MAIN INTERACTIONS IN THE FORMATION ENERGY OF BCC γ(U,Mo) DISORDERED PHASE.

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ABSTRACT

IN THE AIM OF EMPHASIZING THE ROLE OF BONDING ENERGY BETWEEN ATOMS IN THE DECOMPOSITION OF THE METASTABLE GAMMA PHASE AND THE SOLUBILITY OF THIRD ELEMENTS IN U-MO ALLOY, WE DECIDED TO EVALUATE THE THERMODYNAMIC FUNCTIONS OF THE BINARY U-MO AND TERNARY U-MO-X SYSTEMS BY USING FIRST PRINCIPLES CALCULATED TOTAL ENERGIES IN A CLUSTER EXPANSION METHOD. IN THE PRESENT STUDY, WE PERFORMED FIRST-PRINCIPLES ELECTRONIC CALCULATIONS OF 10 TOTALLY RELAXED BCC-BASED ORDERED U-MO STRUCTURES. THEN, WE DECIDED WHICH CLUSTERS SHOULD BE RETAINED IN THE CLUSTER EXPANSION OF THE THERMODYNAMIC FUNCTIONS COMPARING THEIR PERFORMANCE TO REPRODUCE THE EXPERIMENTAL EQUILIBRIUM PHASE DIAGRAM. FINALLY, WE DISCUSSED THE CONTRIBUTION OF THE MULTISITE INTERACTIONS IN THE PROPER DESCRIPTION OF THE ALLOY ENERGETIC. INTERACTION OF THREE BODIES HAS PROVED TO PLAY A FUNDAMENTAL ROLE IN STABILIZATION OF GAMMA PHASE, GIVING AT THE SAME TIME A USEFUL TOOL FOR PREDICTING TERNARY BEHAVIOR.

1. Introduction

Body-centered-cubic uranium alloys are being investigated to develop a nuclear fuel for research nuclear reactors that meets the requirements of low enrichment, high uranium density (>15.0 gU/cm3) and good irradiation behavior. The objective is that the fuel could remain stable in the body centered cubic phase (γ-U bcc solid solution) during fabrication (~500°C) and irradiation (~250°C), i.e., at temperatures at which α-U is the equilibrium phase [1].

Several transition metals, particularly 4d and 5d elements in Group IV through VIII, form high temperature solid solutions with γ-U and this cubic phase can be retained in its metastable state upon cooling. Among them, Mo was recognized as a good candidate, showing a high solubility in γ U (~ 35 at %) and an acceptable amount (~ 20 at. %) needed to stabilize γ U during fuel element fabrication at a working temperature of ~500°C. Small amounts of a third element such as transition metals, 4d and 5d, from groups VII and VIII had a powerful stabilizing effect when added to U-Mo alloys [2, 3].
Hofmann and Meyer [4] have found an empirical relationship between the measured nucleation time for the decomposition of metastable γ U(Mo) phase in α U(Mo) + U_2Mo (the position of the "nose" in the TTT diagram) and the enthalpy of mixing of the γ phase as estimate from semi-empirical method by Miedema et al [5]. From this, it appears that the activation energy of nucleation is proportional to the negative of the enthalpy of mixing. Moreover, they show that this correlation can be extended to the addition of a third element X (transition metals, 4d and 5d, from groups VII and VIII) that replaces atoms of Uranium in the alloy U-Mo. Ternary enthalpy of mixing is estimated as the sum of that in the binary alloys U-Mo and U-X.
Besides, the ultimate effectiveness of third element substitution on γ stabilization depends on the solubility limit of this element in γ-U(Mo) alloy and on the value of enthalpy of mixing in the ternary system. Unfortunately, solubilities of these third elements in the γ-U(Mo) phase are not well known.
A report was published in 2001 [6] which compiles thermodynamic data on the U-Mo alloy, enthalpy and Gibbs energy of formation, and presents them as a function of the uranium composition and temperature in the form of a suitable polynomial. The authors also stated that there were no previous data on the thermodynamic functions of the quenched metastable alloy below the stable γ phase region, and measured the enthalpy increment of quenched $U_{0.823}Mo_{0.117}$ alloy from 299 to 820 K. From this data, together with the estimation of the enthalpy of formation at 298.15 K from Miedema model [5] and the entropy at the same temperature from the method of irreversible thermodynamics, they gave the expression for the Gibbs energy of formation. They finally compared these results with estimations obtained by applying the regular solution model and an empirical approach [7] to nearest neighbours bond energy.
In the aim of emphasizing the role of bonding energy between atoms in the decomposition of the metastable γ phase and the solubility of third elements in U-Mo alloy, we decided to calculate the thermodynamic functions of the binary U-Mo and ternary U-Mo-X systems by using first principles thermodynamics [8]. This formalism establishes that the thermodynamics properties of an alloy can, in principle, be computed as accurately as desired through a technique known as the *cluster expansion*. A cluster is defined as a set of lattice points chosen in such a way that it contains the maximum correlation length to be considered. In the present study, we performed first-principles electronic calculations of 10 totally relaxed bcc-based ordered U-Mo structures and then, we decided which clusters are retained in the cluster expansion of the thermodynamic functions comparing their performance to reproduce the experimental equilibrium phase diagram. Finally, we discussed the contribution of the multisite interactions in the proper description of the alloy energetic.
This paper is organized as follows: First, a brief description of the cluster expansion formalism to calculate phase diagram from first principles is presented. We then show the bcc-based ordered structures chosen and the conditions of first-principles electronic calculations. Finally, the optimal cluster expansion construction and its cluster interactions are discussed.

