



Axial ratio dependence of the stability of self-interstitials in HCP structures

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ABSTRACT

We investigate the effect of the axial ratio (c/a) on the stability of self-interstitial atoms (SIAs) in hexagonal close-packed crystal structures, using hcp-zirconium as a prototype, through density functional theory based *ab initio* calculations. The axial ratio is found to dominate the relative stability of SIAs over volumetric strains. We observe that below the ideal value of 1.633, the basal octahedral configuration is the most stable. Above the ideal value, the off-plane SIAs are more stable than in-plane ones.

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The axial ratio (c/a) is one of the most important structural parameters of a hexagonal-close-packed (hcp) system. The axial ratio determines the most close-packed plane in which the dislocation loop nucleation is energetically favorable, and it affects many properties of the materials including the lattice stabilities [1], elastic moduli [2,3], point defect properties [4], stacking-fault energies [4], ductility/brittleness [5], dislocation nucleation and movements [6–8], fracture mechanism, deformation mechanism [9], element substitutions [10], twinning and extended defects [11], period of the helicoidal magnetic structure [12], domain-structure [13], coincidence orientations [14], interstitials long-range migrations [15], topology of the Fermi surface [16], and energy storage density [17]. There are 28 elements with hcp structures in their α phase. The c/a ratio ranges from 1.472 (Yttrium) to 1.886 (Cadmium). The ideal c/a ratio (1.633) corresponds to the c/a ratio in a face centered cubic structure, which is more isotropic than an hcp structure with non-ideal c/a ratio. The most close-packed plane in hcp is the prism plane $\{10\bar{1}0\}$ for $c/a < 1.633$ and the basal planes (0001) for $c/a > 1.633$.

Self-interstitial atoms (SIAs) are common point-defects of crystalline solids and contribute to mass transport. Compared to vacancies, SIAs have much higher mobility due to smaller migration energy barriers in metallic materials. The relative stability of SIAs is critical in the mass transportation and microstructure evolution. However, the axial ratio dependence of the stabilities as well as relative stabilities of SIAs is still unknown.

With the aim to understand how the c/a ratio affects interstitial stability in hcp metals, we focus on this particular symmetry factor c/a and eliminate any other effects such as chemical composition. Following this logic, we will use one hcp metal and vary the c/a ratio between 1.50 and 1.80 to cover the range of interest. Since

zirconium and its alloys are heavily used in the radiation environment of fission reactors, we choose zirconium as the prototype material [4]. The various c/a ratios were achieved by changing the length of c only while keeping a constant. As a result, there appears to be a uniaxial strain applied. In order to show that the axial effect is not simply strain effects, we have carried out studies of large volumetric strains (about 9%) that are comparable to strains that are responsible for the variable axial ratios.

When one extra atom sits inside an hcp structure to form an SIA configuration, there are eight symmetrical positions where it can rest. We use the conventional notations to denote these eight configurations [18], known as octahedral (O), split $\langle 0001 \rangle$ dumbbell (S), crowdion (C), tetrahedral (T), basal octahedral (BO), basal split (BS), basal crowdion (BC), and basal tetrahedral (BT) configurations. A previous study shows that the SIA configurations of O, S, C, BO, and BS are the five most stable configurations [19] in Zr (Fig. 1). We will only focus on these five configurations since the remaining three configurations are either unstable (BC,T) or with a much higher formation energy (BT).

It is a great challenge to study the properties of SIAs in Zr. From experimental side, both diffuse scattering experiments [20,21] and internal friction measurements [22] have failed to identify the most stable SIA configuration. This is because these quantities are affected by the local environment, including the presence of impurities around the defects. High purity samples are therefore expected to generate reliable results [23]. Models based on classical inter-atomic potentials are problematic in characterizing the SIA stabilities and do not agree with each other [24–29]. Part of the reason is that hcp transition metals, particularly those with c/a ratios different from the ideal value of 1.633, are poorly described by empirical inter-atomic potentials [30]. Precise predictions rely on *ab initio* density functional theory (DFT) calculations.

The formation energy is the energy cost of generating a defect configuration, which is used to quantify the stability of a SIA configuration as compared with the ideal system without any defects.

