



Core electron level shifts in zirconium induced by vacancy, helium and hydrogen

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ABSTRACT

The paper presents a first-principle calculation of the influence of lattice defects (a hydrogen atom, a vacancy and a helium-in-vacancy complex) and their concentration on the core electron binding energies in zirconium atoms. It is shown that the formation of a vacancy or a helium-in-vacancy complex causes core-level shifts of Zr atoms to lower binding energies. Hydrogen dissolution leads to core-level shifts to both lower and higher binding energies. Besides, the effects of electron density redistribution in zirconium (due to the appearance of the defect and, as a consequence, the change of the crystal volume and the lattice relaxation around the defect) on the core electron binding energies are studied.

1. Introduction

Zirconium based alloys are widely used as structural materials for active zones of light water reactors. Water radiolysis under influence of radiation during the operation of these reactors leads to the release of atomic hydrogen, which is actively accumulated in the materials. Moreover, hydrogen, as well as helium is accumulated in structural materials due to (n, p) and (n, α) nuclear reactions. In addition, as a result of a long-term operation of the reactor, an appreciable number of vacancies are formed due to elastic collisions of neutrons with zirconium atoms. Accumulating in the zirconium alloys, these defects impair operational properties of the materials, reducing their plasticity and increasing brittleness [1–3]. The influence of hydrogen, helium and vacancies on the mechanical properties of zirconium and its alloys was investigated from the first principles in [4–8]. However, these studies did not investigate the influence of the defects on the distribution of the electron density of the metal, which is necessary to understand the degradation processes at the microscopic level.

Important information on the influence of impurities on the electron density distribution in a crystal can be obtained from core-level binding-energy shifts [9–11]. Experimentally, these shifts were measured by X-ray photoelectron spectroscopy (XPS) and other spectroscopic methods [12–15]. The most complete information on the core-level shifts (CLSs) can be obtained within the framework of all-electron first-principles full-potential calculations. In the present work, the formation process of the core electron level shifts and the electron density

redistribution in zirconium caused by the formation of vacancies and the presence of H and He atoms is theoretically studied.

2. Theoretical approach and computational details

Self-consistent calculations of core electron energy and electron density distribution of pure Zr and Zr-vacancy (Zr-vac), Zr-H, Zr-He-vac systems were performed using the density functional theory [16,17]. To describe the exchange and correlation effects, the generalized gradient approximation in the form of Perdew-Burke-Ernzerhof (PBE) [18] was used. The Kohn-Sham equations are solved using the all-electron full-potential linearized augmented plane wave (FP-LAPW) method [19,20], as implemented in the FLEUR code [21]. This implementation includes calculations of total energy and atomic forces, which allows carrying out a structural optimization.

The core states were described fully relativistically, while the semi-core (4s and 4p states of Zr) and valence states were treated by the scalar relativistic approximation. Inside the muffin-tin spheres, the wave functions were expanded in spherical harmonics with an angular momentum of up to $l = 8$ for zirconium and 4 for hydrogen and helium. The wave functions in the interstitial region were expanded into augmented plane waves with a cutoff of $k_{\max} = 4.0$ (a.u.)⁻¹, corresponding to the 178 basis LAPW functions per atom. The muffin-tin radii were chosen as 2.5, 1.0 and 1.0 a.u. for Zr, He and H, respectively. Self-consistency was considered to be achieved when the total energy variation from iteration to iteration did not exceed 0.02 meV. For the self-

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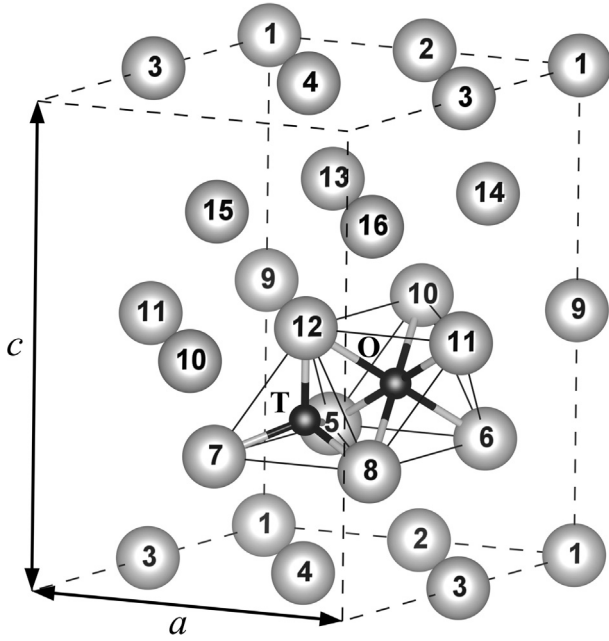


Fig. 1. The calculated supercell of Zr-vac, Zr-He-vac and Zr-H systems with the defect concentration of ~ 6 at.%. a and c are the supercell parameters.

consistent calculations, the Brillouin zone was sampled at 108 k points. The considered systems were relaxed and the atoms were assumed to be in the equilibrium configuration when the force on each atom was below 0.025 eV/\AA .

In our calculations a supercell consisting of a $2 \times 2 \times 2$ block of hcp zirconium unit cells was used (Fig. 1) to study the defect concentration of ~ 6 at.% in zirconium. For convenience of discussion, all the Zr atoms in Fig. 1 are numbered. The supercell of the Zr-H system contained sixteen Zr atoms and one H atom in a tetrahedral (T) or octahedral (O) site. To simulate the Zr-vac system one Zr atom (at number twelve) was removed from the supercell. In the case of the Zr-He-vac system one He atom was placed in the vacancy (instead of the twelfth Zr atom in the supercell). As it was shown in [6,22], this configuration is most energetically favorable. To study the defect concentration of ~ 3 at.% the lateral supercell parameter a for all the considered systems was 1.5 times greater than at the concentration of ~ 6 at.%. Thus, a supercell consisting of a $3 \times 3 \times 2$ block of hcp zirconium unit cells was used.