2. The Cluster Expansion Formalism.

Based in the cluster expansion method [9], the formation energy ΔE_F of any ordered or disordered alloy may be described with a truncated expression of the bilinear form:

$$\langle \Delta E_F \rangle = \sum_{\alpha} V_{\alpha} \quad \xi_{\alpha} \tag{1}$$

in terms of the multisite correlation functions ξ_α and the expansion coefficients V_α which are known in the literature as the effective cluster interactions (ECI). The complete cluster expansion of Eq. (1) is formally exact, however, the utility of this rests in the possibility of identifying a hierarchy of a small number of clusters whose contributions V_α to ΔE_F dominates those of the remaining clusters.

The unknown parameters ECIs of the cluster expansion can then be determined by fitting this expression to a set of formation energies of ordered compounds, for which the corresponding correlation functions are known. These energies can be obtained, for instance, through first-principles electronic calculations. The number of ordered compounds in this set can be equal or greater than the number of V_α parameters to compute. It has been determined that a better cluster expansion is obtained if the system of Eq. (1) is overdeterminated [10], this is, ECIs can be determined from the condition:

$$\sum_{n} \left(\Delta E_F^n - \sum_{\alpha} V_\alpha \ \xi_\alpha^n \right)^2 = minimum \tag{2}$$

where ΔE_F^n stands for the calculated energy of formation of the ordered compound *n*.

After the energy of formation for a given alloy and parent lattice has been determined, it is of interest to examine how phase equilibrium between structures may evolve as a function of temperature and average concentration. The equilibrium states at constant volume and temperature are obtained by minimization of the Helmhotz free energy of formation

$$\Delta F_f = \Delta E_f - T \, \Delta S_{config} \tag{3}$$

where the configurational entropy ΔS_{config} is calculated as a cumulant expansion in terms of subcluster partial entropies of a maximal cluster α_{max} (Cluster Variational Method approach [11]). The entropy per lattice site is thus expressed as

$$\Delta S = k_B \sum_{\alpha}^{\alpha_{\max}} \gamma_\alpha \sum_{\sigma_\alpha} \rho_\alpha(\sigma_\alpha) \ln\left[\rho_\alpha(\sigma_\alpha)\right] \tag{4}$$

where $\rho_\alpha(\sigma_\alpha)$ is the cluster probability, γ_α the so-called Kikuchi-Barker coefficients and k_B the Boltzmann constant. The cluster probability is a function of the correlation functions through the expectation value of an orthogonal expansion [8, 9, 11]. The free energy functional per lattice site may now obtained, for a maximal cluster α_{max} , from Eqns. (1), (3) and (4)

$$\Delta F_f = \sum_{\alpha}^{\alpha_{\max}} \left[V_\alpha \ \xi_\alpha - k_B \ T \ \gamma_\alpha \sum_{\sigma_\alpha} \rho_\alpha(\sigma_\alpha) \ln\left[\rho_\alpha(\sigma_\alpha)\right] \right] \tag{5}$$

At present, there are no selection criteria for choosing neither the right clusters nor the number of known structures that will enter in the cluster expansion. We looked forward the combination of set of clusters and set of ordered structures that best met the following three criteria: the ground state phase diagram should exhibit known stable phases, the calculated equilibrium phase diagram should agree with the experimental ones, and the predicted cluster-expanded energies of ordered compounds in the expansion should agree with the corresponding formation energy calculation via first principles (“exact calculation”).