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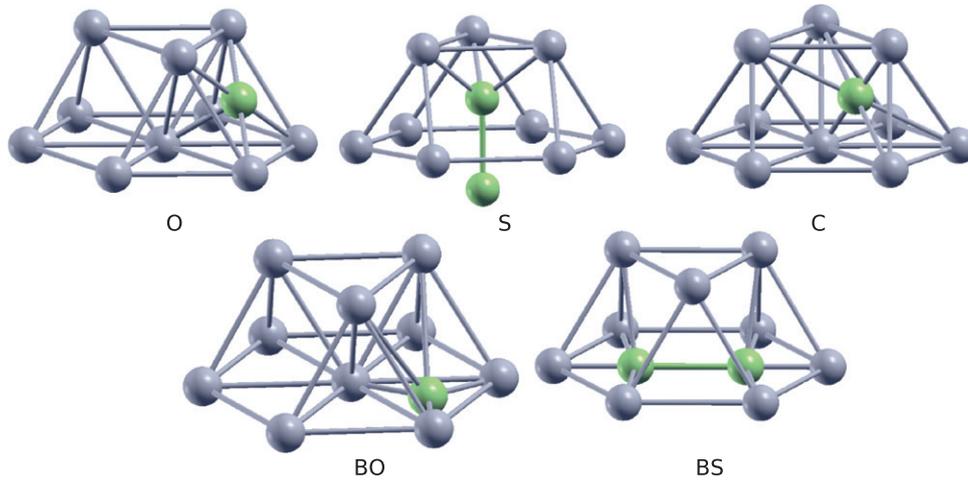


Fig. 1. The five most stable SIA configurations in hcp-Zr at reference state, where green balls represent the SIAs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The difference in formation energies between two SIAs is a measure of their relative stability. At a state under strain ε , which could be uniaxial or volumetric, the SIA formation energies are calculated using the rescaled constant volume method [18,31–33]

$$E^f(\varepsilon) = E\left(N+1; \frac{N+1}{N}V; \varepsilon\right) - \frac{N+1}{N}E(N; V; \varepsilon), \quad (1)$$

where $E(N; V; \varepsilon)$ is the total energy of the ideal bulk (without defects) with N atoms in volume V under uniaxial strain. $E(N+1; \frac{N+1}{N}V; \varepsilon)$ is the total energy of the system with an SIA, which has $N+1$ atoms and the volume is first re-scaled to $\frac{N+1}{N}V$, then a strain ε is applied. The super cell method is used to model the ideal Zr structure and its SIA configurations. We used a super cell containing $5 \times 3 \times 3$ 4-atom-unit cells, with dimensions of a , $\sqrt{3}a$, and c with a total of four atoms, each at (000) , $(1/2 \ 1/20)$, $(01/3 \ 1/2)$, and $(1/25/6 \ 1/2)$, where a and c are lattice constants of hcp-Zr. Such a 180-atom super cell was chosen based on the previous convergence study [19], where the formation and relative formation energies were calculated as a function of super cell size.

DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [34], which is based on the Kohn–Sham Density Functional Theory (KS-DFT) [35], with the generalized gradient approximations developed by Perdew, Burke and Ernzerhof (PBE) for exchange–correlation functions [36]. The core electrons are replaced by the projector augmented wave (PAW) and pseudo-potential approach [37], which has twelve electrons ($4s^2 4p^6 5s^2 4d^2$) explicitly included as valence electrons.

The cutoff energy for the kinetic energy of wave-functions was carefully selected to be 400 eV after convergence tests. To preserve the hcp symmetry in hcp structures, a Gamma-centered k -mesh is required to sample the irreducible Brillouin Zone. A $3 \times 3 \times 3$ Gamma-centered k -mesh was used after k -mesh convergence tests. Integration over eigenvalue was performed by the smearing technique using the Methfessel–Paxton function and a smearing width of 0.05 eV [38], which results in a total energy convergence with fluctuations less than 2.0 meV/cell.

The SIA structures optimized with the conjugate gradient method with constant volume boundary conditions. The criterion to stop the relaxation of the electronic degrees of freedom is set by requiring the total energy change to be smaller than 10^{-5} eV. The optimized atomic geometry is achieved through minimizing Hellmann–Feynman forces on each atom until the maximum force smaller than 0.03 eV/Å. All the parameters selected ensure the

convergence of formation energies with fluctuations less than 0.05 eV/cell.

The lattice constant a of hcp-Zr is predicted as $a = 3.238$ Å and the c/a ratio is 1.600, agreeing with experiments [39] of 3.23 Å, and 1.593 respectively.

The c/a ratio varies from 1.5 to 1.80, with an increment of 0.05. The choice of the range is a compromise between the range of c/a ratio in the 28 HCP elements (1.472 – 1.886) and the mechanical strength of hcp-Zr (–14 GPa to 26 GPa) [40].

