

RERTR 2012 — 34<sup>th</sup> INTERNATIONAL MEETING ON  
REDUCED ENRICHMENT FOR RESEARCH AND TEST REACTORS

October 14-17, 2012  
Warsaw Marriott Hotel  
Warsaw, Poland

**U-Al CALPHAD Phase Diagram: A Comprehensive Description of  
Thermal and Constitutional Point Defects Concentrations in UAl<sub>4</sub>**

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**ABSTRACT**

UAl<sub>4</sub> 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. We investigated the point defect structure of  $\alpha$ -UAl<sub>4</sub> in order to study aluminum diffusion. We performed ab initio calculations within a pseudopotentials method implemented in the Vienna Ab initio Simulation Package (VASP) to obtain point defect formation energies: vacancies ( $V^U$  and  $V^{Al}$ ) and antisites ( $Al^U$  and  $U^{Al}$ ). Using a statistical-thermodynamic model we calculated defects concentrations as function of temperature and deviation from stoichiometry. For stoichiometric UAl<sub>4</sub>, the dominant thermal defects are composed of two antisites. In off-stoichiometric UAl<sub>4</sub>, antisites are the constitutional defects. For U-rich UAl<sub>4</sub>, the thermal defect is called *interbranch*, where one antisite U atom is replaced by five Al vacancies. For Al-rich UAl<sub>4</sub>, the thermal defect is also an *interbranch*, where four antisite Al atoms are replaced by five U vacancies. Our first-principles calculations were used for modeling UAl<sub>4</sub> compound with a Wagner-Schottky-type model in a whole U-Al phase diagram calculated by using the CALPHAD technique. We modified previous databases to consider antisites and vacancies in both sublattices of UAl<sub>4</sub> compound (U,Al,V)<sub>0.2</sub>: (Al,U,V)<sub>0.8</sub>.

**1. Introduction**

UAl<sub>4</sub> 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 UAl<sub>4</sub> phase in an UAl<sub>3</sub>/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 UAl<sub>4</sub> phase at

different temperatures. Thermodynamic and kinetic databases were constructed [2] that could be read with ThermoCalc [3] and DICTRA [4] packages. To further improve our simulation, we have decided to get an insight in the controversy concerning the structure of  $UAl_4$ . The solubility range assessed for  $UAl_4$  (oI4) compound [5] was discussed following experimental results with contradictory conclusions. Borie [6] 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 [7] confirmed a solubility range due to a random occupation of U sites by vacancies, Tougait and Noël [8] 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 [9] we applied first principles methods implemented in the Wien2k code [10]. 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 [11] within a pseudopotentials first principles method implemented in the VASP code [12]. 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 point defect concentration performing structural relaxations around the defect of bulk supercells using the VASP code. The defects we considered are vacancies ( $V^U$  and  $V^{Al}$ ) and antisites ( $Al^U$  and  $U^{Al}$ ), where we use a sublattice notation quoting with  $X^r$  the occupation by the X species (U, Al or V) of a sublattice site occupied by an  $r$  atom in the stoichiometric compound. The calculated energies are taken into account to modify the parameters of the Wagner-Schottky model [13] of  $UAl_4$  phase with two sublattices in the ThermoCalc database used previously.

Using a statistical-thermodynamic model we calculated defects concentrations as a function of temperature and deviation of stoichiometry. For stoichiometric  $UAl_4$ , antisites are the dominant thermal defects. For off-stoichiometric compound, dominant constitutional defects are  $Al^U$  and  $U^{Al}$  in the rich aluminum and rich uranium zones respectively. In the rich uranium zone, the thermal defect is an *interbranch* defect, where an antisite uranium atom ( $U^{Al}$ ) is replaced by five aluminum vacancies. In the rich aluminum zone the thermal defect is also an *interbranch* defect where four antisite aluminum atoms ( $Al^U$ ) are replaced by five uranium vacancies.

