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Ab-initio calculation of enthalpies of formation of intermetallic compounds and enthalpies of mixing of solid solutions

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Abstract

A large number of ab-initio calculations of energies of formation of intermetallic compounds have been performed in the last 15 years. The currently used methods are listed. The paper presents a review of the aluminium based compounds which have been studied. Comparisons of calculated and experimental enthalpies of formation are provided for aluminim-3d and-4d transition metal alloys at equiatomic composition. The modelling of the enthalpies of mixing of solid solutions based on a given lattice is described.

Keywords: A. Aluminides, miscellaneous; Trialuminides; B. Thermodynamic and thermochemical properties; E. Ab-initio calculations

1. Introduction

Ab-initio calculations of energies of formation have been the object of numerous studies in the last 15 years. These studies have been performed with various purposes. The first one was to test the ab-initio methods and to find the more efficient ones. In this goal, comparisons with experimental enthalpies of formation were necessary. Fortunately, in the last 15 years a large number of calorimetric values of enthalpies of formation have been provided by researchers specially by the Kleppa's group (see Refs. [1] and [2] for a review of the investigated compounds). The second goal of ab-initio calculations was the understanding of the alloying behaviour, therefore numerous studies focused on the phase stability and the electronic density of states at the Fermi level. Finally, the more recent ab-initio calculations have shown that predictions of enthalpies of formation are possible, predictions of the ground state in a system, predictions of the relative stabilities of various structures for a same composition. Therefore these calculations can be used when the experiments are very difficult or impossible; moreover they allow us to obtain the energy of formation of metastable states which are the more often not accessible experimentally.

The remainder of this paper is organized as follows. In Section 2, the basis of ab-initio calculations are recalled and the currently used methods are indicated. In Section 3, examples of ab-initio calculations are presented. We have focused our attention on aluminium based alloys because they have been extensively studied and because of their potential applications as structural materials. Section 3.1 presents the studies which have been performed in early transition metal trialuminides. Section 3.2 is devoted to transition metal aluminides at equiatomic composition. In Section 4 the method which is currently used to obtain the enthalpies of mixing in solid solutions is discussed. The conclusions are presented in Section 5.

2. Ab-initio calculations in perfectly ordered compounds

In a solid, where there are upward 10^{24} interacting electrons and nuclei, the resolution of the many body Schrödinger equation for the electronic wavefunctions and energy eigenvalues is a formidable challenge. However, based on the periodicity of the structure of pure elements and perfectly ordered compounds, the Bloch's theorem shows that it is only necessary to solve the many body Schrödinger equation within one unit cell. The basic information that one wishes to obtain from quantum mechanical calculations in solids is the total electronic energy for various arrangements of atoms on various lattices.

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The most sophisticated solutions to the quantum mechanical problem in solids lie within the framework of the density functional theory, DFT [3] using the local density approximation, LDA [4]. The basic notion of these theories is to replace the true interacting many body system with a system of one electron in an effective potential due to all of the other electrons and nuclei. From a fundamental point of view, the one-electron functions are uniquely a tool for calculating the total energy and the electronic density of states; these functions have no particular physical meaning. But this simplification of the problem needs a self-consistent calculation and it is one of the major technical problems in the ab-initio approach. The LDA is not the final solution to the exchange and correlation problem. The most common way for improving the LDA is to use the generalized gradient approximation, GGA [5].

There exist many methods to perform ab-initio calculations of total energies or cohesive energies of pure elements and compounds in the solid state. These are pseudopotential methods [6], plane-wave techniques (linearized augmented plane wave: LAPW [7], full potential linearized augmented plane wave: FLAPW [8]), muffin-tin techniques (augmented spherical wave: ASW [9], linearized muffin-tin orbital: LMTO [7], full potential linearized muffin-tin orbital: FPLMTO [10–12]). In the full potential methods, there is no approximation of the potential anywhere by its spherical average; the potential is represented as accurately as possible by an expansion in local basis functions. More details concerning these methods may be found in the reviews of Finnis [13] and Hafner [14].

