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First Principles Study of Constitutional Point Defects in α UAl₄

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ABSTRACT

We performed first-principles calculations to investigate the point defect structure of α UAl₄. Large 80-atom and 120-atom supercells are employed to obtain fully converged point defect formation energies. Relaxed structures and energies for vacancies and antisites are calculated using a plane-wave pseudopotential method. Our results show that Al antisites and U antisites are the constitutional point defects in Al-rich and U-rich α UAl₄, respectively. Our first-principles calculated Al antisite and U antisite formation enthalpies match the values used recently by others authors for modeling the free energy of UAl₄ compound with a Wagner-Schottky-type model, containing two sublattices with anti-structure type of defect and interaction between defects, in a whole U-Al phase diagram assessed by using the CALPHAD technique.

1. Introduction

UAl₄ intermetallic compound has called research attention due to its possible formation in the interlayer (IL) between Al based matrix and U based alloys in dispersion fuel elements. In a previous work [1] we have satisfactorily simulated the growth of UAl₄ phase in an UAl₃/Al diffusion couple. We built a thermodynamic database using data from the literature and a kinetic database by adjusting parameters from reported experimental growth of the UAl₄ phase at different temperatures. Thermodynamic and kinetic databases were constructed that could be read with ThermoCalc [2] and DICTRA [3] packages. To further improve our simulation, we have decided to get an insight in the controversy concerning the structure of UAl₄. The solubility range assessed for UAl₄ (α I4) compound [4] was discussed following experimental results with contradictory conclusions. Borie [5] had determined the crystallography as body-centered

orthorhombic, spatial group $I2ma$ or $Imma$, and obtained by chemical analysis the composition values in this phase between 81.8 and 83.1 at.% Al. On this basis he postulated the existence of constitutional defects, U vacancies or Al substitutionals at U sites. Afterwards, while Zenou et al [6] confirmed a solubility range due to a random occupation of U sites by vacancies, Tougait and Noël [7] suggested that the compound is stoichiometric with the same techniques. Then, a thorough study of constitutional defects in UAl_4 was still lacking.

In our first investigations of UAl_4 structure [8] we applied first principles methods implemented in the Wien2k code [9]. Spin polarized calculations of structure stabilities led to the conclusion that antisite defects could be stabilized with respect to vacancies in aluminum rich UAl_{4+x} . As we needed to confirm the predictions with calculations in greater supercells, we performed new spin polarized calculations adding spin orbit coupling [10] within a pseudopotentials first principles method implemented in the VASP code [11]. By calculating, within this last approximation, the total energy of the complete set of structures existing in the U-Al binary system, we verified that the correct description of the U-Al ground state is obtained.

In this paper, we evaluate monovacancies and antisite atoms as constitutional defects in UAl_4 structure. We investigate the energetic as a function of defect concentration performing structural relaxations around the defect of bulk supercells using the VASP code. We show the relative stability of antisites with respect to vacancies in both uranium rich and aluminum rich branches of UAl_4 domain and calculate their defect formation enthalpies. The last findings are taken into account to modify the parameters of the Wagner-Schottky model of UAl_4 phase with two sublattices in the ThermoCalc database used previously.

2. Computational details

All density functional theory (DFT) [12, 13] calculations in the present work were performed by the Vienna Ab initio Simulation Package (VASP) [11], making use of the Projector Augmented Waves (PAW) technique [14]. For the exchange correlation functional, the generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE) [15] was applied.

The calculations included fourteen valence electrons for U ($6s^2 6p^6 5f^3 6d^1 7s^2$) and three valence electrons for Al ($3s^2 3p^1$) with a plane-wave cutoff energy of 600 eV for both elements. Spin-polarized (SP) calculations were performed to model the antiferromagnetically ordered UAl_4 [10]. The k-point meshes for Brillouin zone sampling are constructed using the Monkhorst–Pack scheme. In the case of the stoichiometric $oI20$ UAl_4 unit cell, the calculations were performed with a $9 \times 9 \times 9$ k-points grid.

