

Elastic stability and electronic structure of fcc Ti, Zr, and Hf: A first-principles study

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The structural stability and electronic structure of face-centered-cubic Ti, Zr, and Hf were studied by means of first-principles full-potential calculations. The total-energy calculations demonstrate that Ti, Zr, and Hf have a *locally stable* fcc structure, i.e., the elastic stability criteria for a cubic crystal are fulfilled by the calculated elastic constants. The electronic densities of states for the fcc phase are significantly different from those for the corresponding hcp phases, for the three metals involved in this study. In particular, we found that the values of the electronic densities of states at the Fermi level for the fcc phase are approximately 100% higher with respect to the hcp phase.

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Group-IVA elements (Ti, Zr, and Hf) adopt an hcp crystal structure at room temperature and zero pressure. When the temperature is raised, at zero pressure, they transform into a bcc structure before the melting temperature is reached. However, when the pressure is increased, at room temperature, a crystallographic phase transition into the so-called omega structure is observed.¹ At even higher pressures both Zr and Hf show a transformation into the bcc structure. This pressure-induced phase transformation sequence has received extensive experimental as well as theoretical attention.²⁻⁶ The vacancy formation energy in the hcp phase and the Landau free energy for the bcc-hcp phase transformation for this group of elements have been studied recently by means of first-principles calculations.^{7,8} Additionally, a recent first-principles study of the Bain transformation on Ti reports that the calculated total energy shows a minimum at the fcc structure.⁹

The fcc crystal structure does not appear on the usual pressure-temperature phase diagrams of Ti, Zr, and Hf.¹ However, the epitaxial growth of fcc-Ti thin films on NaCl single crystals was reported by Wawner Jr. and Lawless¹⁰ many years ago. More recently, also the epitaxial growth of fcc-Ti thin films on metallic substrates and on semiconductors has been reported: Al(011),¹¹ Ni(001),¹² Al(001),¹³⁻¹⁵ and SiC(0001) (Ref. 16) stimulating a renewed interest in the structural properties of fcc-Ti thin films. Face-centered-cubic Ti is also reported to exist in Ti/Ni and Ti/Al multilayers,^{12,17,18} nevertheless it has been claimed that fcc Ti in Ti/Al multilayers is merely an artifact of the manner in which specimens are prepared for cross-sectional transmission electron microscopy;¹⁹ currently a general agreement has not been reached.^{20,21} Further, evidence for the growth of fcc Hf in Hf/Fe multilayers has been published very recently,²² while to our best knowledge, the growth of fcc Zr has not been reported up to date. These observations stimulated us to study the structural stability and electronic properties of fcc Ti, Zr, and Hf.

In this paper, first we investigate the stabilities of Ti, Zr, and Hf in the fcc phase by performing *ab initio* total-energy calculations for small strains of the fcc structure. Secondly, the electronic structures for the three metals in the fcc structure are analyzed and compared with those corresponding to

the hcp phases. From these results, we will show that Ti, Zr, and Hf have locally stable fcc structures and that the electronic structures for these phases are significantly different from those for the hcp phases.

The Kohn-Sham total energies were calculated self-consistently using the full-potential linearized augmented plane-wave method²³ (LAPW) as implemented in the WIEN97 code,²⁴ where the core states are treated fully relativistically, and the semicore and valence states are computed in a scalar relativistic approximation. The exchange correlation was evaluated within the generalized gradient approximation (GGA), using the recent parameter-free GGA form by Perdew, Burke, and Ernzerhof.²⁵ We have chosen the muffin-tin radii (R_{MT}) of 2.0 a.u. and a plane-wave cutoff $R_{MT}K_{MAX} = 9.0$ leading to about 140 (plane-wave) basis functions. Inside the atomic spheres the potential and charge densities are expanded in crystal harmonics up to $L = 10$. Convergence was assumed when the energy difference between the input and output charge densities was less than 1×10^{-5} Ry.