One of the most widely used methods is the LMTO in the atomic sphere approximation (ASA). However this method does not seem very convenient in systems presenting large size-mismatch and in structures, which are not close-packed. The most accurate and therefore the most computationally intensive techniques are the full-potential methods: FPLMTO, FLAPW, and FLASTO (full-potential linearized augmented Slater-type orbital [15]) which are now extensively used. To conclude this review of the currently used methods, let us quote the Vienna ab-initio simulation package (VASP), which can be used with success in metallic systems. VASP [16–18] is based on the DFT within the LDA or the GGA. It is a plane-wave code. The method used to build the pseudopotentials is derived from the Vanderbilt's [19] recipe for ultrasoft potentials.

In all the computer routines quoted above, one needs only to specify the atomic numbers of the constituent elements and information about their arrangement in space: translation vectors and atomic positions of the species in the unit cell of the structure. The total energy is minimized with respect to the volume (volume relaxation), the shape of the unit cell (cell external relaxation), and the position of the atoms within the cell (cell internal relaxation), with no other restrictions than those imposed by space-group symmetry.

The ab-initio calculations furnish the total energy (or the cohesive energy) at T = 0 K, E^{Φ}. The energy of formation is easily calculated by the relation

$$\Delta_f E = E^{\Phi} - \sum \mathrm{x_i} E_i^O, \tag{1}$$

where E_i^O is the total energy (or cohesive energy) of i in its stable state at $T = 0$ K. In the following we will assume that the enthalpy of formation is equal to the energy of formation.

In addition to the total energies and electronic densities of states, ab-initio calculations allow us to obtain the values of the lattice parameters and the bulk modulus.

3. Examples of ab-initio calculations of enthalpies of formation

Ab-initio calculations have been performed in numerous systems. In the present paper, we will focus our attention on aluminium based alloys because many studies have been performed in these systems and because many experimental determinations of enthalpies of formation of aluminides allow comparisons between experiment and theory. Moreover, aluminides have potential applications in structural materials. A compilation of aluminium based alloys for which ab-initio calculations of enthalpies of formation or structural stability have been performed is presented in Table 1. We apologize for possible omissions. A recent database provided by Johannesson et al. [69] must be added to this review. In this database, the enthalpies of formation of binary combinations of metallic elements were calculated using the LMTO-ASA method within the framework of the GGA. The considered structures were $L1_2$ and $D0_3$ for the compositions A_3B and AB_3, $L1_0$, B2 and B11 for equiatomic composition.

In the following sections, we will discuss the results obtained in the early transition metal trialuminides and in the 3d and 4d transition metal aluminides at equiatomic composition.

3.1. Early transition metal trialuminides

Trialuminides of early transition metals MAl_3 where M is a group III, IV, or V transition metal have been the subject of several investigations. From a practical point of view, these trialuminides are promising structural materials because of their high melting points, low densities, and oxidation resistance. However, most of these compounds crystallize in the $D0_{22}$ (or $TiAl_3$-type) structure. Experiments on many face centered cubic (fcc) metallic alloys reveal that those which develop $L1_2$ atomic order are significantly more ductile than those that form

Table 1
Aluminium based alloys in which ab-initio calculations of enthalpies of formation at $T=0$ K or relative structure stabilities have been performed. IMC: intermetallic compounds, LMTO: linear muffin tin orbital, ASA: atomic sphere approximation, ASW: augmented sperical wave, LAPW: linearized augmented plane wave, FLAPW: fully linearized augmented plane wave, FP: full potential, FLASTO: full potential linearized Slater type orbital, VASP: Vienna ab initio simulation package, PP: pseudo-potentials, DFT: density functional theory, PD: phase diagram