To determine the defect formation energies of isolated point defects we used both a 80-atom $2 \times 2 \times 1$ supercell and a larger 120-atom $3 \times 2 \times 1$ supercell, each containing one single point defect (vacancy or antisite) per supercell. The antisite defect in the case of Uranium antisite (U atom on Al site), unlike Al antisite, was not unique. The site was chosen regarding the proximity of U neighbours, in an attempt to limit U-U interaction. In all these cases, calculations were performed with a $3 \times 3 \times 3$ k-points grid. To take into account the effects of local atomic relaxations around point defects, only first neighbors atom positions are allowed to relax within

each supercell using a conjugate-gradient scheme until the forces acting on the atoms are less than 0.01 eV/Å.

The formation energy of a $U_{1-x}Al_x$ alloy in the antiferromagnetic oI20 UAl_4 structure is defined as:

$$\Delta E_f(U_{1-x}Al_x) = E_T(U_{1-x}Al_x) - (1-x)E_T(U) - xE_T(Al) \quad (1)$$

where $E_T(U_{1-x}Al_x)$, $E_T(U)$ and $E_T(Al)$ are, respectively, the first-principles calculated total energies (per atom) of the alloy, the orthorhombic oC4 U and the cubic cF4 Al. Here x is the atomic composition of Al in the alloy.

3. Results and discussion

3.1. Stoichiometric UAl_4

Before we discuss the results of our calculations for defects in UAl_4 it is useful to analyze how well the thermodynamic properties of the defect-free, stoichiometric UAl_4 are described within the DFT method implemented in the VASP package. In Table I we compare our results for the equilibrium lattice parameters, energy of formation and bulk modulus for UAl_4 obtained using two sets of parameters (GGA+SP and GGA+SP+spin orbit coupling (SOC)) with experimental data as well as with the results of previous *ab initio* calculations.

Table I. Ground-state properties of stoichiometric UAl_4 : equilibrium lattice parameters, bulk modulus B and energy of formation ΔE_f .

Method	Details	lattice parameters (Å)			B(GPa)	ΔE_f (kJ/mol)	Ref
		a	b	c			
experimental	-----	4.40	6.25	13.71	73±5	-25±3	[16]
FLAPW (Wien2K)	GGA+SP	4.38	6.24	13.76	84	-9.97	[10]
	GGA+SP+SOC	4.40 ^a	6.25 ^a	13.72 ^a	----	-18.28	[17]
PAW pseudopotentials (VASP)	GGA+SP	4.35 ^b	6.18 ^b	13.70 ^b	88	-11.97	[10]
	GGA+SP+SOC					-14.14	[10]

^a experimental lattice parameters are used in the calculation without re-calculating relaxation optimization.

^b lattice parameters and bulk modulus optimized during GGA+nonSP calculations remain in these schemes.

We observe the well-known tendency of the GGA to underestimate the lattice constant and overestimate the bulk modulus but not the overestimation of the energy of formation. The difference between the experimental and optimized lattice parameters was around -0.5% and the corresponding bulk modulus difference did not exceed +15%. Although the inclusion of S–O coupling caused a little increment in the underestimation of the lattice parameters (now around -1.1%) and a more substantial overestimation of the bulk modulus (+20%), the resulting energy of formation is improved by 2 kJ/mol (+17%) when PAW pseudopotentials are used.

Let us notice that the lattice shrinkage due to S–O interaction is in fact compensated by strong correlations of f-electrons, which can be treated by GGA + U functionals. The on-site Coulomb repulsion between U-5f electrons might be indeed different in intermetallic compounds and pure metals due to a different occupation and degree of localization of these states. The GGA + U techniques is however difficult to apply for the prediction of energies of formation as they involve adjustable parameters.

Although the observed discrepancy in the energy of formation is significant with regard to the accuracy required in thermodynamic modeling, the ab-initio calculations of the energetic of the UAl_4 compound under study seem to be internally consistent and make possible to correlate the formation energies of the perfect stoichiometric UAl_4 compound and the several off-stoichiometric compounds in order to estimate their point defect formation energies. In this way, neglect the spin orbit coupling in the ab-initio calculations makes no significative difference.

