AB INITIO STUDY OF C14 LAVES PHASES IN Fe-BASED SYSTEMS

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Abstract

Structural properties and energetics of Fe-based C14 Laves phases at various compositions (i.e. Fe_2Fe, Fe_2X, X_2Fe, X_2X, where X stands for Si, Cr, Mo, W, Ta) were investigated using the pseudopotential VASP (Vienna Ab initio Simulation Package) code employing the PAW-PBE (Projector Augmented Wave - Perdew-Burke-Ernzerhof) pseudopotentials. Full relaxation was performed for all structures studied including the reference states of elemental constituents and the equilibrium structure parameters as well as bulk moduli were found. The structure parameters of experimentally found structures were very well reproduced by our calculations. It was also found that the lattice parameters and volumes of the unit cell decrease with increasing molar fraction of iron. Thermodynamic analysis shows that the Fe_2X configurations of Laves phases are more stable than the X_2Fe ones. Some of the X_2Fe configurations are even unstable with respect to the weighted average of the Laves phases of elemental constituents. Our calculations predict the stability of Fe_2Ta. On the other hand, Fe_2Mo and Fe_2W are slightly unstable (3.19 and 0.68 $kJ.mol^{-1}$, respectively) and hypothetical structures Fe_2Cr and Fe_2Si are found unstable as well.

Keywords: C14 Laves phases; Fe-based systems; Lattice stability; Ab-initio calculations

1. Introduction

C14 Laves phase represents a complex intermetallic structure, which can be found in many systems (e.g. Cr-Ta, Cr-Zr, Fe-Mo, Fe-W, Fe-Ta, Ta-V). If present it significantly influences material characteristics. The Fe-based systems are very important for the development of ferritic steels and Laves phases are considered to be promising strengthening phases under certain conditions. In binary systems, these phases can be usually found as stoichiometric but in higher systems they can exhibit some solubility of other elements (Si, Cr). For example, Si has been found to play an important role in the stability of this phase and, because of lack of experimental data concerning the influence of Si on Laves phase in simpler subsystems, a theoretical study of this effect is highly desirable.

In principle, basic properties of any phase are determined by its electronic structure. The purpose of this paper is to study, from first principles, the stability of C14 Laves phases in various binary systems consisting of Fe and some of the following elements: Si, Cr, Mo, Ta or W.

The paper is organised as follows: After the Introduction, we describe our ab initio calculations in Section 2. Section 3 presents the structural and energetic analysis and discussion of the results. Section 4 concludes the paper.

2. Ab initio calculations

Our first-principles calculations were performed by the pseudopotential Vienna Ab initio Simulation Package (VASP) code [1,2] using the Projector Augmented Wave - Perdew-Burke-Ernzerhof (PAW-PBE) pseudopotential [3-5]. The exchange-correlation energy was evaluated within the Generalised Gradient Approximation [6]. Spin polarisation was not included in our calculations, except when noted. Reason for this is the fact that all Laves phases found in the above mentioned systems at ambient temperatures are paramagnetic. From the crystallographic point of view, the C14 Laves phase belongs to the hexagonal structures. It has 12 atoms in its unit cell and its symmetry is described by the space group No. 194 [7, 8].

Optimum calculation settings were achieved starting with the experimentally found lattice parameters. The structure parameters for the reference states (RS) (structures of elemental constituents, which are stable at Standard Ambient Temperature and Pressure (SATP), i.e. FM bcc Fe, NM diamond Si and NM bcc Mo, W and Ta) were taken from [8] and of AFM bcc Cr from [9] (Table 1). For Laves phases in Fe-(Cr,Mo,Si), Fe-Ta and Fe-W

Dedicated to the memory of Professor Zbigniew Moser

systems the lattice parameters from Fe_2Mo, Fe_2Ta and Fe_2W [8] (Table 2), respectively, were implemented. Convergence tests of the total energies with respect to number of k-points have shown that the range of optimum values goes from a grid of 11x11x8 points (Fe_2Mo, W_2Fe and elemental Mo and W in C14 structure) towards 25x25x13 points (Fe_2W). In the case of RS, this range spreads from a grid of 9x9x9 points for FM bcc Fe and NM Si in diamond structure to 23x23x23 points for NM bcc Ta and W.