System	Method	Results	Reference
Al-Ag	LMTO-ASA	fcc compounds, $\Delta_f E$, fcc PD	[20], [21]
	FPLMTO	B20-AgAl, $\Delta_f E$	[22]
Al-Co	FLAPW	B2-AlCo, $\Delta_f E$	[23]
	FPLMTO	B2-AlCo, $\Delta_f E$	[22]
	VASP	$D8_d$-Al_9Co_2, $\Delta_f E$	[24]
Al-Cr	FLAPW	$L1_0$-AlCr, $\Delta_f E$	[23]
	FPLMTO	B32-AlCr, $\Delta_f E$	[22]
	VASP	mC104-$Al_{45}Cr_7$, $\Delta_f E$	[24]
Al-Cu	FLAPW	fcc compounds, $\Delta_f E$, PD	[25]
	FPLMTO	C2/m-AlCu, $\Delta_f E$	[22]
	VASP	C16 and CaF_2-Al_2Cu, $\Delta_f E$	[26]
Al-Fe	FLAPW	B2-FeAl, $\Delta_f E$	[23]
	FLASTO	Fe_3Al, Fe_2Al, FeAl, $FeAl_2$, $FeAl_3$ in various structures, $\Delta_f E$	[27]
	FPLMTO	B2-FeAl, $\Delta_f E$	[22]
	VASP	mC104-$Al_{13}Fe_4$, $\Delta_f E$	[26]
	FLAPW	$D0_3$ and $L1_2$-Fe_3Al, $\Delta_f E$	[28]
Al-Hf	ASW	Al_3Hf, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
	VASP	Al_3Hf, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$ and $\Delta_f E$	[30]
Al-La	ASW	Al_3La, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
Al-Li	FLAPW	fcc and bcc compounds, $\Delta_f E$, PD	[31]
	LMTO-ASA	fcc and bcc compounds, $\Delta_f E$, PD	[32]
	LMTO-ASA	fcc and bcc compounds, $\Delta_f E$	[33]
	LMTO-ASA	fcc compounds, $\Delta_f E$	[34]
Al-Mg	VASP	A12-$Al_{12}Mg_{17}$, $\Delta_f E$	[26]
Al-Mn	FPLMTO	$L1_0$-AlMn, $\Delta_f E$	[22]
	VASP	$D2_h$-Al_6Mn, $\Delta_f E$	[26]
Al-Mo	FPLMTO	B32-AlMo	[22]
	FLASTO	Mo_3Al, MoAl, $MoAl_3$, $MoAl_{12}$, $\Delta_f E$	[35]
Al-Nb	ASW	Al_3Nb, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
	LMTO-ASA	$L1_2$ and $D0_{22}$-Al_3Nb, $\Delta_f E$	[36], [37]
	LMTO-ASA	Al_3Nb, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[38]
	FPLMTO	fcc, bcc, ω, and σ compounds, $\Delta_f E$, PD	[39], [40]
	FPLMTO	ω-AlNb, $\Delta_f E$	[22]
	FLASTO	Nb_3Al, NbAl, $NbAl_3$, $\Delta_f E$	[35]
Al-Ni	ASW	$L1_2$-$AlNi_3$, B2-AlNi, $L1_2$-Al_3Ni	[41]
	LMTO-ASA	$L1_2$-$AlNi_3$, $\Delta_f E$	[42]
	LMTO-ASA	fcc and bcc compounds	[43]
	LMTO-ASA	fcc and bcc compounds, other IMC, $\Delta_f E$, PD	[44]
	FLAPW	B2-AlNi, $\Delta_f E$	[23]
	FLASTO	$AlNi_3$, Al_3Ni_5, AlNi, Al_3Ni_2, Al_2Ni, Al_3Ni in various structures, $\Delta_f E$	[27]
	FPLMTO	B2-AlNi	[22]
	DFT-PP	PD	[45], [46]
	VASP	D020 and oP16- Al_3Ni	[24]
Al-Pd	FPLMTO	B20-AlPd, $\Delta_f E$	[22]
	FLASTO	$AlPd_3$, $AlPd_2$, AlPd, Al_3Pd_2, Al_2Pd, Al_3Pd in various structures, $\Delta_f E$	[35]
Al-Rh	FPLMTO	B2-AlRh, $\Delta_f E$	[22]
	FLASTO	$AlRh_2$, AlRh, Al_3Rh in various structures, $\Delta_f E$	[35]
Al-Ru	FPLMTO	B2-AlRu, $\Delta_f E$	[22]
	FLASTO	$AlRu_3$, AlRu, Al_3Ru_2, Al_2Ru, Al_3Ru in various structures, $\Delta_f E$	[35]
Al-Sc	ASW	Al_3Sc, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
	FLAPW	$L1_2$-Al_3Sc, $\Delta_f E$	[47]
	LMTO-ASA	$L1_2$ and $D0_{22}$ Al_3Sc, $\Delta_f E$	[48]
	LMTO-ASA	Al_3Sc, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[49]
	DFT-PP	fcc-compounds	[50]
	FPLMTO	B2-AlSc	[22]
	VASP	fcc, bcc-compounds and other structures, $\Delta_f E$	[51]
	VASP	$L1_2$-Al_3Sc, $\Delta_f E$	[24]
	DFT-PP	Al_3Sc, relative stability of $L1_2$, $D0_{22}$	[52]

