A first-principle study of Os-based compounds: Electronic structure and vibrational properties

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ABSTRACT

The electronic structure, elastic, and phonon properties of OsM (M=Hf, Ti, Y and Zr) compounds are studied using first-principles calculations. Elastic constants of OsY and specific heat capacity of OsM (M=Hf, Ti, Y, and Zr) are reported for the first time. The predicted equilibrium lattice constants are in excellent agreement with experiment. The calculated values of bulk moduli are considerably high but are much smaller than that of Osmium, which is around 400 GPa. The phase stability of the OsM (M=Hf, Ti, Y and Zr) compounds were studied by DOS calculations and the results suggest that OsY is unstable in the B2 phase. The brittleness and ductility properties of OsM (M=Hf, Ti, Y and Zr) are determined. OsM (M=Hf, Ti, Y and Zr) compounds are predicted to be ductile materials. The electronic structure and phonon frequency curves of OsM (M=Hf, Ti, Y and Zr) compounds are obtained. The position of Fermi level of these systems was calculated and discussed in terms of the pseudo gaps. The finite and small DOS at the Fermi level 0.335, 0.375, 1.063, and 0.383 electrons/eV for OsHf, OsTi, OsY, and OsZr, respectively, suggest that OsM (M=Hf, Ti, Y and Zr) compounds are weak metals.

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1. Introduction

Intermetallic compounds are of interest because of their oxidation resistance, high melting point, strength at high temperatures, superconducting properties [1,2], hydrogen storage capability [3,4], and medical applications [5]. Recently, considerable effort has been directed towards the understanding of structural stabilities and the phase diagrams of the transition metals and compounds formed by Group IV elements T (T=Ti, Zr, Hf) and platinum group elements M (M=Ru, Rh, Pd, Os, Ir, Pt) [6,7].

At high temperature, the Os–Ti and Hf–Os alloys have been studied by direct reaction calorimetry. The formation enthalpies of the intermetallic compounds HfOs and OsTi were measured [6]. The formation enthalpies and structural phase stabilities of several binary transition-metals with the chemical formula XY and XY$_3$ compounds formed by X (X=Ti, Zr, Hf) and platinum group elements Y (Y=Ru, Rh, Pd, Os, Ir, Pt) were estimated using the first-principles local density functional (LDA) approach [7]. The complete phase diagram of the Zr–Os alloy was established by

Eremenko et al. [8] and the alloys containing a small amount of osmium were studied [9]. The microstructure and phase composition of the quenched and aged Zr–Os alloys containing 0.25 to 5 at% of osmium were investigated [10]. A decomposition of the β-phase (centered cubic phase) into the α-phase (hexagonal phase) and a β-phase enriched with osmium occur during quenching in the Zr–0.25 at% Os and Zr–0.5 at% Os alloys. The X-ray diffraction patterns of the Zr–0.25 at% Os alloy contain only the α-phase lines. α-phase lattice parameters in this alloy are about $a=0.3232$ nm, $c=0.5148$ nm, $c/a=1.594$,which coincide with the lattice parameters of the α-phase alloys of pure zirconium. In addition, in the Zr–5 at% Os alloy, only the β-phase is observed by X-ray diffraction analysis with a lattice parameter $a=0.3558$ nm.

The OsTM and TMOs$_2$ compounds have been reported to show no super-hard character, but they behave like ductile materials [11]. The formation enthalpies of 4d and 5d transition metals have been measured by high-temperature direct synthesis calorimetry at 1373 K. They have been compared with the predicted data of Miedema et al. and with those found by *ab initio* calculations [12]. A thermodynamic study of experimental thermochemical and phase diagram data of the Hf–Os alloy was performed employing the CALculation of PHAse Diagrams (CALPHAD) method, and different thermodynamic parameters of the Hf–Os alloys were

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obtained [13].

In order to understand the physical properties and chemical behaviors of the intermetallic compounds for technological applications, a complete investigation of relevant alloy systems is important. In the present work, we focus on investigating the physical properties of Os-based compounds OsM (M=Hf, Ti, Y and Zr), such as elastic constants, band structures, and vibrational properties by the plane-wave pseudopotential density functional theory method through the Quantum ESPRESSO code [14], and also constant-volume specific heat capacity was calculated by the quasi-harmonic approximation (QHA) [15]. We focus especially on the investigation of the stability of OsY in the B2 phase.

This paper is organized as follows. The description of our calculation methods is presented in Section 2. The structural and vibrational properties of OsM (M=Hf, Ti, Y and Zr) compounds are discussed in Section 3, including the comparison with experiment. In Section 3, the electronic structure of these compounds is also investigated. Conclusion is given in Section 4.

2. Method of calculation

2.1. Total energy electronic structure calculations

Many intermetallics with the approximate composition AB crystallize in the B2 structure, which is also known as the CsCl structure (see Fig. 1). In the completely ordered state, A atoms occupy one cubic primitive sublattice and B atoms occupy the rest. This means that each A atom is surrounded by eight B atoms in the nearest neighbor sites, and vice versa. The binary compounds OsM (M=Hf, Ti, Y and Zr) were observed to have the cubic B2 structure [6,10,16,17], which was confirmed by *ab initio* calculations given in Ref. [2]. The structure of OsY was not identified experimentally but it was reported to be B2 phase with a formation energy equals to 0.021 eV/atom [18]. The formation energies were calculated at $T=0$ and $P=0$ for different structures: $L1_1$, B1, B2, B3, and B_h.