3. Results and discussion

3.1 Structure

Calculated structure parameters in comparison with experimental data are shown in Table 1 for RS structures of elemental constituents and in Table 2 for the C14 Laves phases studied. It may be seen that the theoretical results agree well with experimental values.

Table 1. *Calculated and experimental lattice parameters of the RS structures (AFM stands for antiferromagnetic, FM for ferromagnetic and NM for nonmagnetic state, V_{at} denotes the volume per atom).*

Structure	This work (relaxed)			Experiment		
	a (a.u.)	V_0 (a.u.^{3})	B_0 (Mbar)	a (a.u.)	V_{at} (a.u.^{3})	Ref.
AFM bcc Cr	5.3947	78.5015	1.86	5.44	80.4946	[8]
FM bcc Fe	5.3589	76.9466	1.94	5.40 5.4160	78.7320 79.4339	[9] [10]
NM bcc Mo	5.9513	105.3921	2.71	59.4340	104.9723	[8]
NM diam. Si	10.3354	138.0030	0.90	102.6290	135.1209	[8]
NM bcc Ta	6.2531	122.2539	2.01	62.3970	121.4672	[8]
NM bcc W	5.9915	107.5396	3.15	59.8060	106.9582	[8]

Table 2. *Calculated and experimental structure parameters and bulk moduli (B_0) of the C14 Laves phases in the Fe-X systems (X = Si, Cr, Mo, Ta, W).*

| Structure	a (a.u.)	c/a	V_{at} (a.u.^{3})	$4f$-z	$6h$-x	B_0 (Mbar)
Fe_2Fe	8.5562	1.5976	72.2224	0.0804	0.8260	2.62
Fe_2Cr	8.6291	1.5938	73.9032	0.0775	0.8250	2.68
Cr_2Fe	8.7111	1.6095	76.7794	0.0621	0.8287	2.38
Cr_2Cr	8.7701	1.6512	80.3841	0.0464	0.8289	2.38
Fe_2Mo	8.8485	1.6146	80.7275	0.0695	0.8273	2.88
Fe_2Mo exp [8]	8.9668	1.6299	84.8053	0.063 [a]	0.83 [a]	- - -
Mo_2Fe	9.6076	1.5838	101.3668	0.0612	0.8280	2.11
Mo_2Mo	9.7465	1.6466	110.0248	0.0413	0.8298	2.42
Fe_2Si	8.6043	1.6601	76.3173	0.0714	0.8265	2.13
Si_2Fe	9.6519	1.3569	88.0536	0.0230	0.8214	1.43
Si_2Si	10.5905	1.2334	105.7317	0.0718	0.8158	0.89
Fe_2Ta	8.9710	1.6347	85.1753	0.0656	0.8293	2.68
Fe_2Ta exp [8]	9.1841	1.6284	91.0364	0.063 [a]	0.83 [a]	- - -
Ta_2Fe	10.0163	1.5921	115.4628	0.0329	0.8294	1.58
Ta_2Ta	10.3003	1.5922	125.5696	0.0623	0.8292	2
Fe_2W	8.8403	1.6219	80.8705	0.0686	0.8279	3.11
Fe_2W exp [8]	8.9522	1.6242	84.0975	0.063 [a]	0.83 [a]	- - -
W_2Fe	9.7322	1.5896	105.7456	0.0595	0.8291	2.26
W_2W	9.8110	1.6515	112.5596	0.0417	0.8301	2.82

[a] *As the corresponding experimental data were not found in [8], the values of C14 $MgZn_2$ Laves phase were used here.*

The deviations in atomic volume are within the range from -3.1 to 2.1 % for RS (from Fe to Si) and from -3.8 to -6.4 % for Laves phases (from Fe_2W to Fe_2Ta). We have also found unambiguous trends in the geometry of Laves phase configurations (i.e. Fe_2Fe, Fe_2X, X_2Fe, X_2X) depending on the amount of Fe atoms in unit cell and on the size (or number of electrons) of X atom. These trends are demonstrated in Figure 1.

