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First-principles study of the structural, electronic and elastic properties of W_5Si_3

Xiaoma Tao, Philippe Jund*, Catherine Colinet, Jean-Claude Tédenac

Institut Charles Gerhardt, Universite Montpellier 2, Pl. E. Bataillon CC150334095 Montpellier, France

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ABSTRACT

We present a study of the structural, electronic, and elastic properties of the W_5Si_3 compound by using density-functional theory. The lattice constants, formation enthalpies, elastic constants and elastic moduli of W_5Si_3 have been calculated and compared to the available experimental values: the calculated lattice constants and formation enthalpy are in good agreement with the experimental data. Concerning the mechanical behavior, the high B/G ratio indicates that W_5Si_3 compounds are prone to ductile behavior. The total and partial density of states as well as the bonding charge densities in the (001) and (100) planes have been determined in order to get some insight on the bonding mechanism in W_5Si_3. Finally, using the Debye model, the Debye temperature, heat capacity, and thermal expansion have also been calculated and are in agreement with experimental results.

1. Introduction

Transition metal silicides (TMS) are very attractive for their various unique physical and mechanical properties. Generally, the transition metal silicides have high melting points, high strengths, and high creep resistance at elevated temperature, and show good resistance to oxidation [1–5]. Especially, among the transition metal silicides, the refractory metal silicides are very interesting for their ultrahigh-temperature properties which explains why some refractory metal silicides have been studied recently experimentally and theoretically [4–9]. For example, in our previous work [9] the structural, electronic, and elastic properties of Ta_5Si_3 have been studied via ab initio simulations. As a member of the refractory metal elements, tungsten has the highest melting point and forms two intermetallic compounds (WSi_2 and W_5Si_3) [10] in the W–Si binary system.

Like the Mo_5Si_3 compound, the crystal structure of W_5Si_3 is tetragonal with space group: I4/mcm (No. 140) [10]. The thermodynamic properties (formation enthalpy [11,12] and thermal expansion [13]) of W_5Si_3 have already been investigated. The integrated interdiffusion coefficients [14] and the activation energies for the interdiffusion [15] of W_5Si_3 phase have been studied as well. Because of the strong covalent-dominant atomic bonds and the high hardness inherent to the tungsten silicides, intermetallic W_5Si_3 coatings have outstanding abrasive and adhesive wear resistance [16]. In addition, very recently, superconducting properties have been reported for W_5Si_3 [17]. Unfortunately, there are few studies focused on the electronic and mechanical properties of W_5Si_3. However, as a potential ultrahigh-temperature compound, the structural, electronic and elastic properties of W_5Si_3 are very important and essential for the design and development of new materials. In order to lift this lack of numerical data, the density functional theory (DFT) and the quasiharmonic Debye model have been employed to study the physical and mechanical properties of W_5Si_3.

The remainder of this paper is organized as follows. In Section 2, the method and calculation details are described. In Section 3, the phase stability, the electronic and structural properties, the elastic constants as well as some thermodynamic properties are presented and discussed. Finally, some conclusions are drawn in Section 4.

2. Computational details

Similarly to what we have done in our previous study [9], first-principles calculations are performed using the scalar relativistic all-electron Blöchl's projector augmented-wave (PAW) method [18,19], as implemented in the highly-efficient Vienna Ab initio Simulation Package (VASP) [20,21]. For the GGA exchange-correlation function, the Perdew–Wang parametrization (PW91) [22,23] is employed. For comparison, the LDA exchange-correlation function [24] is also used for the calculation of the equilibrium volume and the formation enthalpy. Here we have adopted the standard version of the PAW potentials for W, and Si atoms. A plane-wave

* Corresponding author.
E-mail address: pjund@univ-montp2.fr (P. Jund).

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Table 1
Crystallographic structural data for the three prototypical structures considered for the W_5Si_3 compounds.

Prototype	Pearson symbol	Space group	Strukturbericht	Atomic Wyckoff positions		
W_5Si_3	tI32	I4/mcm (140)	$D8_m$	W(1)	16k	$(x, y, 0)$
				W(2)	4b	$(0, 1/2, 1/4)$
				Si(1)	8h	$(x, x+1/2, 0)$
				Si(2)	4a	$(0, 0, 1/4)$
Mn_5Si_3	hP16	$P6_3/mcm$ (193)	$D8_8$	Mn(1)	4d	$(1/3, 2/3, 0)$
				Mn(2)	6g	$(x, 0, 1/4)$
				Si(1)	6g	$(x, 0, 1/4)$
Cr_5B_3	tI32	I4/mcm (140)	$D8_1$	Cr(1)	16l	$(x, x+1/2, z)$
				Cr(2)	4c	$(0, 0, 0)$
				B(1)	4a	$(0, 0, 1/4)$
				B(2)	8h	$(x, x+1/2, 0)$

energy cutoff of 500 eV is held constant for all the calculations. Brillouin zone integrations are performed using Monkhorst-Pack k-point meshes [25] with a k-point sampling of $9 \times 9 \times 9$ for the Cr_5B_3-type and W_5Si_3-type structures and of $7 \times 7 \times 9$ for the Mn_5Si_3-type structure. The Methfessel-Paxton technique [26] with a smearing parameter of 0.2 eV is also used. The total energy is converged numerically to less than 1×10^{-6} eV/unit. After structural optimization, calculated forces are converged to less than 0.01 eV/Å.

