Figs. 2d and 3d and also elevated density of valence charge between them, as compared to that of interatomic region (the top panel in Fig. 2d). A comparative study of the distributions of the charge density in the Zr–He, Zr–H, and Zr–He–H systems shows that the hydrogen dissolution in the Zr–He system insignificantly influences the bond between Zr and He atoms (the charge density between them is almost unchanged). On the other side, introduction of helium in the Zr–H system weakens the bonds of the metal with hydrogen (the charge density between these atoms decreases by almost 20% (the top panels in Figs. 2c and 2d)). All these conclusions completely agree with the result of our study of DES of the system under consideration.

To reveal the specific features of the interaction of hydrogen and helium with zirconium and also their mutual influence on one other, we performed a detailed analysis of the charge density of zirconium due to the presence of impurity. In Figs. 2–4, panels (e–g, h–j) show negative and positive, respectively, values of the difference of densities $\rho(\mathbf{r})$ of the system

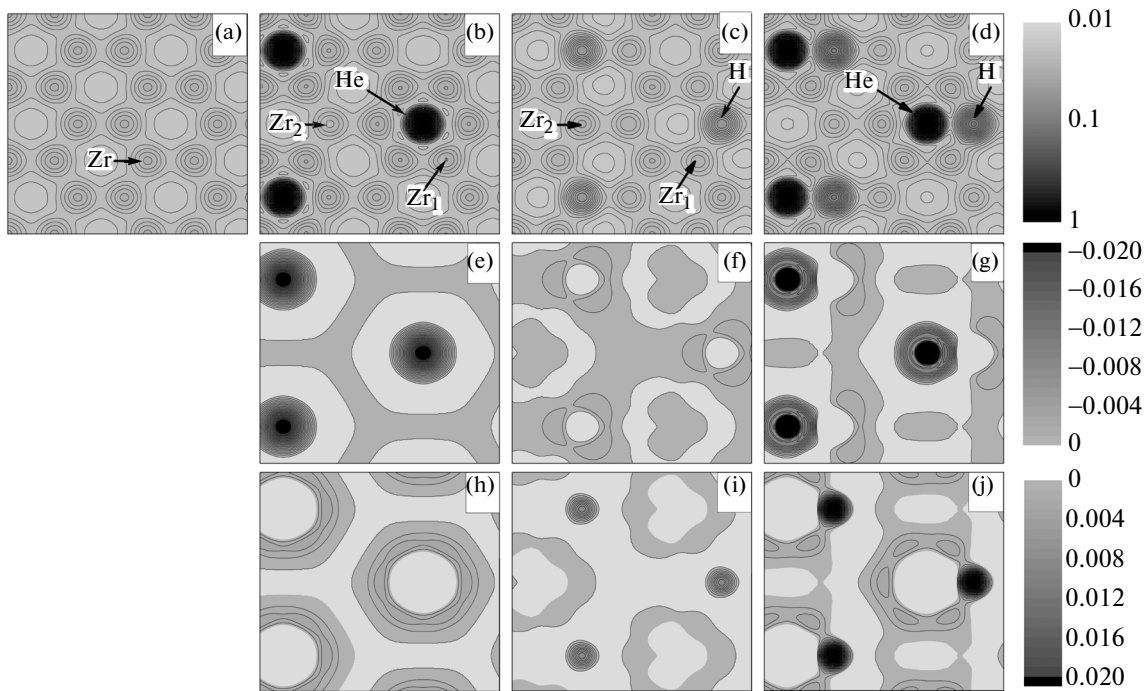


Fig. 3. Distribution of valence charge density $\rho(\mathbf{r})$ of (a) pure hcp zirconium and (b) the Zr–He, (c) Zr–H, and (d) Zr–He–H systems in the plane passing through a helium atom and parallel to (0001) basal plane of the hcp structure. Panels (e–g) show negative and panels (h–j) show positive values of the difference of the valence charge densities $\Delta\rho(\mathbf{r})$ for the Zr–He, Zr–H, and Zr–He–H systems, respectively.