The calculations were carried out with a sufficiently large number of k points in the first Brillouin zone (BZ). We used a $13 \times 13 \times 13$ k -point mesh, yielding a different number of k points in the irreducible wedge of the BZ depending on the structure: 84 for the bcc and fcc, 135 for the hcp, and 144 for the omega phase. We investigate the convergence of the total energy on increasing the number of k points for each structure. For example, an increase from 13^3 to 15^3 points in the first BZ for hcp Zr leads to a total-energy difference of less than 0.01 mRy. Special attention was paid to convergence of results for the elastic constants calculations, especially for the fcc structure with a tetragonal distortion at constant cell volume for which the energy differences are only fractions of 1 mRy. For the tetragonally and trigonally distorted fcc phases, we used 550 and 670 k points in the irreducible part of the BZ, respectively. The corrected tetrahedron method²⁶ was used for Brillouin-zone integration.

For the cubic structures (fcc and bcc) the total energy was calculated as a function of cell volume V . For the hcp and omega structures the total energy was calculated as a function of V and c/a . We performed calculations for seven different volumes and for seven different c/a ratios, in order to optimize both V and c/a . The calculated total energy as a

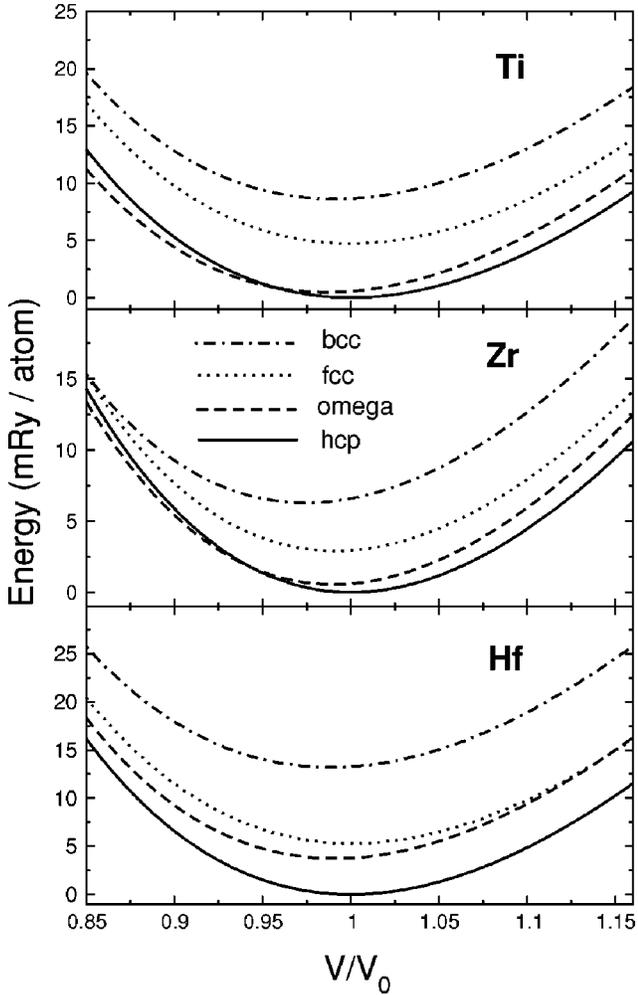


FIG. 1. Calculated total energies for the hcp, omega, bcc, and fcc phases of titanium, zirconium, and hafnium as a function of atomic volumes. The energy of the hcp phase at the equilibrium volume here is the reference level, and is set to zero. The lines are fits of the equation of state to the calculated energy values (see text).

function of volume was fitted to the Murnaghan equation of state;²⁷ from this process the equilibrium volume (V_0) and the bulk modulus (B) were obtained. The fits to the calculated total energy as a function of volume for Ti, Zr, and Hf, with the hcp, omega, fcc, and bcc structures, are presented in Fig. 1. The energy is referred to the ground state, the minimum of the hcp structure, E_0^{hcp} , and the volume is normalized to the calculated equilibrium volume of the hcp structure, V_0^{hcp} . It is important to note that in the three metals the predicted ground states correspond to the hcp structure as is observed experimentally. From the Fig. 1, we can see that for the three metals the phase ordering at the equilibrium volume is the same, increasing in energy hcp, omega, fcc, and bcc. In the case of Ti and Zr we find the pressure-induced hcp-omega transition at 0.96 and 0.94 of V_0^{hcp} , in good agreement with the experimental observations.⁴ For Hf this transition occurs at a volume smaller than the range studied in this work. In Table I, we summarize the calculated equilibrium volumes and bulk moduli for the hcp phases, the equilibrium

TABLE I. Calculated equilibrium volume for Ti, Zr, and Hf in the hcp and fcc phases (in $\text{\AA}^3/\text{atom}$), bulk moduli for the hcp phase, and the energy difference between the fcc and hcp phases, $\Delta E = E_0^{\text{fcc}} - E_0^{\text{hcp}}$. Experimental values from Ref. 1 are shown in parentheses.