## 2. Method

The overall procedure and formalism follows the description of Colinet *et al* [14]. We consider a deviation  $\delta$  from the stoichiometry in an  $UAl_4$  alloy in the form  $U_{1/5-\delta} Al_{1/5+\delta}$ , in a two sublattice model where the N sites in both sublattices (U and Al) of  $UAl_4$  structure may be occupied by one of the three species uranium, aluminum or vacancies (V). Each sublattice hosts  $N^U = N/5$  and  $N^{Al} = 4 N/5$  species, where the superscript denotes the sublattice. In this way, each sublattice is occupied by  $n_i^r$  atoms or vacancies ( $r=U$  or  $Al$ ;  $i = U, Al$  or  $V$ ).

Within the frame of canonical ensemble the number of U and Al atoms is kept fixed to  $n_U = n_U^U + n_U^{Al}$  and  $n_{Al} = n_{Al}^U + n_{Al}^{Al}$ . On the other hand, the number of vacancies in the alloy  $n_V = n_V^U + n_V^{Al}$  and the total number of lattice sites may change. The distribution of the species in the

two sublattices can be described as a function of the atomic concentrations defined with respect to the total number of U and Al atoms  $N_{at} = n_U + n_{Al}$  as  $x_i^r = n_i^r / N_{at}$ .

In this way, we have six atomic concentrations:  $x_U^U, x_{Al}^U, x_V^U, x_U^{Al}, x_{Al}^{Al}, x_V^{Al}$ .

The defect concentrations  $x_d^r$  to take into account are four: antisites ( $x_{Al}^U$  and  $x_U^{Al}$ ) and vacancies ( $x_V^U$  and  $x_V^{Al}$ ) and they have been written [14] as a function of temperature and deviation from stoichiometry:  $x_d^r = x_d^r(T, \delta)$ .

The constraints concern the number of Al sites, which is four times the number of U sites, and the fixed total number of U and Al atoms (Equations 1 to 3):

$$\sum_i x_i^{Al} = 4 \sum_i x_i^U \quad (1)$$

$$x_U = x_U^U + x_U^{Al} = 1/5 - \delta \quad (2)$$

$$x_{Al} = x_{Al}^U + x_{Al}^{Al} = 4/5 + \delta \quad (3)$$

The equilibrium state at T and P is determined by the minimum in free energy G per atom, or in  $\Delta G_f$  per atom related to a reference state:

$$\Delta G_f = \Delta H_f - T \Delta S_f \quad (4)$$

where the difference at the right side is performed between formation enthalpy and T times formation entropy. Formation enthalpy can be written as a linear function of defect concentrations in the Wagner–Schottky model (a sublattice model for a non interacting point defects gas) [13]:

$$\Delta H_f = \Delta H_f^d = \Delta H_f^{UAl_4} + H_d x_d \quad (5)$$

where  $\Delta H_f^d$  is the formation enthalpy per atom of an N atoms (N = 80 or 120) antiferromagnetic  $UAl_4$  supercell containing one point defect of  $d$  type, and  $\Delta H_f^{UAl_4}$  is the formation enthalpy of the perfectly ordered  $UAl_4$  without defects, both calculated via first principles;  $H_d$  is the formation enthalpy of isolated point defects of  $d$  type obtained from the calculated energies (Section 4) and  $x_d$  is the defect atomic concentration.

$\Delta S_f$  is obtained assuming a random distribution of the species in both sublattices:

$$\Delta S_f = -5k_B \left( \sum_d x_d^U \ln x_d^U + \sum_d x_d^{Al} \ln x_d^{Al} - \frac{1+x_v}{5} \ln \frac{1+x_v}{5} - \frac{4(1+x_v)}{5} \ln \frac{4(1+x_v)}{5} \right) \quad (6)$$