As the c/a ratio varies, configuration O shows a maximum formation energy at $c/a = 1.55$ Table 1. After that, the formation energy decreases as c/a increases, and the rate of decrease increases Fig. 2. At $c/a = 1.80$, the formation energy is $E_o^f = 1.379$ eV, which is the lowest among other SIAs. There is a general trend that the formation energies decrease with the increment of the c/a ratio after the maxima around the ideal c/a ratio. Such axial ratio effect on the formation energies of SIAs could be understood as follows. When the c/a ratio increases, the distance between two neighboring atomic layers increases, and the separation of atoms in these layers is enlarged. Because the total electronic charge is fixed, the overall electronic charge density decreases. As a consequence, the formation energy decreases.

The change of the formation energy for the in-plane configurations (BO and BS) is weakly sensitive to the c/a ratio when $c/a > 1.633$. This could be understood as that the formation energies of in-plane configurations are the result of forming bonds among atoms in the basal plane. The bond lengths with other in-plane atoms are shorter, and thus stronger than those off-plane atoms. When the c/a ratio increases, the distance between two neighboring atomic layers increases, which enlarges the separation of atoms in adjacent layers. The overall electronic charge density therefore decreases. Since the size of the basal plane is conserved, the electronic charge densities on the basal plane changes less than in the off-planes. As a result, the formation energies of in-plane configurations are more inert to the change of the c/a ratio.

On the contrary, the off-plane configurations (O, S, and C) are much more sensitive to the variation of the c/a ratio since these

Table 1

The maximum formation energies E^f (in unit of eV) of SIAs and the corresponding c/a ratio from *ab initio* studies of hcp-Zr.

	O	S	C	BO	BS
E^f	2.986	3.329	3.369	2.864	3.231
c/a	1.55	1.55	1.60	1.65	1.65

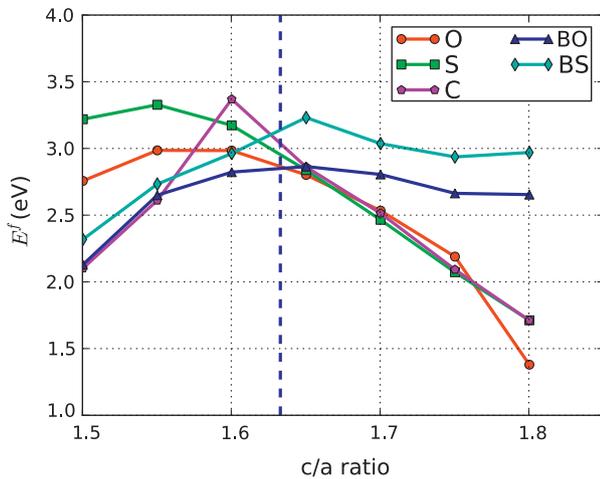


Fig. 2. Formation energy of SIAs with respect to the c/a ratio.

SIAs are located between the adjacent basal planes. They introduce more electronic bonds off the basal plane. Due to the variation of the c/a ratio, the electronic bonding in off-plane direction will be greatly affected by the change of the electronic charge density. As a consequence, formation energies of off-plan SIAs decrease more drastically than those of in-plane SIAs.

It is worthy to note that the sensitivity of the SIAs stabilities to the c/a ratio was also checked in a previous study within a small range of 1.593 and 1.60, and the same results were reported [33].

It is interesting to find that these three off-plane configurations show similar decreasing rates in the formation energy when c/a is greater than 1.633, and the configuration O decreases faster when $c/a > 1.75$. The similarity of the rate of decrease beyond the ideal c/a ratio could be due to the fact that the rate of attenuation of electronic charge density along the c direction is the same in all three cases and the electronic charge density along the c direction dominates the formation energies of off-plane SIAs.

The response of the formation energies of the off-plane and in-plane counterparts are somehow symmetrical with the ideal $c/a = 1.633$ as the c/a ratio changes. The formation energy curves of counterpart configurations, O and BO, S and BS, have crossovers around the ideal c/a . Such symmetry could be result of the bonding symmetry around the ideal c/a ratio.