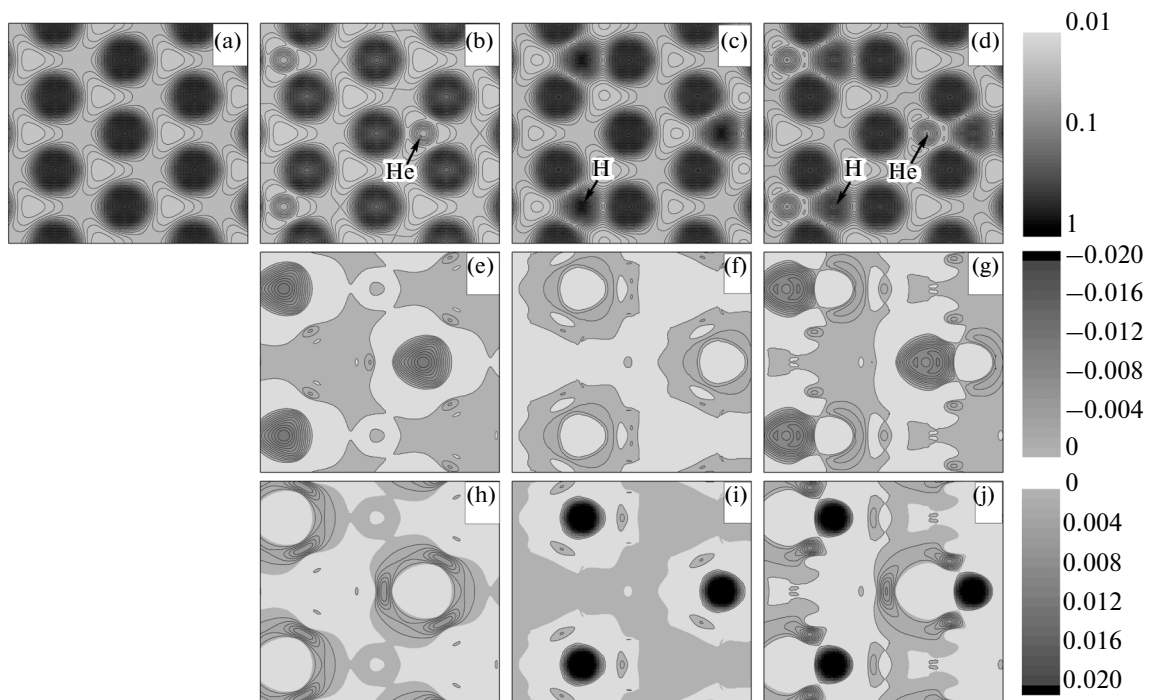


Fig. 4. Distribution of valence charge density $\rho(\mathbf{r})$ of (a) pure hcp zirconium and (b) the Zr–He, (c) Zr–H, and (d) Zr–He–H systems in the plane parallel to (0001) basal plane of the hcp structure and passing through a hydrogen atom. Panels (e–g) show negative and panels (h–j) show positive values of the difference of the valence charge densities $\Delta\rho(\mathbf{r})$ for the Zr–He, Zr–H, and Zr–He–H systems, respectively.

under consideration and their components. For example, for the Zr–He–H system, this value is found by formula

$$\Delta\rho(\mathbf{r}) = \rho_{\text{Zr-He-H}}(\mathbf{r}) - \rho_{\text{Zr}}(\mathbf{r}) - \rho_{\text{He}}(\mathbf{r}) - \rho_{\text{H}}(\mathbf{r}).$$

Thus, in panels (e–g), we can see the regions of the Zr crystal from which the valence charge goes out, and, in panels (h–j), we can see the regions where the valence charge comes due to the existence of the impurity.

It is seen from the difference of densities $\Delta\rho(\mathbf{r})$ shown in panels (e–j) that the existence of the impurity in the interstitial sites of the hcp lattice of zirconium leads to noticeable redistribution of the valence charge density of the metal that damps as the distance from the impurity increases. In particular, helium almost completely displaces electrons of zirconium (Fig. 2e) from the octahedral interstitial site that helium occupies to the interatomic region of Zr atoms of the first coordination sphere (Fig. 2h). In addition, helium brings about a nonuniform redistribution of the charge density in MT spheres of nearest Zr atoms (Figs. 2e and 2h). As a result, the valence charge in MT spheres of these Zr atoms increases by $0.022e$ as compared to that characteristic of pure zirconium. In this case, the charge in the MT sphere of helium only increases by $0.007e$ with respect to analogous value for a free helium atom.