Minimizing  $\Delta G_f$  and taking into account the relation among concentrations, we can write the set of equations (7) to (10) that allows us to obtain  $x_d^r(T, \delta)$  from defect formation enthalpies  $H_V^U, H_V^{Al}, H_{Al}^U$  and  $H_U^{Al}$ :

$$\frac{5^5 x_V^U (x_V^{Al})^4}{4^4 (1+x_v)^5} = \exp \left( -\beta (H_V^U + 4H_V^{Al}) \right) \quad (7)$$

$$\frac{x_V^U x_U^{Al}}{x_V^{Al} x_U^U} = \exp \left( -\beta (H_V^U + H_U^{Al} - H_V^{Al}) \right) \quad (8)$$

$$\frac{x_V^{Al} x_{Al}^U}{x_V^U x_{Al}^{Al}} = \exp\left(-\beta(H_V^{Al} + H_{Al}^U - H_V^U)\right) \quad (9)$$

$$\delta = x_{Al}^U - x_U^{Al} + \frac{1}{5}(4x_V^U - x_V^{Al}) \quad (10)$$

### 3. Computational Details

All density functional theory (DFT) [15, 16] calculations in the present work were performed by the Vienna Ab initio Simulation Package (VASP) [12], making use of the Projector Augmented Waves (PAW) technique [17]. For the exchange correlation functional, the generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE) [18] 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  $UAl_4$  [11]. 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 neighbors, 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 and second 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.

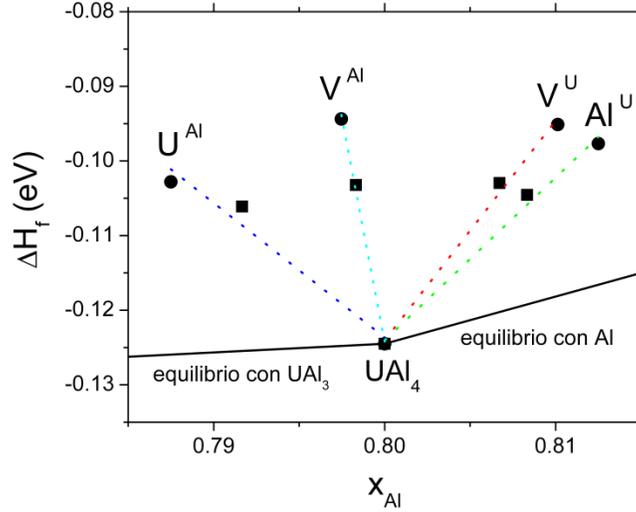
### 4. Results and Discussion

#### 4.1. Defect Concentrations

##### 4.1.1. Constitutional defects at $T=0K$

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 constitutional defects. The pressure effect on the defect formation enthalpies is very small [14], 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 ( $V^{Al}$ ), U vacancies ( $V^U$ ), Al antisites ( $Al^U$ ) and U antisites ( $U^{Al}$ ), are plotted as four branches. 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.** Enthalpies 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.

A linear relationship between  $\Delta H_f^d$  y  $x_{Al}$  is predicted, as in Fig. 1, from equation (10) and after the Wagner–Schottky model for predicted formation enthalpies of off-stoichiometric  $UAl_4$  alloys containing defects in eq. (5) [13].  $H_d$  values listed in Table I can be obtained from Fig. 1 slopes, for the four constitutional defects in  $UAl_4$ .

**Table I.** First-principles calculated formation enthalpies  $H_d$  of isolated point defects in oI20  $UAl_4$ . Reference states: cubic cF4 Al and orthorhombic oC4 U.

Defect type	Designation	$H_d$ (kJ/mol)	$H_d$ (eV/atom)
Al antisite	$Al^U$	219.02	2.27
U antisite	$U^{Al}$	190.08	1.97
U vacancy	$V^U$	235.42	2.44
Al vacancy	$V^{Al}$	237.36	2.46