In the next set of experiments, we studied the effect of volumetric strain to show that the axial effect is not simply strain effect. While the volumetric strains are applied, the three orthogonal directions undergo the same strains within the elastic region, which is from -0.03 to 0.03 in this study. The formation energy $E^f(\varepsilon)$ varies with respect to the applied volumetric strain ε (ranged from -0.0873 to 0.0927) for all SIA configurations (Fig. 3). A positive volumetric strain indicates the dilation of the volume and a negative volumetric strain implies a shrinkage. The formation energies of SIA configurations decrease with positive volumetric strain. When strains are negative, the formation energies of the S and C configurations increase to their maximum of 3.212 eV and 3.444 eV, respectively, at $\varepsilon = -0.061$, then decrease. The rest of the SIAs have the maxima at $\varepsilon = -0.091$. The volumetric strains do not change the relative stability of all the SIA configurations.

The behavior of the formation energies of SIA responding to the volumetric strain can be understood as follows. As the volumetric strain increases, the separation between atoms increases, which results in a decrease of the electron charge density. The interactions (strength of the bonds) between atoms are weakened. As a result, the formation energy decreases with respect to the strain.

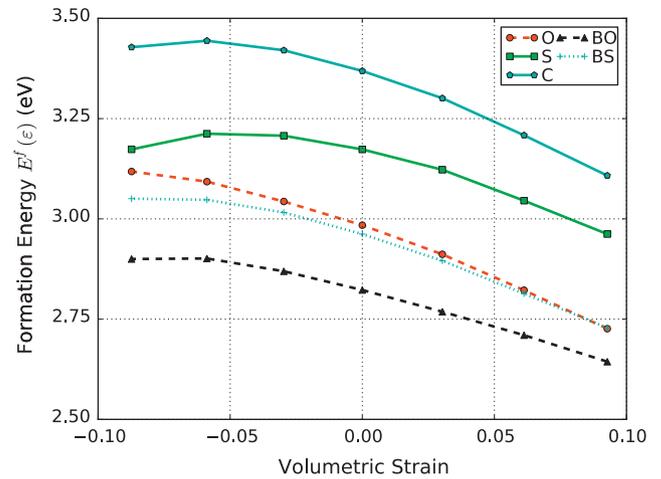


Fig. 3. The variation of formation energies of SIAs with respect to the volumetric strains.

The basal octahedral configuration is the most stable configuration in all the studied strains except the tensile uniaxial strain along the c direction. Under the tensile uniaxial strain, all the tested off-plane SIA configurations (O, S, and C) have lower formation energies than the in-plane configurations (BO and BS). The knowledge of the conclusive formation energies of these SIAs could provide a solid ground for further studies on the evolutions of these SIAs using transition state theory and Kinetic Monte Carlo methods.

When a single Zr crystal is irradiated, it has the expansion in the a direction and contraction in the c direction [41]. Because the BO and BS are the two most stable configurations, the in-plane SIA configurations could be dominant compared to the off-plane configurations. The diffusion between the BO and BS is within the basal plane, i.e., two-dimensional. The difference of the formation energy is 0.09 eV. Since E^f could be used as a rough estimation of the diffusion energy barrier, the in-plane diffusion could be dominant.

A SIA generated by radiation will become an in-plane SIA during relaxation due to the energy landscape. Thus there is a movement from off-plane to in-plane. This could provide an explanation of the experimental observation that alignment of c loops in bands parallel with the basal planes in neutron-irradiated Zr [42]. Furthermore, the 2D diffusion in-plane will transport the SIA along the basal plane. This process is repeated until there is a measurable expansion in the a direction and contraction in the c direction, as observed in single crystal zirconium [41,43]. Although dislocation loops, small defect clusters, and dislocation climb processes are responsible for the growth through complex mechanisms, our results suggest a mechanism of radiation growth [28] caused by 2D diffusion, from the aspect of the stability of the SIAs. Interestingly, our results fit in a recent radiation growth model [44] in which the radiation growth is governed by the production of SIA clusters and their migration along basal planes.

In summary, we studied the axial ratio effect on the stabilities of self-interstitial atom (SIA) configurations in hcp-zirconium using *ab initio* DFT calculations. Although the physical parameters of Zr were used as a prototype in the calculations, based on our analysis of change of the electron charge density, our results could be general for other hcp crystals. We found that the basal octahedral (BO) configuration is the most stable configuration except when $c/a > 1.633$, where off-plane configurations are more stable. The second most stable configuration is the basal split-dumbbell (BS) for the axial ratio less than 1.633, with the formation energy difference of 0.09 eV. The volumetric strains do not change the

relative stability of SIAs. The axial ratio is the dominating factor over volumetric strain. Our results suggest the diffusion of SIAs is two-dimensional within the basal plane, between BO and BS configurations. Our results could provide a guide for further transition state theory and Kinetic Monte Carlo studies on the evolutions of these SIAs.

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