Conversely, the hydrogen dissolution in zirconium increases the electron density in the tetrahedral interstitial site that it occupies (Fig. 2i) and decreases the electron density in the interatomic region of Zr atoms of the first coordination sphere (Fig. 2f). The calculations show that the MT sphere of an isolated hydrogen atom contains the electron charge of $0.290e$, and this charge increases to $0.503e$ in the Zr–H system. This indicates the transfer of the electron density from the interatomic region of zirconium to the MT sphere hydrogen. In the MT spheres of Zr atoms closest to hydrogen, the valence charge increases as compared to that of pure zirconium by $0.012e$ for the atoms in the tetrahedron base and by $0.002e$ for the atom in the tetrahedron vortex, which seems to indicate different types of coupling of hydrogen with these atoms.

It is seen from the difference of the densities $\Delta\rho(\mathbf{r})$ that, in the Zr–He–H system, the influence of impurities under consideration on the electron density of zirconium is, as a whole, the same as that in the Zr–He and Zr–H systems: hydrogen increases the electron density of zirconium in the region of the interstitial site that it occupies, and helium decreases the electron density. The combined influence of H and He on the electron density of zirconium is observed most noticeably in the interatomic region of Zr atoms of the first coordination sphere of the impurities.

The valence charge in the MT spheres of H and He atoms increases by $0.025e$ and $0.001e$, respectively, as compared to the value in the Zr–H and Zr–He systems; i.e., introduction of He into the Zr–H system

leads to additional transfer of the electro charge to the MT-sphere of hydrogen, and the dissolution of H in the Zr–He system does not almost change the charge state of helium. In this case, the valence charge increases by $0.028e$ in the MT-spheres of nearest Zr atoms and decreases by $0.0203e$ in other MT-spheres of Zr atoms as compared to that of pure zirconium.

An analysis of the redistribution of the valence electron density in the basal planes passing through impurity atoms in the Zr–He, Zr–H, and Zr–He–H systems shows that the presence of helium is a determining factor in the formation of the distribution of the electron density of the Zr–He–H system, while the effect of hydrogen has predominantly local character.

4. CONCLUSIONS

The ab initio calculations of the structures of the Zr–He, Zr–H, and Zr–He–H systems and also pure Zr were performed in terms of the density functional theory. An analysis of the results shows that the H and He impurities variously change the electronic structure of zirconium as their concentrations are of ~ 6 at %. For example, He 1s states form a narrow band lying below the Zr conduction band bottom by approximately 12 eV. On the other side, hydrogen, dissolving in zirconium, does not form additional band, unlike helium, but splits off a band of hybridized $s^{\text{H}}-(s, p, d)^{\text{Zr}}$ states from the zirconium conduction band bottom, forming a chemical bond. It is found that, as atomic helium is introduced in Zr, its unoccupied 2s states take part in the formation of a weak chemical bond with zirconium atoms. In addition, helium amplifies the covalent component of the bond between Zr atoms of the first coordination sphere, which likely can be a factor of zirconium embrittlement as a result of introducing helium.

Considering the Zr–He–H system as a result of dissolution of hydrogen in the Zr–He system or introduction of helium in the Zr–H system, we revealed that the existence of the hydrogen does not markedly influence the interaction of helium with the metal, whereas the introduction of helium decreases the Zr–H bond energy. Disposing in neighboring interstitial sites of the zirconium lattice (the Zr–He–H system), hydrogen and helium atoms form chemical bonds not only with zirconium atoms but also with each other. The he introduction in the Zr–H system leads to additional electron charge transfer to the MT-sphere of hydrogen, and the dissolution of H in the Zr–He system almost does not change the charge state of helium.

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