(*continued on next page*)

Table 1 (*continued*)

System	Method	Results	Reference
Al-Sr	VASP	$D1_3$-Al_4Sr, $\Delta_f E$	[24]
Al-Ta	ASW	Al_3Ta, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
Al-Tc	FPLMTO	B32-AlTc, $\Delta_f E$	[22]
	FLASTO	$AlTc_2$, AlTc, Al_3Tc_2, Al_3Tc, $Al_{12}Tc$, in various structures, $\Delta_f E$	[35]
Al-Th	FLAPW	$AlTh_2$, $\Delta_f E$	[53]
Al-Ti	FLAPW	$L1_0$-AlTi	[54]
	ASW	Al_3Ti, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
	LMTO-ASA	$D0_{22}$-Al_3Ti, tetragonal distortion	[55]
	FLAPW	$L1_2$ and $D0_{22}$-Al_3Ti, $\Delta_f E$	[47]
	LMTO-ASA	$L1_2$, $D0_{22}$, and $D0_{19}$-Al_3Ti, $\Delta_f E$	[56]
	LMTO-ASA	$L1_2$, $D0_{22}$, and $D0_{19}$-$AlTi_3$, $\Delta_f E$	[57]
	FPLMTO	fcc compounds, $\Delta_f E$	[58]
	FPLMTO	fcc and hcp compounds, $\Delta_f E$, PD	[59]
	LMTO-ASA	$L1_2$ and $D0_{22}$-Al_3Ti, $\Delta_f E$	[60]
	FPLMTO	Al_3Ti, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[61]
	FLAPW	$D0_{19}$-$AlTi_3$, $L1_0$-AlTi, $D0_{22}$-Al_3Ti, $\Delta_f E$	[62]
	FPLMTO	AlTi, relative stability of B19, B2, B33, $L1_0$, ω	[39]
	FLASTO	$AlTi_3$, AlTi, Al_2Ti, Al_3Ti in various structures, $\Delta_f E$	[27]
	FPLMTO	$L1_0$-AlTi, $\Delta_f E$	[22]
	VASP	$D0_{22}$, Al_3Ti	[24]
	PP	Al_3Ti, relative stability of $L1_2$, $D0_{22}$	[52]
	VASP	Al_3Ti, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$, $\Delta_f E$	[63]
Al-V	ASW	Al_3V, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
	FLAPW	$L1_0$-AlV, $\Delta_f E$	[62]
	FPLMTO	AlV, relative stability of B19, B2, B33, $L1_0$, ω	[39]
	FPLMTO	$L1_0$-AlV, $\Delta_f E$	[22]
	FLASTO	AlV_3, AlV, Al_3V in various structures, $\Delta_f E$	[27]
	VASP	Mc104-$Al_{45}V_7$, $\Delta_f E$	[24]
	VASP	$L1_2$ and $D0_{22}$-Al_3V, $\Delta_f E$	[64]
Al-Y	ASW	Al_3Y, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
	LMTO-ASA	$L1_2$, $D0_{22}$, $D0_{19}$-Al_3Y, $\Delta_f E$	[36], [37]
	VASP	$CeCu_2$ and C15-Al_2Y, relative stability and $\Delta_f E$	[65]
	FPLMTO	B33-AlY, $\Delta_f E$	[22]
	FLASTO	AlY_3, AlY_2, AlY, Al_2Y, Al_3Y in various structures, $\Delta_f E$	[35]
Al-Zn	DFT-PP	fcc compounds, $\Delta_f E$, PD	[25]
Al-Zr	ASW	Al_3Zr, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[29]
	LMTO-ASA	$L1_2$, $D0_{22}$, $D0_{19}$-Al_3Zr, $\Delta_f E$	[36], [37], [48]
	FPLMTO	Al_3Zr, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$	[61]
	FPLMTO	AlZr, relative stability of B19, B2, B33, $L1_0$, ω	[39]
	FLASTO and DFT-PP	several IMC, $\Delta_f E$	[66]
	FPLMTO	B33-AlZr, $\Delta_f E$	[22]
	VASP	Al_3Zr, relative stability of $L1_2$, $D0_{22}$, $D0_{23}$ and $\Delta_f E$	[67]
	FPLMTO	fcc compounds, $\Delta_f E$, PD	[68]