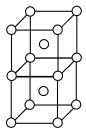
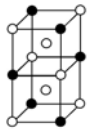
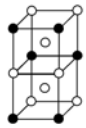
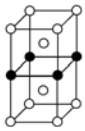
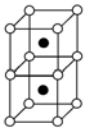
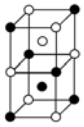
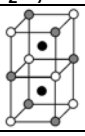
Name: Formula:	**A2, (bcc)** **A ; B**	**DO_3** **A_3B ; AB_3**	**$L6_0$** **A_3B ; AB_3**
Crystal Structure			
Bravais lattice	I	P	P
Atoms in the unit cell	(0,0,0)	A: (0, 0, 0) B: (0, 1, 0) B: (1/2, 1/2, 1/2) B: (1/2, 1/2, 3/2)	B: (0, 0, 0) A: (0, 0, 1) A: (1/2, 1/2, 1/2) A: (1/2, 1/2, 3/2)
Unit cell vectors	(1,0,0) (0,1,0) (0,0,1)	(0, 1, 1) (1, 0, 1) (1, 1, 0)	(1, 0, 0) (0, 1, 1) (0, -1, 1)
Space Group number Pearson´s symbol	229 cI2	225 cF16	123 tP4
Name: Formula:	**$C11_b$** **A_2B ; B_2A**	**B2** **AB**	**B32** **AB**
Crystal Structure			
Bravais lattice	P	P	P
Atoms in the unit cell	A: (0, 0, 0) A: (0, 0, 1) B: (1/2, 1/2, 1/2)	A: (0, 0, 0) B: (1/2, 1/2, 1/2)	A: (0, 0, 0) B: (0, 1, 0) A: (1/2, 1/2, 1/2) B: (1/2, 1/2, 3/2)
Unit cell vectors	(1,0,0) (0,1,0) (1/2, ½, 3/2)	(1, 0, 0) (0, 1, 0) (0, 0, 1)	(0, 1, 1) (1, 0, 1) (1, 1, 0)
Space Group number Pearson´s symbol	139 tI6	221 cP2	227 tP4
Name: Formula:	**L21** **A_2BC;** **AB_2C;ABC_2**		
Crystal Structure			
Bravais lattice	P		
Atoms in the unit cell	A: (0, 0, 0) B: (1/2, ½, ½) C: (1/4, 1/4, 1/4) C: (3/4, 3/4, 3/4)		
Unit cell vectors	(0, 1, 1) (1, 0, 1) (1, 1, 0)		
Space Group number Pearson´s symbol	225 cF16		

Table 1. Crystal structure information for the bcc compounds considered in the cluster expansion.

3. The total energy of ordered compounds.

First principles total energy calculations were carried out for a total of 10 bcc-based ordered structures. Structure information is shown in Table 1, while formation energies are plotted in Figure 1. In selecting bcc-based structures a natural candidate was U_2Mo structure, which existence was experimentally shown in U-Mo system [12]. The calculation were performed within the generalized gradient approximation [13], including relativistic corrections, using the Full Potential Linearized Augmented-Plane-Wave (FP-LAPW) method implemented in the WIEN 97.8 code [14], with a *k* mesh of 286 k points in the Brillouin irreducible zone. With regards to the cubic structures, the criterion to obtain the total energy was to minimize it as a function of lattice parameter. For tetragonal structures the process was to minimize *a* parameter keeping *c* constant then, taken this minimum *a*; minimize the *c* parameter and finally minimize the cell volume for the *c/a* value previously obtained. The process was repeated till convergence was achieved.

4. Binary calculations results.

The formation energy ΔE_F of ordered compounds were computed from their total energies as [15]:

$$\Delta E_f = E_T - \left(c_U \; E_U + c_{Mo} \; E_{Mo}\right) \tag{10}$$

where E_T , E_U and E_{Mo} are the total energy of the compound, Uranium and Molybdenum respectively. These values are shown in the ground state phase diagram of Figure 1 (circles). There are two features of this phase diagram that are worth to emphasize. The calculated energies of formation predict only one stable compound (U_2Mo) and an asymmetry that would stabilize the disordered alloy in the Uranium rich side as it is observed in the experimental bcc phase diagram of U-Mo (see Figure 2 [12]).