The formation enthalpies of OsZr, OsHf, and OsTi are found to be all negative. This is an indication of the stability of these compounds in the B2 structure [6]. The calculations of the total energies were performed with the Quantum ESPRESSO (QE) code [14]. The exchange-correlation potential was treated with the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE-GGA) [19]. Ultrasoft pseudopotentials from the Quantum Espresso library are used for most elements, including Ti, Y, Zr, and Os. Publicly available pseudopotentials are used for the OsHf compound, including ultrasoft Os and Hf pseudopotentials created by the Rappe group [20]. The energies were calculated at zero temperature and pressure. The accuracy of the first-principles calculations depends on the choice of convergence conditions, such as forces and stress tensors and the sets of special **k**-points. In our calculations, the scheme of Monkhorst and Pack [21] was used for the Brillouin zone **k**-point sampling. The energy cutoff for the expansion of the eigenfunctions was set to 40 Ry. To evaluate the electronic charge density, the kinetic energy cutoff was set to 400 Ry. The irreducible wedge of the first Brillouin zone was sampled using 1000 **k**-points. Integration up to the Fermi surface was performed using the Methfessel–Paxton smearing technique [22] with a smearing parameter of $\sigma=0.02$ Ry. With these choices, the total energy was converged to 10^{-5} Ry and the maximum force allowed on each atom was 0.002 Ry/a.u. Having obtained self-consistent solutions of the Kohn–Sham equations, the lattice-dynamical properties were calculated within the framework of the self-consistent density functional perturbation theory [23]. To obtain the complete phonon dispersions and density of states, eight dynamical matrices were calculated on a $(4 \times 4 \times 4)$ **q**-point mesh. These dynamical matrices were calculated using the Fourier
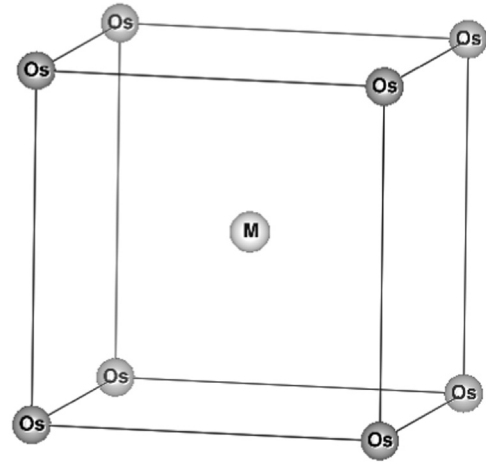

Fig. 1. Crystal structure of OsM (M=Hf, Ti, Y and Zr) in the B2 phase. OsM unit cell contains two atoms, Os and M, one occupies the position 1a (0,0,0) and the other the position 1b (0.5,0.5,0.5).

deconvolution on this mesh. The ground state of OsM (M=Hf, Ti, Y and Zr) compounds was obtained by optimizing the total energy as function of the lattice parameters.

2.2. Elastic constants calculations

The elastic constants of a material describe its response to an applied stress or, conversely, the stress required to maintain a given deformation, and can be used to evaluate the elastic properties. These properties are related directly to mechanical stability. The elastic constants provide an estimation of the melting temperature and the strength [24].

The calculated elastic parameters are obtained from the energy variation $\frac{\Delta E}{V}$ described in Ref. [25].

For the strain under hydrostatic pressure $\boldsymbol{e}=(\delta, \delta, \delta, 0, 0, 0)$, the total energy change is transformed to:

$$\frac{\Delta \boldsymbol{E}}{\boldsymbol{V}}=\frac{9}{2}\boldsymbol{B}\delta^2, \tag{1}$$

where B is the bulk modulus and given by the following equation:

$$B = \left(C_{11} + 2C_{12}\right)/3. \tag{2}$$

By applying the volume-conserving monoclinic strain $\boldsymbol{e}=(0, 0, \delta^2/(4-\delta^2), 0, 0, \delta)$, the total energy variation is given by the following formula:

$$\frac{\Delta \boldsymbol{E}}{\boldsymbol{V}}=\frac{1}{2}\boldsymbol{C}_{44}\delta^2+\boldsymbol{O}\left(\delta^4\right). \tag{3}$$

In the final step, we used the volume-conserving rhombohedral strain tensor given by $\boldsymbol{e}=(0, 0, (1+\delta)^{-2}-1, 0, 0, \delta)$, which transforms the total energy to

$$\frac{\Delta \boldsymbol{E}}{\boldsymbol{V}}=6\boldsymbol{C}'\delta^2+\boldsymbol{O}\left(\delta^3\right), \tag{4}$$

where C' is defined by $\boldsymbol{C}'=\left(\boldsymbol{C}_{11}-\boldsymbol{C}_{12}\right)/2$.

Several sets of $\frac{\Delta E}{V}$ were calculated by varying δ in steps of 0.002. These data were fitted by a quadratic polynomial, and then the elastic constant is obtained from Eqs. (1)–(4).

Shear modulus (G) is derived using the following relation:

$$G=\frac{C_{11}-C_{12}+3C_{44}}{5}. \tag{5}$$