The most obvious tendency may be observed in behaviour of the lattice parameters (*a, c*) and atomic volumes (V_{at}) which increase with the concentration of X atoms involved except of the case of *c* parameter in Fe-Si system. This common trend results from the fact that Fe atoms are ones of the smallest particles studied in this work [11]. The differences in the size between the Fe and X atoms affect the distances between the individual lines in Figure 1(c) as here the effects of mutual interplay of *a* and *c* are "integrated" into the value of atomic volume. We can see there that the values of V_{at} of all structures increase in the series Fe-Cr, -Si, -Mo, -W and -Ta – individual curves in Figure 1(c) do not intersect. This tendency is similar to trends in empirical atomic radii [11] which give the order Si, W, Fe, Cr, Mo, Ta. What are the reasons for

disagreement in case of Si and W? The answer concerning W is simple. As we do not study separate atoms but bulk material our results should be compared rather with other experimental data e.g. covalent radii [12-16], metallic radii [12] or valence shell orbital radii [17]. These data show that V_{at} of W in bounded state moves toward higher values. The best agreement with our results was found in the case of the valence d-orbital radii in [17] (0.72 Fe, 0.86 Cr, 1.38 Mo, 1.47 W and 1.55 Ta (a.u.)), which increase exactly in the same order as our atomic volumes V_{at}. However it must be taken into account that there are several ways how to define radius for atoms. The further question is why such small atoms as Si provide a Laves phase with so relatively large V_{at}. In case of Si, although the atoms themselves are relatively small, covalent bonds can increase the average atomic volume quite a lot (cf. V_{at} = 138 a.u.^{3} in diamond structure). For metallic constituents, we may conclude that the effective atomic sizes (here valence d-orbital radii) play an important role in determining of the atomic volume of studied configurations.

We can also see that even the internal parameters describing positions of atoms in the unit cell depend
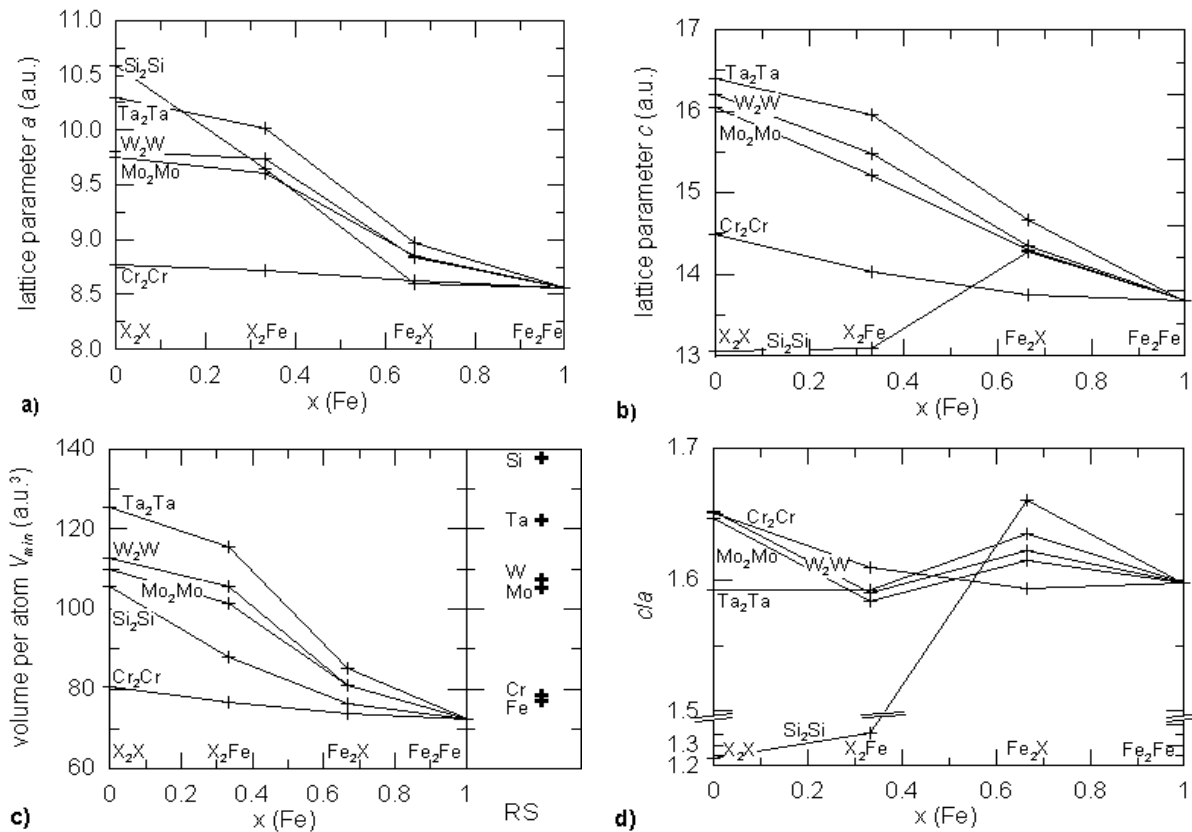
Figure 1. *Concentration dependence of the a, c, V_{at} and c/a for C14 Laves phases in Fe-X systems (X = Si, Cr, Mo, Ta, W). The right-hand side of Fig. 1(c) shows the atomic volumes in the reference-state structures of elemental constituents. Numerical values are given in Table 2.*