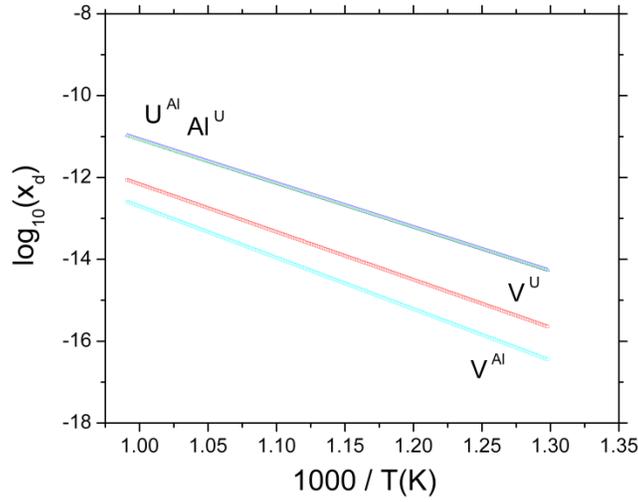
#### 4.1.2. Thermal defects in stoichiometric $UAl_4$

The stoichiometric  $UAl_4$  compound is perfectly ordered at  $T=0$  K, but thermal defects are generated as temperature increases. Assuming  $\delta=0$ , eq. (10) imposes the constraint that thermal defects must be generated in combinations that keep composition fixed. The simplest defects reactions that verify this constraint are four. Table II lists the reactions together with their reaction enthalpies calculated from enthalpies in Table I.

In Figure 2 we plot the defect concentrations obtained after the resolution of eq. (7) to (10) for the stoichiometric compound for T values between 770 K and 1000 K. Thermal defects that appear first as T increases are those with less formation enthalpy per defect. In Table II it is shown that the minimum value corresponds to the so called  $H_{2D}$  reaction. Thus, the antisites are the dominant thermal defects, as it can be seen in Figure 2.

**Table II.** Enthalpies  $H_D$  of the defects formation reactions in stoichiometric  $UAl_4$ .  $N_d$  is the number of defects generated through the reaction.

Designation	Reaction	$H_D$ (eV)	$H_D$ (eV)/ $N_d$
$H_{2D}$	$0 \rightarrow U^{Al} + Al^U$	4.24	2.12
$H_{5D}$	$0 \rightarrow V^U + 4V^{Al}$	12.28	2.456
$H_{6D}$	$0 \rightarrow Al^U + 5V^{Al}$	14.57	2.43
$H_{9D}$	$0 \rightarrow 4U^{Al} + 5V^U$	20.08	2.23



**Figure 2.** Defects concentrations  $x_d$  in stoichiometric  $UAl_4$  as a function of temperature, calculated from the set of equations (7) to (10).

#### 4.1.3. Thermal and constitutional defects in off- stoichiometric $UAl_4$

Eq. (10) establishes the concentration of constitutional defects, antisites or vacancies, in the state of maximum ordering in off- stoichiometric  $UAl_4$ :

$$\begin{aligned} \delta < 0 &\rightarrow x_{U^{Al}}^{Al}(const) = |\delta| \text{ or } x_{V^{Al}}^{Al}(const) = 5|\delta| \\ \delta > 0 &\rightarrow x_{Al^U}^U(const) = \delta \text{ or } x_{V^U}^U(const) = \frac{5}{4}\delta \end{aligned}$$

In order to decide about the relative stability of antisites and vacancies we can compare their formation enthalpies. The relationships  $H_{U^{Al}}^{Al} < 5H_{V^{Al}}^{Al}$  and  $H_{Al^U}^U < \frac{5}{4}H_{V^U}^U$ , show that antisites are the constitutional defects at both sides of stoichiometry.

At  $T \neq 0$ , we have to evaluate the formation of thermal defects in off-stoichiometric  $UAl_4$ . The constraint of fixed composition imposes that formation of defects will take place in combinations such that the sum of the number of constitutional plus thermal defects verifies eq. (10). Thermal defects in Table II are still possible, but now there are more possibilities due to the presence of off-stoichiometric constitutional defects. This is, constitutional antisites are replaced by vacancies or vice versa. This kind of defects are called *interbranch* [14] since their formation process can be understood as a transition of the alloy from an stable branch to an unstable

branch. The formation of these defects implies the disappearance of constitutional defects. Possible *interbranch* reactions and their associated enthalpies are listed in Table III.