Metal	V_0^{hcp}	B^{hcp} (GPa)	V_0^{fcc}	ΔE (mRy)
Ti	17.4 (17.6)	112 (106)	17.4	4.8
Zr	23.4 (23.3)	95 (95)	23.1	3.3
Hf	22.4 (22.3)	109 (108)	22.5	4.0

volumes for the fcc phases, and the energy difference between the minimum energy of these two phases $\Delta E = E_0^{\text{fcc}} - E_0^{\text{hcp}}$. The calculated equilibrium volumes and bulk moduli for the hcp phases are in good agreement with the experimental values (see Table I) for the three metals; the errors in the equilibrium volumes and bulk moduli are not larger than 1% and 10%, respectively, as is expected for first-principles calculations where the GGA is used. It is interesting to note that the smallest value for ΔE is observed for Zr, although this element shows the largest difference in volume.

The stabilities of fcc Ti, Zr, and Hf have been analyzed using the elastic constants. A cubic crystal has three independent elastic moduli; these can be taken to be the bulk modulus (B) and two shear moduli, $G' = (C_{11} - C_{12})/2$ and $G = C_{44}$.^{28,29} In this way, the conditions for elastic stability of a cubic lattice are^{29,30}

$$B = (C_{11} + 2C_{12})/3 > 0,$$

$$G' = (C_{11} - C_{12})/2 > 0,$$

$$G = C_{44} > 0. \quad (1)$$

The bulk modulus B was determined by fitting the calculated total energy as a function of volume to the Murnaghan equation of state, as was mentioned above. The shear elastic constants were calculated from the total energy as a function of volume conserving tetragonal (for G') and trigonal (for G) strains at the calculated equilibrium lattice parameter, following Ref. 28. The calculated lattice parameters and bulk moduli for the three fcc metals are presented in Table II. We can see that the elastic stability criteria for a cubic crystal [Eq. (1)] are fulfilled by the calculated elastic constants for the three metals. Therefore, Ti, Zr, and Hf have a locally stable fcc structure, in agreement with the observations of fcc Ti (Refs. 10,11,13, and 16) and fcc Hf.²² The observation of fcc Zr has not been, to our best knowledge, reported yet, consequently the present results represent a prediction of a metastable phase of Zr.

TABLE II. Calculated lattice parameters and bulk moduli for Ti, Zr, and Hf in the fcc phase.

Metal	a_0 (\AA)	B (GPa)	G' (GPa)	G (GPa)
Ti	4.11	107	22	61
Zr	4.52	91	21	53
Hf	4.48	103	28	67

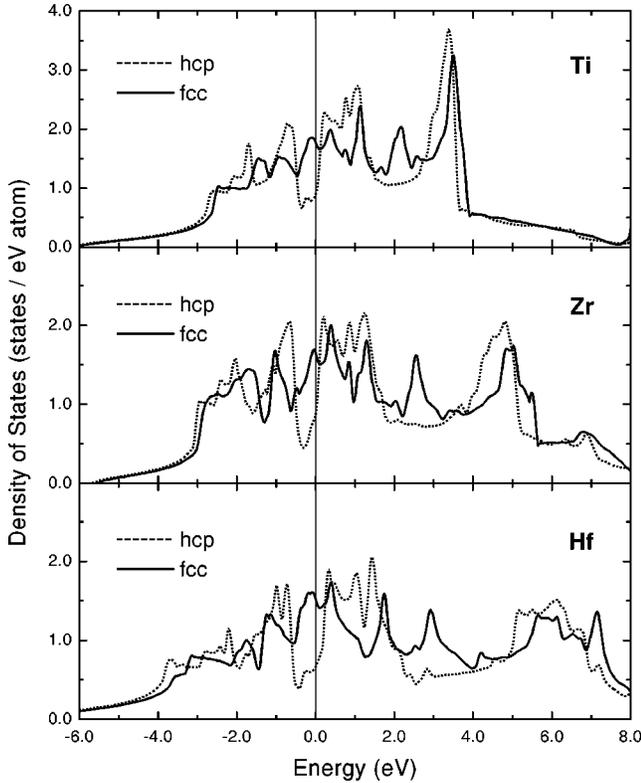


FIG. 2. Densities of states for the hcp (dashed line) and fcc (solid line) phases at the calculated equilibrium volume for titanium, zirconium, and hafnium.