$D0_{22}$ order, presumably due to the lack of a sufficient number of slip systems in the $D0_{22}$ structure. Consequently the $L1_2$ alloys are more likely to be suitable in structural applications because of their mechanical properties.

From a theoretical point of view, many studies have been performed to understand the relative stabilities of $L1_2$, $D0_{22}$, and $D0_{23}$ structures in the early transition metal trialuminides. The first extensive study was performed by Carlsson and Meschter [29] using the ASW method, this study gave the main features because these authors considered the ideal and the distorted structures. However they did not introduce the atomic displacements in the $D0_{23}$ structure and therefore could not find that the ground state of $HfAl_3$ compound is $D0_{23}$ structure [30]. Further studies were performed and gave more information. The main conclusions which can be derived from all these studies are the following:

1. For Sc, Y, and La trialuminides, the $L1_2$ structure is more stable than the ideal $D0_{22}$ structure. The tetragonal distortion of the $D0_{22}$ structure led to a decrease of the total energy, however the distorted $D0_{22}$ structure remains less stable than the $L1_2$ structure.
2. For V, Nb, and Ta trialuminides, the ideal $D0_{22}$ structure is already more stable than the $L1_2$ structure. The distortion of the $D0_{22}$ structure increases its stability with respect to the $L1_2$ one.

3. In the case of Ti, Zr, and Hf trialuminides, the situation is more complicated. Many studies have been performed in these systems (see Table 1). Amador et al. [61] in Al_3Ti and Al_3Zr and recently Colinet and Pasturel in Al_3Ti [63], Al_3Zr [67], and Al_3Hf [30] have shown the importance of the relaxations on the structural stability. The $L1_2$ structure is more stable than the ideal $D0_{22}$ and $D0_{23}$ structures. It is certainly the reason for which $L1_2$ is obtained in a metastable state by the rapid quenching of melts or by the precipitation of saturated fcc solid solution. The distortion of the lattice stabilizes the $D0_{22}$ structure with respect to the $L1_2$ one in Al_3Ti and Al_3Hf compounds and the $D0_{23}$ structure in Al_3Zr compound. In the completely relaxed stage, the $D0_{23}$ structure appears the more stable structure for the three systems. This is in agreement with the experimental phase diagrams of Al-Zr and Al-Hf systems [70]. Recent experimental phase diagram determinations have been performed in the Al-Ti system [71,72], a low temperature structure $Al_{24}Ti_8$, whose Pearson symbol is tI32, was reported for 75 at% of aluminium.

Comparisons of calculated and experimental values of the enthalpies of formation of Al_3Ti, Al_3Zr, and Al_3Hf compounds have been done by Colinet and Pasturel [63,67,30]. These comparisons have shown a good agreement between the two sets of values.