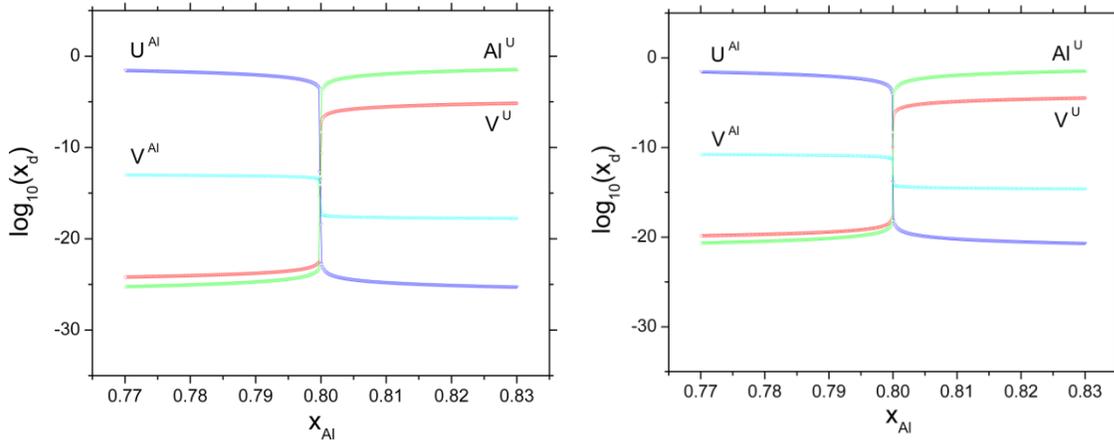
**Table III.** Enthalpies  $H_D$  of *interbranch* defects reactions: constitutional defects are eliminated and antisites are replaced by vacancies.  $N_d$  stands for the number of defects generated through the reaction.

Designation	Reaction	$H_D$ (eV)	$H_D$ (eV)/ $N_d$
$H_{IU}$	$4Al^U \rightarrow 5V^U$	3,12	0,62
$H_{IAI}$	$U^{Al} \rightarrow 5V^{Al}$	10,33	2,07

Figure 3 shows the defect concentrations as a function of concentration obtained from the resolution of eq. (7) to (10), for  $T=823$  K and  $T=1000$  K.

The dominant constitutional defects for the off-stoichiometric compound are  $Al^U$  and  $U^{Al}$  at both sides of stoichiometry.

A comparison between the values of formation enthalpies by defect in Tables II and III allows us to decide about the most favorable defects reactions. In the rich uranium zone the most favorable reaction is  $H_{IAI}$ , the thermal defect is in consequence an *interbranch* defect where an U antisite is replaced by five Al vacancies. In the rich aluminum zone the most favorable reaction is  $H_{IU}$ , and the thermal defect is an *interbranch* where four antisite aluminum atoms are replaced by five uranium vacancies.



**Figure 3.** Defect concentrations as a function of Al composition at (a)  $T=823$  K. (b)  $T=1000$  K.

#### 4.2. Calphad Phase Diagram

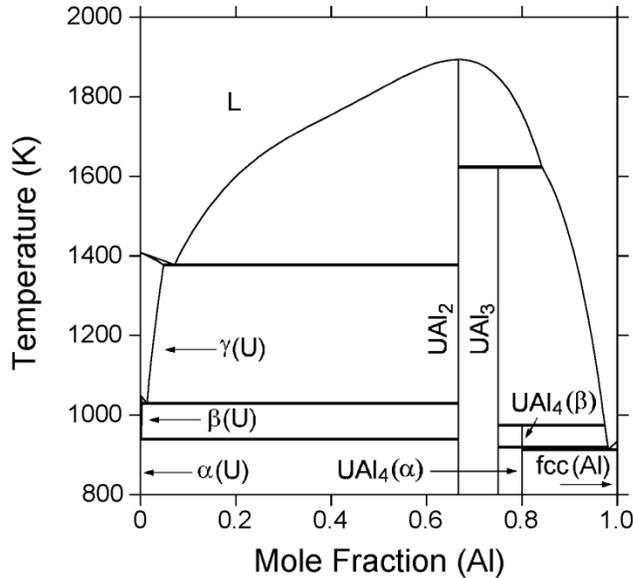
The whole phase diagram of U-Al system was assessed by Wang et al. [19] using the CALPHAD technique [20]. We have used these model parameters, with one exception, for the thermodynamic assessment of the growth of the  $UAl_4$  phase in an  $UAl_3/Al$  diffusion couple [1]. In that work,  $UAl_4$  compound was considered as a phase with solubility in the uranium sublattice and assessed with the two sublattice model. In a recent work [21], we allowed solubility in both sublattices, but the modelization we used took into account antisite defects only:  $(U,Al)_{0.2}:(U,Al)_{0.8}$ .