The calculated lattice parameter for fcc Ti (4.11 Å, see Table II) is very close to the experimental value (4.15 Å) which has been obtained from a strain analysis of quantitative low-energy electron-diffraction data for Ti thin films on Al(001).¹³ For fcc Hf we have obtained an equilibrium lattice parameter of 4.48 Å, which is 3% lower than the experimental value of 4.64 Å which was determined from x-ray-diffraction measurements on Fe/Hf multilayers.²² For fcc Zr we have obtained a lattice parameter of 4.52 Å and comparison is not possible because experimental data is not available. However, this value can be useful in searching for a substrate on which the epitaxial growth of fcc Zr could be obtained. Unfortunately, no metal with an fcc ground state has a lattice parameter close to the value of 4.52 Å. Nevertheless, regarding the (001) surface of the fcc structure match with the (001) surface of the bcc structure, under an in-plane rotation of 45° ($a_{\text{bcc}} = a_{\text{fcc}}\sqrt{2}/2$), using this rule, the value of $a_{\text{fcc}} = 4.52$ Å becomes $a_{\text{bcc}} = 3.20$ Å. From this result, we find that Mo, W, and Nb, which have the bcc structure and lattice parameters of 3.15, 3.16 and 3.30 Å, respectively, are good candidates for use as substrates on which fcc Zr could be grown epitaxially.

In Fig. 2, we present the calculated electronic densities of states (DOS) for Ti, Zr, and Hf in the hcp and fcc structures. The solid lines correspond to the fcc phases and the dotted lines to the hcp phases; the zero of the energy axis is at the

TABLE III. The DOS at the Fermi energy E_F (in states eV^{-1} atom^{-1}) for Ti, Zr, and Hf in the two phases hcp and fcc at the calculated equilibrium volume (see Table I).

Metal	hcp	fcc	$\Delta N(E_F)$
Ti	0.90	1.75	94%
Zr	0.87	1.66	91%
Hf	0.68	1.49	119%

Fermi level (E_F). The bandwidths of both fcc and hcp phases increase from Ti to Hf as a consequence of the partial delocalization of the d electrons from Ti(3 d) to Hf(5 d) through Zr(4 d). For the three metals the fcc DOS are shifted slightly to higher energies with respect to the hcp DOS. However, considerable differences in intensities and positions of the peaks are observed, for example, while the hcp DOS have a minimum around 2–3 eV, the fcc DOS present a salient peak in this energy region for the three metals. For the hcp phases the E_F lies in a minimum of the DOS curves. In contrast, for the fcc phases the E_F lies in the three cases (Ti, Zr, and Hf) in a region of high DOS. For Ti and Zr the values of the DOS at E_F corresponding to the fcc are $\sim 90\%$ higher than those corresponding to the hcp structure, while for Hf this difference reaches 119% (see Table III). From this result, differences can be expected between the electronic properties of the fcc and hcp phases for the three metals (Ti, Zr, and Hf), in particular in the properties depending directly on $N(E_F)$, such as the electronic specific heat and the magnetic susceptibility.

Finally, we return briefly to the controversy about the structure of Ti in Ti/Al multilayers,^{18–21} which was mentioned above. Considering the large difference between the calculated $N(E_F)$ for hcp Ti and fcc Ti (94%), we suggest that experimental determination of $N(E_F)$ in Ti/Al multilayers can be useful to distinguish between hcp Ti and fcc Ti.

In summary, we have calculated the elastic constants and electronic structures of fcc Ti, Zr, and Hf using the full-potential LAPW method. We found that the elastic stability criteria for a cubic crystal are fulfilled by the calculated elastic constants, i.e., the three studied transition metals have a locally stable fcc structure. The electronic structures for the fcc phases were analyzed and compared with those for the hcp phases, for the three metals. We found significant differences between the electronic structures for the fcc and hcp phases despite similar equilibrium volumes. In particular, the value of $N(E_F)$ for the fcc structure is approximately 100% higher than that for the hcp structure. Consequently, differences can be expected between the electronic properties of the fcc and hcp phases for Ti, Zr, and Hf.

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