In order to find the minimal cluster expansion that is able to predict both the ground state of Fig. 1 and the experimental bcc phase diagram of Fig. 2, we considered all the clusters shown in Figure 3 with a hierarchy of clusters up to fifth neighbors in five successive sets: p1 + p2 (A), p1 + p2 + t112 (B), p1 + p2 + p3 + t112 (C), p1 + p2 + p3 + t112 + t113 (D) and p1 + p2 + p3 + p5 + t112 + t113 (F) (where: p_i is the ith neighbor pair and t_{ijk} is the triplet that involves i^{th}, j^{th} and k^{th} neighbors pairs). Thermodynamic equilibrium was obtained minimizing Helmhotz free energy as a function of site occupation and with the constraint of chemical potentials via the CVM method in all five approaches and they are illustrate in Figure 4. It can be seen that only D and F approaches reproduce the important experimental feature of the stabilization of U_2Mo phase, exhibiting at the same time a more accurate phase boundary for the equilibrium Mo+γU(Mo). Although D and F approaches almost exhibit the same fit of the two phase field Mo + γU(Mo), F approach fits better the transformation temperature γU(Mo) + U_2Mo.

The effective cluster interactions (ECI) corresponding to F approach as a function of their size are shown in Fig. 5 and the cluster-expanded energy of formation for the considered ordered compounds (filled diamonds) and for the random bcc alloys (line) are shown in Fig. 1. Clearly, the choice of clusters yields the same ground states as the calculated energies. The short-range pair interactions dominate the miscibility gap observed both in our calculation and in the experimental diagram between the terminal solid solution Mo(U) and the γU(Mo) phase but, the asymmetry of the gap and the stabilities of the gamma phase and the compound U_2Mo are due to the presence of triplet interactions, in particular that including first and third neighbors (t113). It is also

remarkable that irregular tetrahedron approach fails to predict the correct phase diagram for this system [16, 17]. This allows us to assert that the irregular tetrahedron interaction plays no significant role in stabilizing γU(Mo) phase.

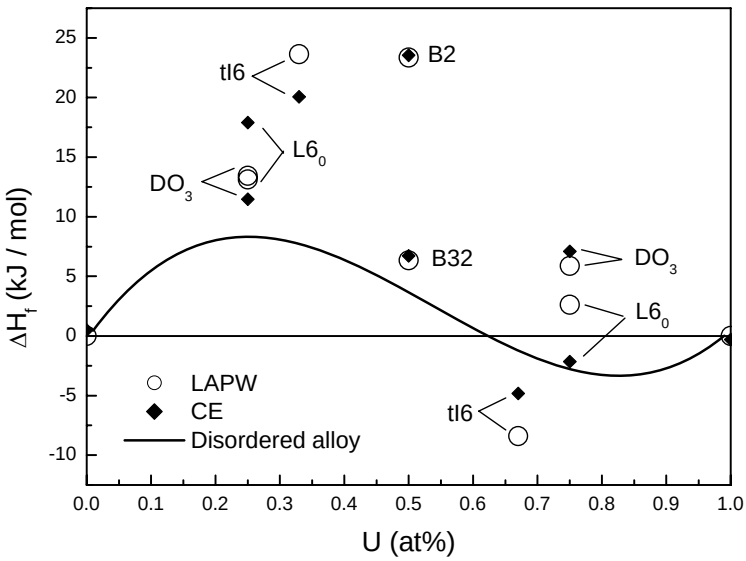


Figure 1. Ground state bcc phase diagram of U-Mo alloys. The ab initio calculations are represented by the circles while the cluster-expanded energies of formation are represented by filled diamonds. The curve stands for the corresponding energy of formation of disordered γU(Mo) alloy.

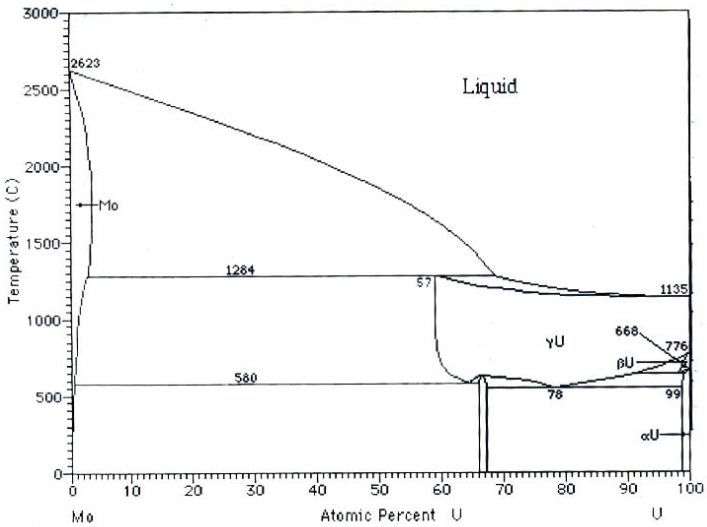


Figure 2. The experimental phase diagram of U-Mo.

