

An ab-initio study of the effects and stability of vacancies, anti-sites and small radius atoms (B, C, N and O) in the B2-FeAl structure

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Keywords: Iron-aluminides, atomic and structural defects, electronic properties, ab initio calculations

Abstract. Atomistic modeling based on Density Functional Theory (DFT) within the framework of the Generalized Gradient Approximation (GGA) is used to show the effects of defects such as vacancy, boron, carbon, nitrogen and oxygen substituting Fe or Al atoms in the B2-FeAl structure. The site preference of each type of defect is determined from a comparison of total energy calculations using a supercell structure, consisting of 16-atoms, within which each the various defects are introduced. The changes in lattice parameter and bulk modulus associated to the presence of the defects in the FeAl matrix are also studied.

1. Introduction

B2-FeAl alloys are considered as potential candidates for medium and high temperature structural applications because they present excellent oxidation resistance, low densities, good mechanical properties at high temperatures, and low raw material cost [1-10]. It is well established that their properties are highly sensitive to the type and concentration of defects (for example thermal vacancies) as well as the deviation from the stoichiometry [11-16]. As for many intermetallic compounds, the application of these alloys at room temperature is however limited by their low ductility [11, 13]. Several theoretical and experimental works have demonstrated that the mechanical and embrittlement properties can be improved by small addition of carbon, boron, and 3d-4d transition metals elements [17-25]. For example, FeAl alloys present an intrinsic intergranular brittleness in their 'pure' state and change their fracture mode, when boron-doped, toward a less brittle fracture taking place in a transgranular manner [26-28]. It was also reported that the presence of carbon in these alloys may enhance the ductility by reducing the susceptibility of the alloy to the hydrogen embrittlement [29,30]. Considerable strengthening can also be achieved at room temperature if very fine carbides are distributed evenly in the FeAl matrix [20]. These improvements in strength are attributed to the solid solution strengthening of the interstitial carbon atoms at low concentrations and to the precipitation hardening at high concentrations of carbon atoms.

Unfortunately, there are few studies related to the role of structural defects on the electronic structures and atomic bonding in FeAl alloys, which should also help to give a better understanding of their behavior and mechanical properties. In particular, as these materials are sensitive to quench-in vacancies, the combination of small radius atoms (C, B, N, O) with vacancies has not been fully addressed and is of a particular interest. The attempt of the present work is to present a systematic study of the vacancies and atomic defect additions in the FeAl alloys from quantum mechanical calculations based on the Density Functional Theory (DFT). To this purpose, we have used the Full-Potential Linearized Augmented Plane Wave (FP-LAPW) method which is well known to enable accurate calculations within the supercell approach and has already been used for studying defects in the bulk as well as surfaces properties [31-33]. This approach authorizes a systematic study by comparing the site preference and anti-site configurations from total energy calculations.

The present paper consists of the following sections. Section II details the parameters of the calculations related to the FP-LAPW method. Section III discusses the changes in formation energies associated with different types of structural defects. Their effects on the lattice parameter and bulk modulus modifications are also determined. Finally, section IV gives a global summary with some concluding remarks.

2. Computational method

The present calculations are done within the framework of the density functional theory (DFT), according to which the many-body problem of interacting electrons and nuclei is mapped to a series of one-electron equations; the so-called Kohn–Sham (KS) equations [34, 35]. The self-consistent calculations for all structures were carried out using a scalar-relativistic version of the Full-Potential Linearized Plane Waves (FP-LAPW) method [36]. The Gradient Conjugate Approximation (GGA) of Perdew *et al* [37] (PBE) to the density-functional theory was taken to include the exchange-correlation energy to the total energy. Inside the muffin-tin spheres, the wavefunctions, electron charge densities, and potentials are expanded in terms of spherical harmonics, while for the interstitial region between the spheres plane-wave expansions are used. The core states were treated fully relativistically in the frozen core approximation. The muffin-tin radii were taken as 0.8464, 0.87285, 0.8993, 0.9257, 0.9522, and 1.1109 Å for B, C, N, O, Al, and Fe, respectively. The supercell structures used in the calculations were constructed from 16-atoms (8Fe, 8Al) of the B2-FeAl structure. The B2-structure is defined as the α -sublattice of Fe atoms and β -sublattice of Al atoms, like the cubic CsCl-structure (space-group symmetry is $Pm-3m$ (221)). The vacancy and X atom ($X=C, B, N$ and O) substitute the Fe or Al atoms (corner, center, and faces in the equivalent positions), with symmetry conservation to avoid large calculations. The four possible structural defects associated with the B2-FeAl structure itself (anti-sites and vacancies) studied here are given in Figs. 1(a)-(d). The case where a small radius atom X ($X = B, C, N, O$) is present in Fe or Al vacancy sites - thus substituting Fe or Al atoms - is shown in Figs. 1(e)-(f).