In this paper, the thermodynamic description of the U-Al system was revised, based on the results concerning point defects in the previous sections. In order to reflect the influence of all point defects, vacancies were added into the thermodynamic modeling of the  $UAl_4$  phase. Based on the first principles calculations,  $UAl_4$  compound is modeled as  $(U,Al,V)_{0.2}:(U,Al,V)_{0.8}$ . The selection of adjustable coefficients follows the idea of a Wagner–Schottky-type model containing two sublattices. In accordance with this, adjustable coefficients are related to the formation enthalpy of these type of defects. They can be calculated using the  $H_d$  values in Table I, and the experimental value of  $\Delta H_f^{UAl_4}$ . Results are shown in Table IV along with the values proposed in Ref. [19] and [1].

**Table IV.** Formation enthalpies of antisites and vacancies in the  $UAl_4$  crystal structure.

	Ref [19]	Ref [1]	This work
$\Delta H_f^{UU_4}$ (kJ/mol)	----	1.5	114±3
$\Delta H_f^{AlAl_4}$ (kJ/mol)	15	1.5	17±3
$\Delta H_f^{UV_4}$ (kJ/mol)	-	-	901±3
$\Delta H_f^{VAl_4}$ (kJ/mol)	-	-	31±3

With the set of model parameters given in Ref. [19], and incorporating the values of the parameters in Table IV, the calculated phase diagram of U-Al system is shown in Figure 4.



**Figure 4.** Calculated phase diagram of U–Al system.

The  $UAl_4$  phase in equilibrium with Al and  $UAl_3$  phases shows no solubility, suggesting that there should be interaction between defects in this compound and that thermal defects could play a significant role.

## Conclusions

In this work, we evaluated vacancies and antisite atoms as constitutional defects in  $UAl_4$  structure. We investigated the energetic as a function of point defect concentration performing structural relaxations around the defect of bulk supercells using the VASP code. The defects we considered were vacancies ( $V^U$  and  $V^{Al}$ ) and antisites ( $Al^U$  and  $U^{Al}$ ).

Using a statistical-thermodynamic model we calculated defects concentrations as a function of temperature and deviation of stoichiometry. For stoichiometric  $UAl_4$ , antisites are the dominant thermal defects. For off-stoichiometric compound, dominant constitutional defects are  $Al^U$  and  $U^{Al}$  in the rich aluminum and rich uranium zones respectively. In the rich uranium zone, the thermal defect is an *interbranch* defect, where an antisite uranium atom ( $U^{Al}$ ) is replaced by five aluminum vacancies. In the rich aluminum zone the thermal defect is also an *interbranch* defect where four antisite aluminum atoms ( $Al^U$ ) are replaced by five uranium vacancies.

The calculated energies were 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. In order to reflect the influence of both point defects, vacancies were added into the thermodynamic model of the  $UAl_4$  phase. Based on the results in first principles calculations in the present work,  $UAl_4$  compound is modeled as  $(U,Al,V)_{0.2}$ :  $(U,Al,V)_{0.8}$ .

## Acknowledgements

This work was partially supported by Gerencia Materiales of the Comisión Nacional de Energía Atómica, Argentina; ANPCyT under grant PICT-2011-1861; CONICET under grant PIP 00965 2010-2012; and UNSAM under grant C063.

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