3.2. *Transition metal aluminides at equiatomic composition*

In recent years, the transition metal aluminides at equiatomic composition have been the subject of several studies. Using the FLAPW method, Zou and Fu [23] determined the enthalpies of formation of the compounds AlTi, AlV, and AlCr in the $L1_0$ structure and of AlFe, AlCo, and AlNi in the B2 structure. Using the FPLMTO method, Nguyen-Manh et al. [39] studied the relative stabilities of $L1_0$, B19, B2, B33, and ω structures in AlTi, AlZr, AlV, and AlNb compounds. Later Nguyen-Manh and Pettifor [22] systematically studied the relative stabilities of several structures for 3d and 4d aluminides at equiatomic composition, they determined the ground state in each system and provided the energy of formation of this ground state. Recently, Watson et al. [27,35] studied the 3d and 4d aluminium systems and obtained the enthalpies of formation of various structures. Moreover, a large number of enthalpies of formation of aluminides in B2 and $L1_0$ structures were calculated using the LMTO-ASA method by Johannesson et al. [69]. Figs. 1 and 2 present these results respectively for the 3d and 4d aluminides at equiatomic composition. Additionally, the values obtained by Asta et al. [50] using VASP for B2-AlSc, by Lu et al. [43] and Pasturel et al. [44] using the LMTO-ASA method for B2-AlNi have been included in Fig. 1. Experimental values of enthalpies of formation of aluminides are available and are also reported in Fig. 1 and 2. These values are taken from the review of de Boer et al. [73] and from the compilation of Desai et al. [74] These values are also those obtained more recently by Meschel and Kleppa [75] for AlSc and AlCo, by Meschel and Kleppa [1] for AlFe and AlNi, by Jung and Kleppa [76] for AlRu and AlRh, by Jung et al. [77] for PdAl, by Meschel and Kleppa [78] for AlHf.

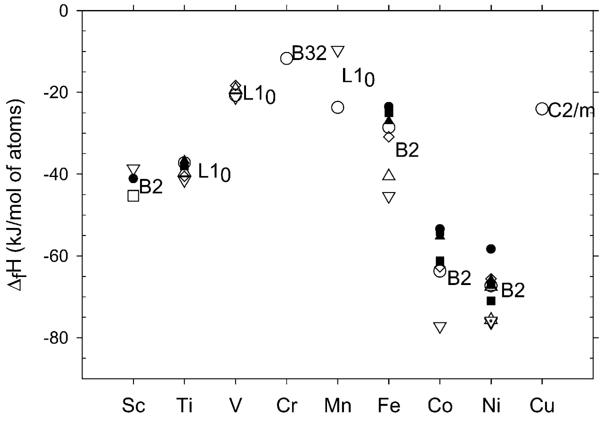

Fig. 1. Calculated and experimental values of 3d-aluminides at equiatomic composition. Empty symbols: calculated values: circles [22], triangles up [27], triangles down [69], squares [51] for AlSc, triangle up dotted [43] and triangle down dotted [44] for AlNi, diamonds [23]. Full symbols: experimental values: circles [75, 1], squares [73], triangles up [74].

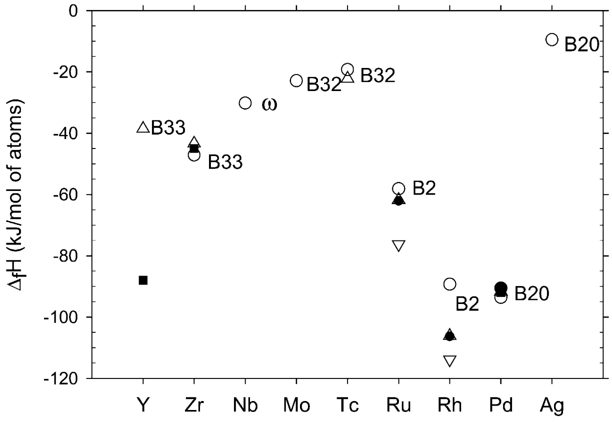

Fig. 2. Calculated and experimental values of 4d-aluminides at equiatomic composition. Empty symbols: calculated values: circles [22], triangles up [35, 66], triangle down [69]. Full symbols: experimental values: circles [76, 77, 78], squares [73].