on the molar fraction of Fe in a regular way. (Fig. 2) The internal parameters 6h-x and 4f-z describe positions of atoms in 6h sublattice in direction of both x and y axes within the range of 0.8158-0.8301 and in 4f sublattice in the direction of the axis z in the interval 0.0230-0.0804, respectively. It is obvious that these parameters strongly depend on the composition of the structure. Except of Fe-Si system, the 6h-x parameter slightly increases with decreasing concentration of Fe atoms. The 4f-z parameter, on the other hand, reveals the opposite tendency in most cases. There are some exceptions from this trend in the Fe-Ta and Fe-Si system which may correspond to the irregularities in trends in c/a ratio (Fig.1(d)).
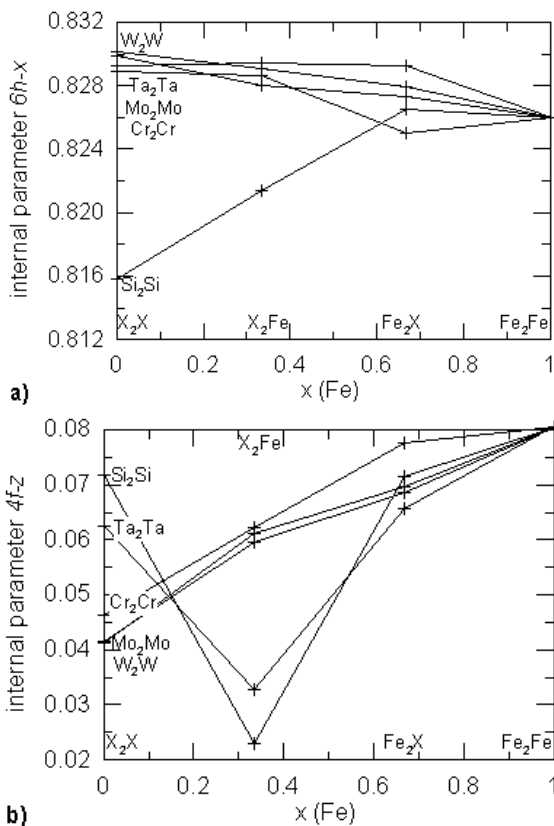
Figure 2. *Concentration dependence of the 6h-x and 4f-z internal parameter for C14 Laves phases in the Fe-X systems (X = Si, Cr, Mo, Ta, W).*

To study the distance in coordination spheres of atoms and kind of the Nearest Neighbours (NN), the values of the 6h-x and 4f-z parameters must be considered. In the case of sublattices in Laves phases studied, we found that the 1st NN atoms do not lie in the same distance from the central atom. They form some kind of shells whose widths are listed in Table 3.

The interplay of internal and lattice parameters can be seen in Figure 3 where the deviations from the trends observed earlier are not manifested and we get

Table 3. *The average 1st NN distances (r) and the widths of the 1st NN shells (w) for C14 Laves phases in the Fe-X systems (X = Si, Cr, Mo, Ta, W).*