As mentioned in our previous work [9], the Vinet [27] equation of state is used to obtain the equilibrium volume (Ω_0), the total energy (E), the bulk modulus (B) and the pressure derivative of the bulk modulus ($\partial B/\partial P$).

The formation enthalpy of the W_5Si_3 alloys can be calculated from the following equation:

$$\Delta H(W_5Si_3) = E(W_5Si_3) - 5E(W) - 3E(Si) \quad (1)$$

where $E(W_5Si_3)$, $E(W)$ and $E(Si)$ are the equilibrium first-principles calculated total energies of the corresponding W_5Si_3 compound, of W with bcc structure and of Si with diamond structure, respectively.

For the calculation of the elastic constants and the thermodynamic properties of W_5Si_3, the procedure is similar to the one described in detail in Ref. [9] and is therefore not recalled here.

3. Results and discussion

3.1. Phase stability

In the present work, three prototype structures of W_5Si_3 compounds have been taken into account: the W_5Si_3-prototype structure ($D8_m$), the Cr_5B_3-prototype structure ($D8_l$) and the Mn_5Si_3-prototype structure ($D8_8$) (the corresponding crystal information has been listed in Table 1). The calculated lattice constants and formation enthalpies of the W_5Si_3 compounds with these three crystal structures are listed in Table 2. Comparing with

Table 2
The calculated lattice constants and formation enthalpies for the W_5Si_3 compounds compared to the available experimental data.

Phase	Prototype	Lattice parameters		Formation enthalpy (eV/atom)	Source
		a(Å)	c(Å)		
W_5Si_3	W_5Si_3	9.6756	4.9637	−0.145	GGA
		9.5519	4.8811	−0.237	LDA
		9.645 [10]	4.97 [10]	−0.163 [11]	Exp.
	Mn_5Si_3	7.2839	5.1018	−0.044	GGA
		7.1900	5.0185	−0.130	LDA
	Cr_5B_3	6.1920	12.2975	−0.002	GGA
		6.1145	12.0795	−0.079	LDA

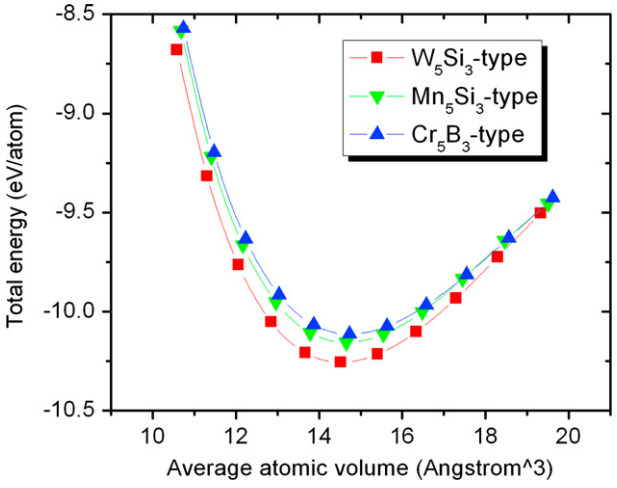

Fig. 1. Total energy vs volume for the three prototype structures of W_5Si_3.

the experimental lattice constants, the calculated lattice constants of the W_5Si_3-prototype structure ($D8_m$) compound are in very good agreement with the experimental values [10]. It can also be seen from Table 2, that the lattice constants obtained with the GGA are closer to the experimental values than those obtained with the LDA. For the other two prototypes, there are no experimental values available to compare with. The calculated formation enthalpies of the three structures indicate that the W_5Si_3-prototype structure is the stable phase in agreement with experiment [10]. The total energy vs volume curves of the three prototype structures are shown in Fig. 1, and from this figure it can be seen clearly that the W_5Si_3-prototype phase is the stable phase. Previously we have shown that the Cr_5B_3-prototype structure is the stable phase for Ta_5Si_3 while the W_5Si_3-prototype structure is the high-temperature phase [9] for this compound. The present calculated formation enthalpies of the W_5Si_3-prototype structure are −0.145 eV/atom (GGA) and −0.237 eV/atom (LDA). It can be seen that the GGA result is in very good agreement with the experimental value of −0.163 eV/atom [11].

3.2. Electronic structure

In order to get some insight on the bonding mechanism of the W_5Si_3 compounds, the total (TDOS) and partial (PDOS) density of

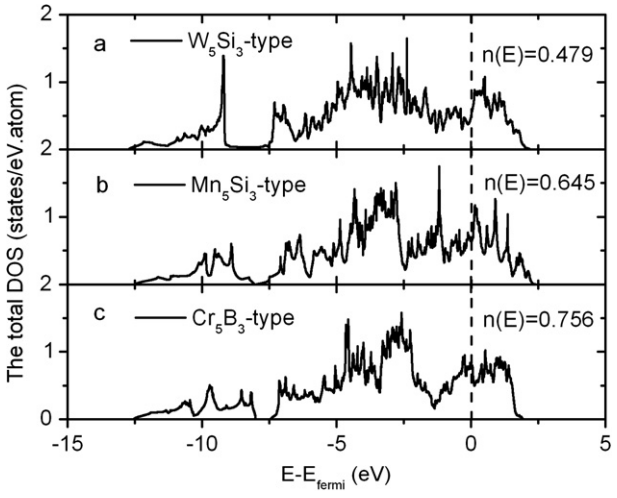

Fig. 2. Total density of states for the three prototypes W_5Si_3.