Some conclusions may be deduced from inspection of Figs. 1 and 2. With a few exceptions, the agreement between the experimental and the calculated values is satisfying. The results obtained using the LMTO-ASA method deserve some comments. On the one hand, the values obtained for compounds which possess the B2 structure are more negative than the experimental values and than the other calculated values (except for AlSc compound). On the other hand the values obtained for the compounds which possess the $L1_0$ structure are in very good agreement with the other calculated values and the experimental ones. As indicated in section 2, the LMTO-ASA method is maybe not well suited for structures which are not close-packed such as the B2 structure.

For AlSc, AlTi, AlV, AlZr, AlRu, AlPd compounds, the agreement between all calculated and experimental values of the enthalpies of formation is very good. For some compounds, however, there are discrepancies. In the case of B2-AlFe the calculated values are all more negative than the experimental ones, particularly in the case of Fe based alloys, as has been discussed recently by Lechermann et al. [28]. In the cases of B2-AlCo and B2-AlNi, the calculated values of the enthalpies of formation are in agreement with some experimental ones but not with the values obtained by Meschel and Kleppa [75,1] which are less negative. In the case of B2-AlRh, there is a large difference between the value of the enthalpy of formation calculated by Nguyen-Manh et al. [22] and two experimental values [75,73]. In the case of B2-AlY there is a large discrepancy between the values calculated by Watson et al. [35] and the experimental value reported by de Boer et al. [73]. In conclusion, other experimental and calculated values of enthalpies of formation will be welcome to solve the above mentioned discrepancies.

The case of Al-Nb system deserves one comment: at equiatomic composition the equilibrium between the $D0_{22}$ and the σ phase is the more stable state. The first metastable state is the ω-NbAl whose enthalpy of formation determined by Nguyen-Manh et al. [39] is reported in Fig. 2.

4. Ab-initio calculation of enthalpies of mixing of solid solutions

In solid solutions based on a given lattice, the situation is rather more complex. The strategy which is now extensively used consists of performing ab-initio calculations of total energies of perfectly ordered compounds based on the lattice. The result of such calculations is the ground state at $T=0$ K, let's say the formation of perfectly ordered compounds or the phase separation between the constituent elements. The calculations of the thermodynamic data at finite temperature need the modelling of the total energies results and the use of a statistical treatment.

The modelling is performed by using the Connolly and Williams method (CWM), which has been introduced by Connolly and Williams [79]. This method has been extended by several researchers, in particular by de Fontaine and coworkers [80] who called the method the structure inversion matrices (SIM) and by Zunger and coworkers [81] who called the method the renormalization approach.

Connolly and Williams [79] started from a formal description of the solid solution with a generalized Ising Hamiltonian of the form [82]:

$$E_{tot}^{S} = \sum_{n=0} V_n \sigma_1 \sigma_2 \ldots\ldots\ldots \sigma_n \tag{2}$$

where σ_n is the spin variable, which takes the values +1 or −1 depending of the occupancy of site n. The V_n are called effective cluster interactions (ECI). The summation in Eq. (2) runs over all cluster types that can be formed by combining sites on the entire crystal including the "empty cluster". The correlation function of the cluster α of n sites are defined by:

$$\xi_\alpha = < \sigma_1 \sigma_2 \ldots\ldots\ldots \sigma_n > . \tag{3}$$

In a given structure S, the correlation functions, ξ_α^S, are found by inspection of the structure. If the number of equivalent clusters per lattice site is denoted m_α, the configurational energy can be expressed as:

$$E_{tot}^{S} = \sum m_\alpha V_\alpha \xi_\alpha^S. \tag{4}$$

Knowing the correlation functions in each considered structure, the linear system formed by Eq. (4) can be inverted and yield to the V_α. Of course, it is necessary that the number of studied superstructures is greater or at least equal to the number of cluster interactions, which have to be determined. Hence, by choosing a set of ordered structures and by arbitrarily truncating the summation in Eq. (4), a set of multisite interactions can be obtained from:

$$V_\alpha = \frac{1}{m_\alpha} \sum_S \left[\xi_\alpha^S\right]^{-1} E_{tot}^S \tag{5}$$
$$\text{for } \phi < \alpha < \alpha_{max}, V_\alpha = 0 \text{ for } \alpha_{max} < \alpha < \infty,$$

ϕ is the empty cluster. Equation (5) must be understood in a symbolic sense. For a given α_{max}, the best set of cluster interactions is chosen as the one that minimizes the predictive error in the energy according to:

$$\sum_S w_S \left[E_{tot}^S - \sum_\alpha m_\alpha V_\alpha \xi_\alpha^S \right]^2 = \text{minimum}. \tag{6}$$

According to researchers, various weight factor, w_S, were introduced [43,83,32]. The optimum set of ECIs is obtained by studying the convergence of the predictive error involved in the predicting energy values and also the convergence of the formation energy of the random alloy at equiatomic composition. This latter is also a significant check because it is obtained as a by-product in the used method. Let us recall that, in substitutional disordered structures, all atomic positions are equivalent so that all correlations can be expressed in terms of the one point correlation function, ξ_1:

$$\xi_\alpha^{dis} = (\xi_1)^{n_\alpha} \tag{7}$$

where n_α is the number of sites contained in the α cluster. The total energy of the disordered configuration, according to the CWM, is then given by:

$$E_{tot}^{dis} = \sum_{\alpha}^{\alpha_{max}} m_\alpha V_\alpha (\xi_1)^{n_\alpha}. \tag{8}$$

Such a method was used in several systems such as Al-Li [31,32], Al-Ti [59], Al-Ni [43,44], Al-Nb [40], Al-Ag [20,21], Al-Zr [68].

The rate of convergence of the cluster expansion is a major problem in the use of the CWM. It has been emphasized by Zunger [81] that the cluster expansions for systems with lattice relaxation converge more slowly than cluster expansions for unrelaxed systems. To solve this problem, the reciprocal space cluster expansion was proposed by Laks et al. [84]. In practice, the reciprocal-space expansion is applied to the pairs whereas the three-body and higher figures are described by a real-space expansion. This method was used by Müller et al. [25] in Al-Cu and Al-Zn systems.

The statistical treatments, which allow to obtain the thermodynamic data at finite temperature, are the cluster variation method (CVM) [85–90] or Monte-Carlo simulations [91–92]. The CVM was often used [20,21,31,32,40,43,44,59]. One may quote that the Al-Zn miscibility gap and the Al rich part of the Al-Cu phase diagram have been calculated by Müller et al. [25] using Monte Carlo simulations.

5. Conclusions

In the last 15 years, research concerning ab-initio calculations of enthalpies of formation at T = 0K in metallic systems has been very active. However very few calculations were performed in lanthanide and actinide based alloys. Moreover the treatment of Fe and Fe based alloys such as Fe_3Al still pose problems [28]. Calculations in more complex phases than the one based on fcc, bcc and hcp structures have already been performed [93–96]. The final goal of ab-initio calculations of enthalpies of formation is the ab-initio determination of the phase diagram in a given system. However it appears that, until now, ab-initio calculations of phase diagrams have been restricted to the relatively simple; indeed a phase diagram calculation needs the calculation of the Gibbs energies of all phases in competition and therefore a finite temperature treatment. The used methods are the CVM or Monte Carlo simulations, additionally the electronic and vibrational effects must be taken into account. Therefore the complete ab-initio calculation of a complex phase diagram is not close at hand. However, phase diagram calculations in systems, where experimental data are missing, could be performed in the future by combination of CALPHAD routines and ab-initio calculations of formation energies or energies of mixing.

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