Structure	r (a.u.)			w (a.u.)		
	2a	4f	6h	2a	4f	6h
No. of atoms in shell	12	16	12	12	16	12
Fe₂Fe	2.48	2.67	2.44	0.41	0.41	0.54
Fe₂Cr	2.50	2.68	2.46	0.41	0.36	0.52
Cr₂Fe	2.50	2.72	2.49	0.40	0.17	0.45
Cr₂Cr	2.53	2.76	2.54	0.34	0.50	0.54
Fe₂Mo	2.55	2.76	2.53	0.40	0.19	0.48
Mo₂Fe	2.75	2.98	2.73	0.46	0.22	0.50
Mo₂Mo	2.81	3.07	2.82	0.39	0.67	0.61
Fe₂Si	2.51	2.71	2.49	0.35	0.19	0.56
Si₂Fe	2.65	2.87	2.63	0.61	0.81	0.66
Si₂Si	2.88	3.05	2.82	0.78	0.92	0.61
Fe₂Ta	2.59	2.81	2.58	0.40	0.15	0.47
Ta₂Fe	2.85	3.12	2.87	0.44	0.84	0.63
Ta₂Ta	2.95	3.20	2.94	0.49	0.22	0.52
Fe₂W	2.55	2.76	2.53	0.40	0.18	0.49
W₂Fe	2.78	3.02	2.77	0.46	0.21	0.50
W₂W	2.83	3.09	2.84	0.39	0.70	0.60

smooth concentration dependencies of average 1st NN distances from central atom on composition.

We can draw the following conclusions concerning the 1st NN distances in various sublattices:

• In each configuration of C14 Laves phase, the 1st NN distance increases in series 6h, 2a and 4f except for the Ta₂Fe, Mo₂Mo and W₂W where the 2a sublattice reveals slightly lower average 1st NN distance than the 6h sublattice.

• The 2a sublattice has the Coordination Number (CN) 12 and the 1st NN consist of six 6h and six 4f atoms in all Laves phase configurations studied. The average distances between the central atom and the 1st NN atom reveal smooth dependence on Fe composition, see Figure 3(a). The width of the 1st NN shell ranges from 0.34 a.u. for Cr₂Cr to 0.78 a.u. for Si₂Si configuration.
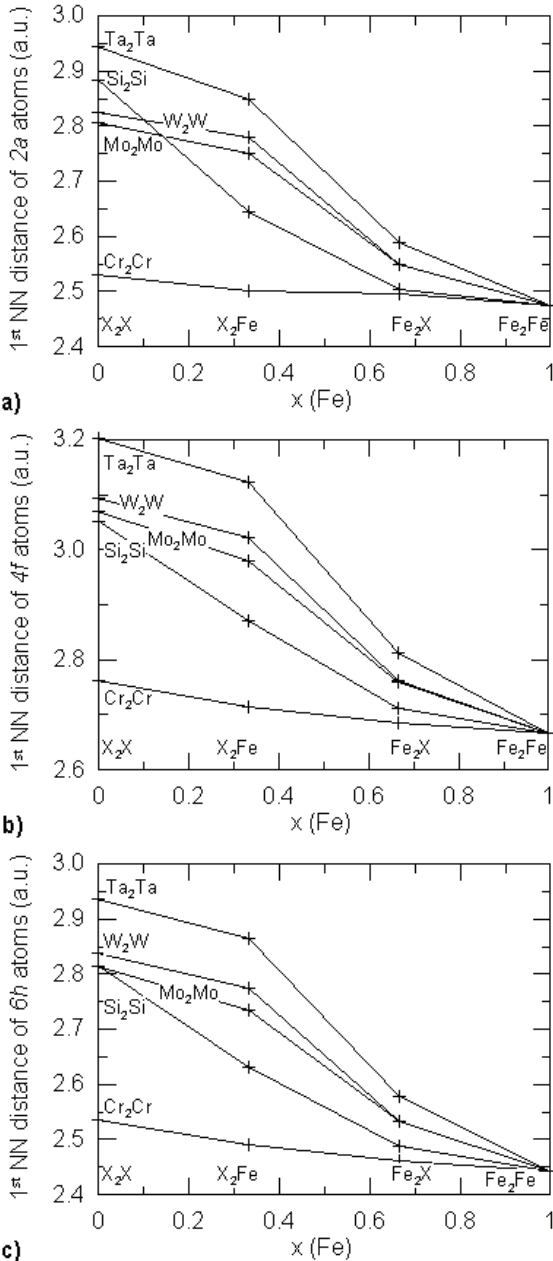
• The 1st NN coordination shell of the 6h sublattice (CN=12) consists of two 6h, two 2a, two 6h, four 4f and two 4f atoms (in the order of increasing distances) and it reveals only tiny changes in its arrangement in the C14 Laves phases studied. There is only some rearrangement between the furthest six (4+2) 4f atoms found in the Fe-rich configurations. On the other hand, the X-rich configurations prefer to arrange these six 4f atoms in the opposite order, i.e. in subgroups of 2 and 4 atoms. Let us note that there are some anomalies in Si₂Fe and Si₂Si:
- In Si₂Fe the couple of 4f atoms substitutes the