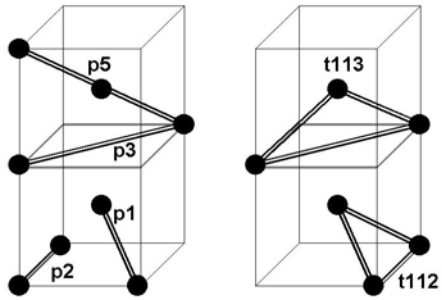


Figure 3. Real-space depiction of the clusters used in the expansion.

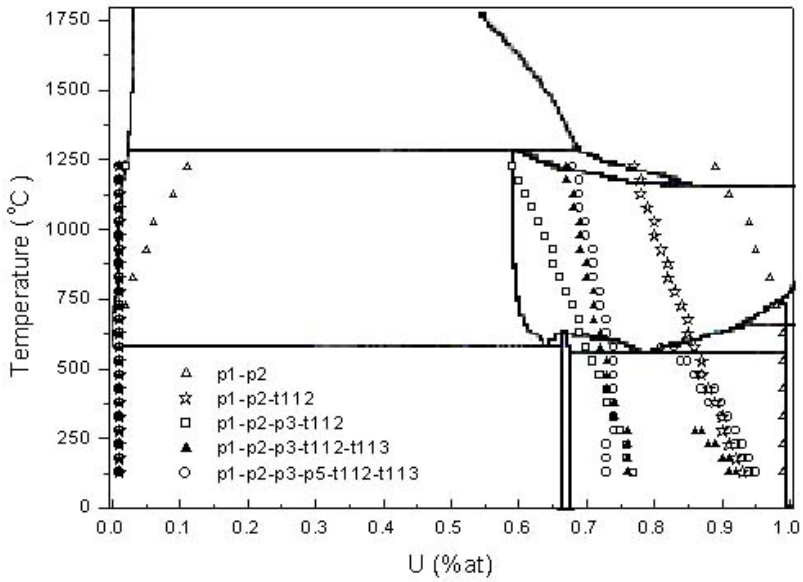


Figure 4. Comparison between the experimental and calculated bcc phase diagrams of U-Mo. Five sets of calculations are shown with a hierarchy of clusters up to fifth neighbors.

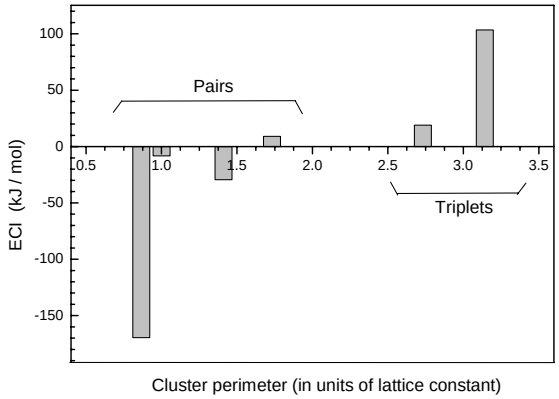


Figure 5. Effective cluster interactions for bcc-based Uranium-Molybdenum alloys. In the case of the three-body multisite ECIs, we have used the perimeter of the triplet as a measure of the range of the interactions.

5. Approach to ternary calculation: U-Mo-Pt.

New FP LAPW calculations at T=0K were performed in order to obtain values of formation energies for bcc binary U-Pt and Mo-Pt compounds and ternary U-Mo-Pt compounds ($L2_1$ structure, cF16, $AlCu_2Mn$ type). They are shown in Table 2.

Structure	E_F (k_BK)
B2 UPt	-6933,5835
B32 UPt	-10103,7176
U_3Pt	7182,9022
Upt_3	47305,8488
B2 PtMo	2100,2730
B32 PtMo	26,8254
Pt_3Mo	-751,1191
$PtMo_3$	14588,2976
L21 U_2PtMo	-1689,8046
L21 Pt_2UMo	-2347,9348
L21 Mo_2PtU	1244,8970

Table 2. Formation energies of U-Pt and Mo-Pt binary comopunds and $L2_1$ ternary compounds.