The binding energy of Zr core electrons in the considered systems was calculated as

$$\Delta E_{\text{Zr-X}} = E_{\text{F}} - E_{\text{core}}, \quad (1)$$

where E_{F} is the Fermi energy of the Zr-X system (X is the vacancy, hydrogen or helium) and E_{core} is the energy of Zr core electron. The CLS δE was obtained as

$$\delta E = \Delta E_{\text{Zr-X}} - \Delta E_{\text{Zr}}, \quad (2)$$

where ΔE_{Zr} is the core electron binding energy of pure Zr.

To study the mechanism of the origin of the CLS in the considered systems, we divided the system formation process into three stages: (1) the appearance of the defect in the ideal metal lattice and (2) the subsequent change of the crystal volume (lattice parameters optimization) with (3) the relaxation of atomic positions in the lattice. The CLSs caused by the defect occurrence (δE_{def}), the change of the lattice parameters (δE_{vol}) and the lattice relaxation (δE_{relax}) were calculated as

$$\delta E_{\text{def}} = \Delta E_{\text{Zr-X}}^0 - \Delta E_{\text{Zr}}, \quad (3)$$

$$\delta E_{\text{vol}} = \Delta E_{\text{Zr-X}}^{\text{opt}} - \Delta E_{\text{Zr-X}}^0, \quad (4)$$

$$\delta E_{\text{relax}} = \Delta E_{\text{Zr-X}} - \Delta E_{\text{Zr-X}}^{\text{opt}}, \quad (5)$$

where $\Delta E_{\text{Zr-X}}^0$ and $\Delta E_{\text{Zr-X}}^{\text{opt}}$ are the binding energies of Zr core electrons of the Zr-X system with lattice parameters of pure zirconium and with optimized ideal lattice parameters, correspondingly.

The defect formation in a crystal causes the redistribution of its valence electron density (valence charge transfer δQ to or from Zr atoms) which in turn leads to the change in the binding energy of core electrons [9,23]. Therefore, to study in detail the nature of the CLS, we calculated the change of the electron charge δQ in the Zr MT-sphere due to the defect formation, as well as its partial components δQ_{def} , δQ_{vol} and δQ_{relax} arising at the above-mentioned stages

$$\delta Q = Q_{\text{Zr-X}} - Q_{\text{Zr}}, \quad (6)$$

$$\delta Q_{\text{def}} = Q_{\text{Zr-X}}^0 - Q_{\text{Zr}}, \quad (7)$$

$$\delta Q_{\text{vol}} = Q^{\text{opt}}_{\text{Zr-X}} - Q_{\text{Zr-X}}^0, \quad (8)$$

$$\delta Q_{\text{relax}} = Q_{\text{Zr-X}} - Q^{\text{opt}}_{\text{Zr-X}}, \quad (9)$$

where Q is the valence charge in the MT-spheres of the pure Zr (Q_{Zr}) and the Zr-X system with lattice parameters of pure Zr ($Q_{\text{Zr-X}}^0$) and with optimized lattice parameters for ideal ($Q_{\text{Zr-X}}^{\text{opt}}$) and relaxed ($Q_{\text{Zr-X}}$) atomic configurations in the supercell.

3. Results and discussion

3.1. Vacancy

The first coordination sphere of a vacancy includes nine Zr atoms (Fig. 1): atoms 9, 10 and 11 are located in the same basal plane as the vacancy; atoms 5, 7, 8 and 13, 15, 16 lie in the neighboring basal planes above and below the vacancy, respectively. Atoms 6 and 14 belong to the second coordination sphere. The third and fourth coordination spheres contain, correspondingly, atom 4 and atoms 1, 2, and 3. The CLSs δE calculated for the Zr atoms of the above-mentioned coordination spheres from Eq. (2) are presented in Fig. 2. It is seen that the vacancy formation leads to a shift of the core electron levels to lower binding energies by 0.06 – 0.26 eV depending on the coordination sphere number. The value of the CLS depends weakly on the quantum numbers of the electron states. Therefore, only the $3d_{3/2}$ state of Zr is considered further below.

Fig. 3a shows the contributions of the vacancy occurrence (δE_{def}), decrease in the crystal volume (δE_{vol}) and atom displacements from the

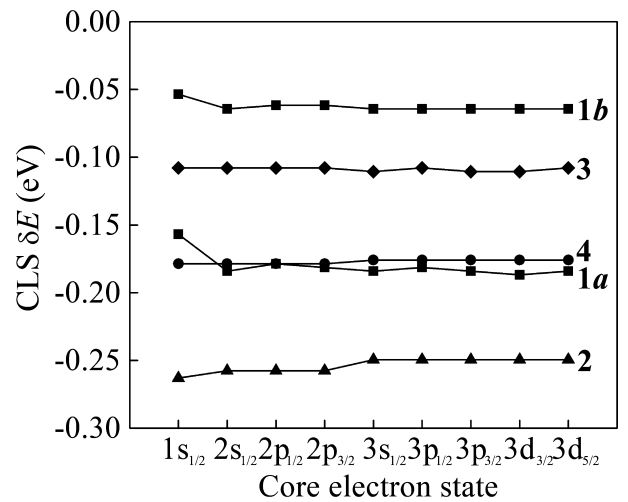


Fig. 2. The CLS δE of Zr atoms in the Zr-vac system. Numbers indicate the vacancy coordination spheres. Letters a and b denote the atoms of the first coordination sphere lying in the same basal plane with the vacancy and in the neighboring basal planes, respectively.

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