first two 6*h* atoms in the shell i.e. the number of 4*f*/6*h* atoms is increased/lowered here by two. This fact can be a consequence of the significant decrease in 4*f-z* parameter which causes that the atoms of the 4*f* sublattice become to be the nearest surrounding of the 6*h* atoms.

- Si₂Si reveals, on the other hand, a shift of the first two 6*h* nearest atoms to the farthest position of the coordination sphere.

However, even in spite of these rearrangements in

Figure 3. *Concentration dependences of the average 1ˢᵗ NN distances for the 2a, 4f and 6h sublattice for C14 Laves phases in the Fe-X systems (X = Si, Cr, Mo, Ta, W).*

the 1ˢᵗ NN coordination shell of the 6*h* sublattice we can still see a smooth dependence of the average 1ˢᵗ NN distances on composition (Fig. 3(c)). The width of the 1ˢᵗ NN shell ranges from 0.45 a.u. for Cr₂Fe to 0.66 a.u. for Si₂Fe configuration.

• The 4*f* sublattice (CN=16) reveals many rearrangements of the order of three 2*a*, six 6*h*, three 6*h*, three 4*f* and one 4*f* atom in the 1ˢᵗ NN coordination shell but there are no evident rules here. Again, the concentration dependences of the average NN distances are quite smooth.

Using ab initio methods, the values of bulk moduli of RS and Laves phases can be calculated and their values are listed in Tables 1 and 2. The composition dependence of bulk moduli is shown in Figure 4. It can be seen there that bulk moduli of Laves phases in all systems studied exhibit a strong composition dependence. The least influence of molar fraction of Fe can be found in Fe-Cr system which can be caused by similar size of atoms of these elements. Bulk moduli of both binary and pure constituent Laves phases also strongly depend on the kind of X component and their values decrease in the same order as in case of the RS, i.e. from W, Mo, Ta to Si, except for Fe-Cr system, which can be caused by magnetic ordering of Cr and Fe RS. The values of bulk moduli of pure element structures and of the Laves phases are very close in case of NM elements, i.e. bulk moduli of Mo, W, Si and Ta Laves phase are 89.3 %, 89.5 %, 98.9 % and 99.5 % of the RS value, respectively. On the other hand the bulk moduli of NM Cr and Fe Laves phase are much higher than those of magnetic RS (i.e. 128.0 % and 135.1 % of RS value, respectively).
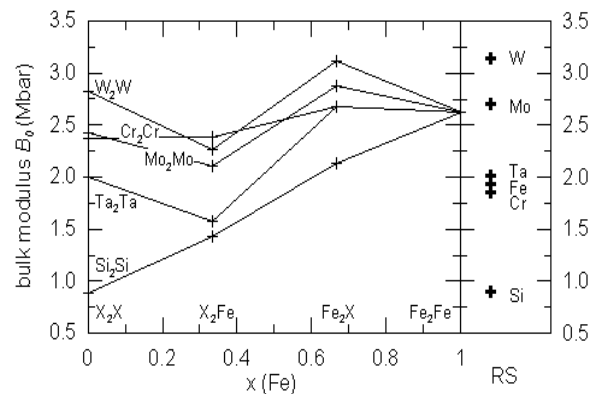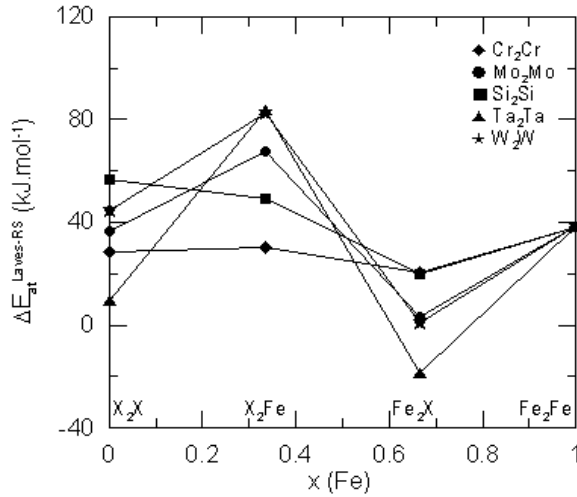