3.2. Structural defects in UAl_4

At $T = 0$ K, the point defect structure of an ordered compound is solely governed by enthalpy, and the point defects stable at this temperature are called structural defects. The pressure effect on the defect formation enthalpies is very small [18], then in what follows we shall neglect this effect and consider that the defect formation enthalpies are equivalent to the defect formation energies.

In Figure 1, the predicted formation enthalpies of off-stoichiometric UAl_4 alloys containing each of the four possible types of constitutional point defects, Al vacancies (Va^{Al}), U vacancies (Va^U), Al antisites (Al^U) and U antisites (U^{Al}), are plotted as four branches, respectively. The branch giving the lowest formation enthalpy corresponds to the most stable defect structure; Figure 1 thus shows that the stable constitutional point defects in Al-rich and U-rich oI20 UAl_4 are Al antisites and U antisites, respectively.

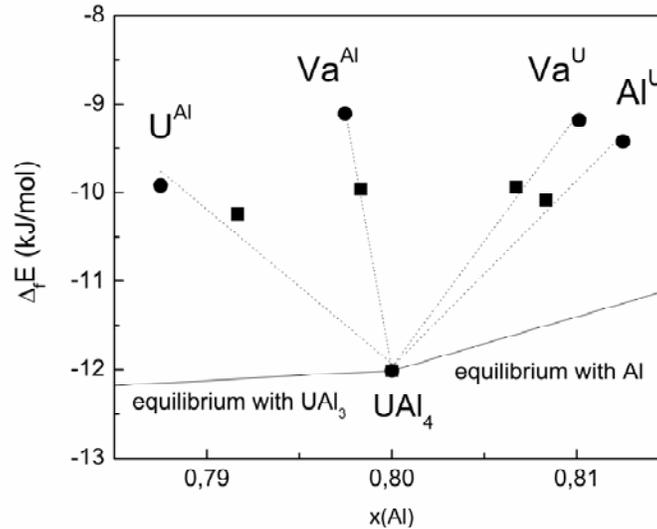


Figure 1. Energies of formation of the supercells $2 \times 2 \times 1$ (●) and $3 \times 2 \times 1$ (■) containing one defect. The reference states are the element U in the orthorhombic oC4 structure and the element Al in the cubic cF4 structure.

As it can be notice from Figure 1, the predicted formation enthalpies of off-stoichiometric UAl_4 alloys containing defects look like a linear relationship with the excess or deficiency of aluminum according to the Wagner–Schottky model (a gas of non-interacting point defects on well-defined sublattices) [19] where the formation enthalpy (per atom) of an off-stoichiometric UAl_4 alloy is a linear function of the point defect concentration:

$$\Delta H_f^d = \Delta H_f^{UAl_4} + H_d x_d \quad (2)$$

where ΔH_f^d is the formation enthalpy (per atom) of a N-atom (N = 80 or 120) antiferromagnetic oI20 UAl₄ supercell containing one point defect of type *d*, $\Delta H_f^{UAl_4}$ is the formation enthalpy of perfectly ordered defect-free oI20 UAl₄, H_d is the formation enthalpy of isolated point defects of type *d* in stoichiometric oI20 UAl₄ and x_d is the atomic concentration of defects. For N-atom supercells (N = 80 or 120), we have $x_d = 1/(N - 1)$ for a vacancy defect and $x_d = 1/N$ in the case of an antisite defect.

By fitting equation (2) to the results in Figure 1 we obtain the values of H_d reported in Table II for the four possible types of constitutional point defects in oI20 UAl₄.

Table II. First-principles calculated formation enthalpies H_d of isolated point defects in oI20 UAl₄. Reference states: cubic cF4 Al and orthorhombic oC4 U.

Defect type	Designation	H_d (kJ/mol)	H_d (eV/atom)
U vacancy	Va ^U	284	2.94
Al antisite	Al ^U	211	2.18
Al vacancy	Va ^{Al}	1158	12.01
U antisite	U ^{Al}	174	1.80

3.3. Thermodynamic modeling

Recently, the whole phase diagram of U-Al system was assessed by Wang et al. [20] using the CALPHAD technique [21]. We have used all these model parameters, with one exception which is later explained in the text, for the thermodynamic assessment of the growth of the UAl₄ phase in an UAl₃/Al diffusion couple [1]. In that work, UAl₄ compound is considered as a phase with solubility and assessed with the two-sublattice model. The solubility is accepted in the uranium sublattice: (U,Al)₁(Al)₄.