A first approach to γU(Mo, Pt) phase ternary composition field of estability was performed, including pairs till second neighbours, and clusters till tetraedron interaction. Thermodynamic equilibria was obtained for 2300K, 1700K y 1400K. Calculated Pt solubility in γ U(Mo) phase is negligible between 1400 K and 2300 K. We show in Figure 6 the partial equilibrium diagram calculated at 1700K.

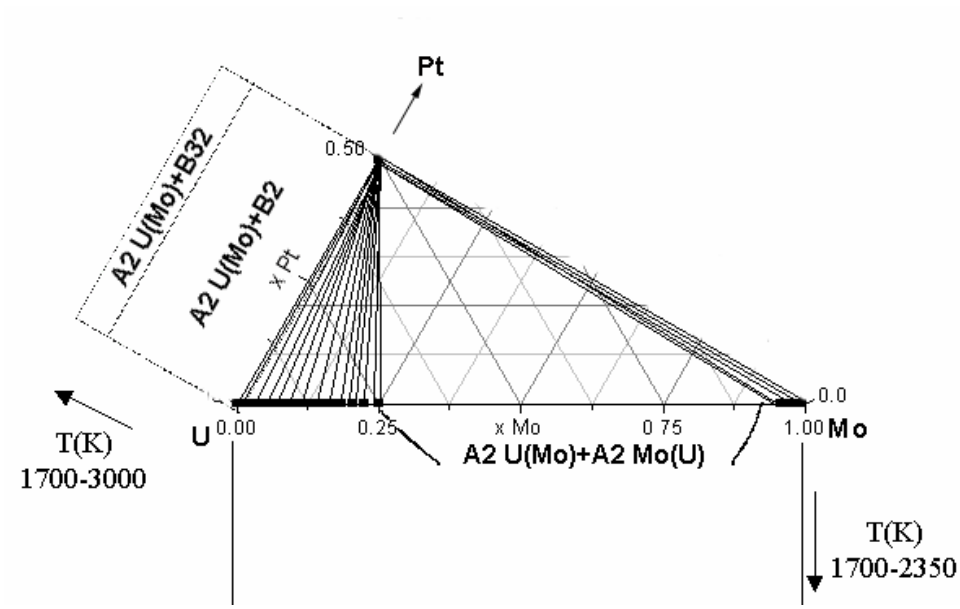


Figure 6. Calculated partial equilibrium diagram for U-Mo-Pt in the tetraedron approach.

Recent experimental data [18] show that an U-7wt%Mo-0,9wt%Pt alloy with short time lasting heat treatment below descomposition temperature exhibits α-UMo phase with no Pt content, U_2Mo with no Pt content, and metastable retained γ U(Mo,Pt). Although γ U(Mo,Pt) is metastable at that temperature, this measurement indicates that the phase accepts at least 0,99at% Pt in solution at stability temperatures. This result disagrees with our ternary calculations, but is at the same time another evidence showing that tetraedron approach is not a good one to reproduce U-Mo-Pt thermodynamic features. In the binary system,it was necesary to take into acount the estabilization of the U2Mo phase and the related triplet interaction with third order pairs. Thus, we are able to propose that triplets with third order pairs are also needed for an accurate description of the ternary U-Mo-Pt system equilibria.
Besides, experimental results suggests that a ternary compound should be formed, as Pt alloy content was not accepted in the two U-Mo binary phases. This agrees with the stabilization tendency of binary U-Pt compounds and ternary $L2_1$ U_2PtMo compound showed in FP LAPW calculations. It should be nevertheless noted that our calculations only include bcc compounds, and we have not calculated compounds with another crystalline structure.

6. Conclusions

It was demonstrated that the stability of γU(Mo) phase is dominated by a three-body multisite interaction consisting in two pairs of first neighbors and one pair of third instead of pairs interactions as was previously proposed. In consequence, it should be noted that the ultimate effectiveness of third element substitution on γ stabilization depends on how much this element modified the mentioned multisite interaction.

7. Acknowledgements

This work was partially supported by the Secretaría de Ciencia y Tecnología del Gobierno Argentino under grant BID 1201/OC-AR, PICT Nº 12-11186 (program 2004-2006).

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