Figure 4. *Concentration dependence of the bulk modulus for C14 Laves phases in the Fe-X systems (X = Si, Cr, Mo, Ta, W).*

3.2 Energetics

Total energy of formation per atom may be obtained as

$$\Delta E_{at}^{\text{Laves}-\text{RS}} = E_{at}^{\text{Laves}} - (x_{\text{Fe}}E_{at}^{\text{RS}_{\text{Fe}}} + (1-x_{\text{Fe}})E_{at}^{\text{RS}_X})$$

where E_{at} stands for total energy per atom and x_{Fe} denotes the molar fraction of Fe.

Figure 5. *Concentration dependence of $\Delta E_{at}^{\text{Laves}-\text{RS}}$ for C14 Laves phases in the Fe-X systems (X = Si, Cr, Mo, Ta, W) (fully relaxed results).*

All equilibrium total energy differences $\Delta E_{at}^{\text{Laves}-\text{RS}}$ are summarised in Table 4 and Fig. 5 which shows that the only stable configuration is the Fe_2Ta one. But there are two other structures Fe_2W and Fe_2Mo which are only slightly unstable in comparison with the remaining configurations. These three structures revealing the highest tendencies to stability are the only ones among the Fe-X systems studied which

have been experimentally found.

The comparison in Table 4 shows that our calculated data for C14 Laves phase of elemental constituents are in perfect agreement with ab initio calculated data published in [18]. The agreement with experimental data is worse. This is given by the fact that experiments are not performed at 0 K temperature.

4. Conclusions

The purpose of this work was to understand, with the help of ab initio electronic structure calculations, the relations between the electronic structure, size of the atoms and the thermodynamic as well as structural properties of the C14 Laves phases. We demonstrate that the structure parameters and heats of formations strongly depend on the molar fraction of Fe atoms and that the calculated equilibrium parameters correspond very well to the experimental values. Analysis of our results shows that both geometric and electronic factors are important for stabilization of the C14 Laves phase in the iron-based systems.

Our ab initio electronic structure calculations reveal that the C14 Laves phase is unstable at zero temperature in both Fe-Mo and Fe-W system which is in contradiction with experiments. However, the absolute value of the total energy of formation is very low. We suppose that the instability at higher temperatures is suppressed by the entropy effects. But, on the other hand, some other C14 Laves phases (e.g. Fe_2Ta) are stable even at low temperatures. We have found that the phase stability related to the reference state is significantly influenced by occupations of sublattices.

Table 4. *Ab initio calculated total energies of formation $\Delta E_{at}^{\text{Laves}-\text{RS}}$ ($kJ.mol^{(-1)}$ of atoms) of various Laves phase configurations with respect to the weighted ratio of the RS compared with literature data.*

Elem. X	Fe₂X		X₂Fe	X₂X	
	VASP	Exp.	VASP	VASP	Calc.
Cr	20.22	- - -	30.10	28.63	27.8 [18]
Mo	3.19	-14.1 [19]	67.38	36.60	36.5 [18]
Si	19.91	- - -	48.92	56.52	53.6 [18][a]
Ta	-18.61	-6.3±1.9 [20] [b]	83.70	9.35	9.7 [18]
		-19.7 [21]			
		-19.25±2.79 [22]			
		-19.27 [23]			
W	0.68	-7.61±3.14 [24]	82.60	44.40	43.8 [18]
Fe	- - -	- - -	- - -	38.27	31.1 [18]

[a] *This value was obtained using the energy difference $E^{bcc} - E^{diamond} = 0.53\ eV = 51.1\ kJ/mol$ [25], as the value of energy of formation of Laves phase in Si obtained in Ref. [18] was related to bcc Si.*

[b] *The sample showed significant amount of second phases in X-ray diffraction analyses [20].*

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