The selection of adjustable coefficients follows the idea of a Wagner–Schottky-type model containing two sublattices with anti-structure type of defect and interaction between defects. The interaction between defects is a second order correction of the gas model of non-interacting point defects and can be treated separately. In accordance with this, two adjustable coefficients are related to the formation enthalpy of the anti-structure type of defects: the formation enthalpies of pure elements in the oI20 UAl₄ crystal structure. They can be calculated using equation (2), the H_d values in Table II, and the value of experimental $\Delta H_f^{UAl_4}$ (Table I).

Results are shown in Table III along with the values proposed in Ref. [20] and [1].

Table III. The formation enthalpy $\Delta H_f^{UAl_4}$ ($\Delta H_f^{AlAl_4}$) of the pure U (Al) element in the oI20 UAl₄ crystal structure.

	Ref [20]	Ref [1]	This work
$\Delta H_f^{UAl_4}$ (kJ/mol)	----	1.5	114±3
$\Delta H_f^{AlAl_4}$ (kJ/mol)	15	1.5	17±3

As it can be seen from the table, the values obtained in this work are in agreement with those in Ref. [20] (the high value of $\Delta H_f^{UAl_4}$ in this work is similar to the proposal of no solubility in the aluminium sublattice). However there is a substantial difference with those values proposed by

ourselves in Ref. [1]. That proposal was driven in order to fit the experimental data reviewed by Kassner et al. [4] with a UAl_4 solubility range between 81.3 and 83.8 at.% Al at $T = 823$ K. With the set of model parameters given in Ref. [20], but substituting the values of the parameters $\Delta H_f^{UAl_4}$ and $\Delta H_f^{AlAl_4}$ with those obtained in this work, the calculated phase diagram of U-Al system is shown in Figure 2. The UAl_4 phase in equilibrium with Al and UAl_3 phases shows no solubility indicating that the point defects in this compound would be only thermal defects.

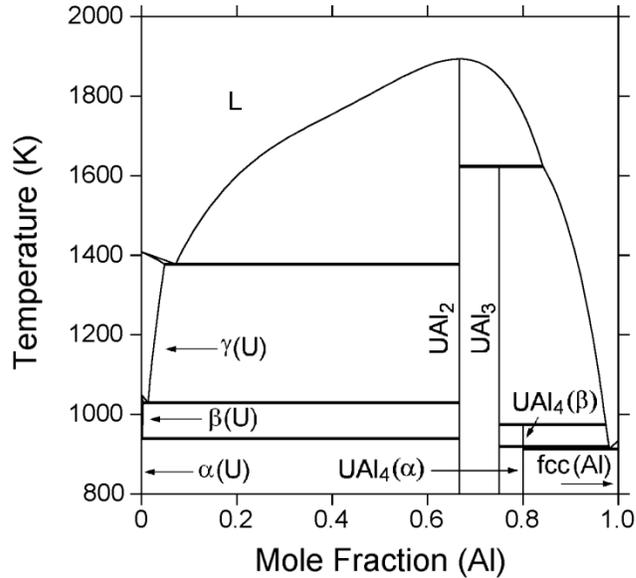


Figure 2. Calculated phase diagram of U–Al system.

As the interdiffusion coefficient in the simulated growth of UAl_4 phase in a UAl_3 /Al diffusion couple depends of tracer diffusion coefficient and thermodynamic factor of aluminum in the UAl_4 phase, the new findings of this study indicate the need to reassess that simulation.

4. Conclusions

In the present study, we obtained the formation enthalpies of isolated point defects in stoichiometric UAl_4 by means of first-principles supercell calculations. Our results show that Al antisites and U antisites are the constitutional point defects in Al-rich and U-rich UAl_4 , respectively. Using the Wagner-Schottky model along with the formation enthalpies calculated in this work into the CALPHAD model, we also obtained the phase diagram of U–Al system. The diagram calculated suggests that the UAl_4 phase in equilibrium with Al and UAl_3 phases has predominantly thermal defects.

5. References

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