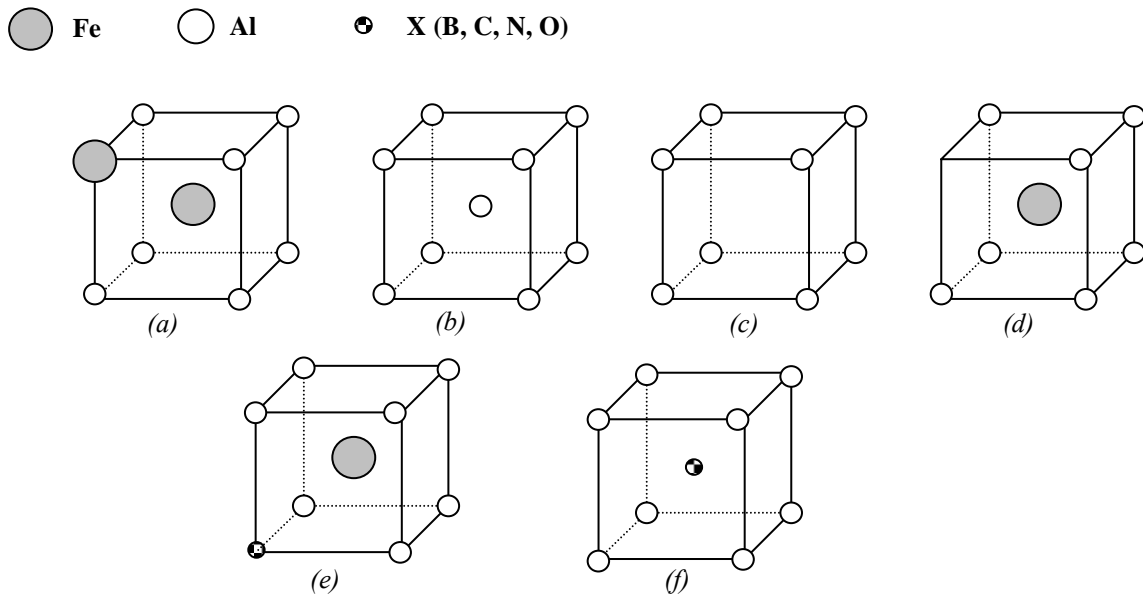


Fig. 1 (a) Al anti-site, (b) Fe anti-site, (c) vacancy in Al site, (d) vacancy in Fe site, (e) and (f) X atom ($X = B, C, N, O$) in Fe and Al site, respectively.

3. Results and discussion.

Simple, double, and triple vacancies. The energetics of vacancies are studied by calculating the heat of formation (per vacancy) of $A_{8-n}B_n$ systems with n vacancies (ΔH_A), assuming that a given system is in thermal equilibrium with Fe and Al crystals that act as reservoirs of Fe and Al atoms, respectively. The energy costs to successively replace n Fe or n Al atoms by n vacancies are calculated from the formation energy (per vacancy) needed to create n vacancies in the A_8B_8 systems. The resulting chemical reactions allow us to define (ΔH_A) and (ΔE_A) as follows:

$$\Delta H_A(n) = \frac{1}{n} [E(A_{8-n}B_8) - [(8-n)E(A) + 8E(B)]] \quad (1.a)$$

$$\Delta E_A(n) = \frac{1}{n} [E(A_{8-n}B_8) - E(A_8B_8)] + E(A). \quad (1.b)$$

Here, (A , B) are (Fe, Al) or (Al, Fe) atom-pairs, $E(A_{8-n}B_8)$, $E(A_8B_8)$, $E(A)$, and $E(B)$ are the total energy of the $B2-A_{8-n}B_8$, $B2-A_8B_8$, A and B systems, respectively. The heat of formation ΔH_A (Eq. 1.a) plotted in Fig. 2(a), which can also be regarded as the binding energy necessary to dissociate the supercells into individual atoms, is always negative. This means that formation of FeAl matrix from the *fcc*-Al and *bcc*-Fe crystals, with vacant sites in the Fe or Al sublattices, is preferred to phase separation. Fig. 2(a) also shows that the formation of vacancies in the Fe sublattices is more favorable than in the Al sublattices. However, it could be suspected that large vacancies (double and triple) in the Al sublattice are not favorable since the formation energy approaches positive values (phase separation). In order to obtain further information about the energetics of the vacancy formation, the variation of the formation energy ΔE_A (Eq. 1.b) as a function of the number of vacancies, n , is plotted in Fig. 2(b). This energy is more appropriate to study the energy cost needed to create n vacancies in the FeAl matrix. The reported values confirm that it is easier to create single, double, and triple vacancies in Fe sublattice than in Al sublattice, as found above for ΔH_A , suggesting that the vacancy concentration further increases with increasing Al content than with increasing Fe content; in good agreement with the experimental observations^{38, 39}. It is also interesting to note that single and triple vacancies in the Fe sublattice are more favorable than pair vacancies. Comparatively, in the case of the Al sublattice, ΔE_A decreases monotonically with the number of vacancies. In addition, it can be noticed that large concentration of vacancies in Al sublattice has smaller energy cost than for low concentration.

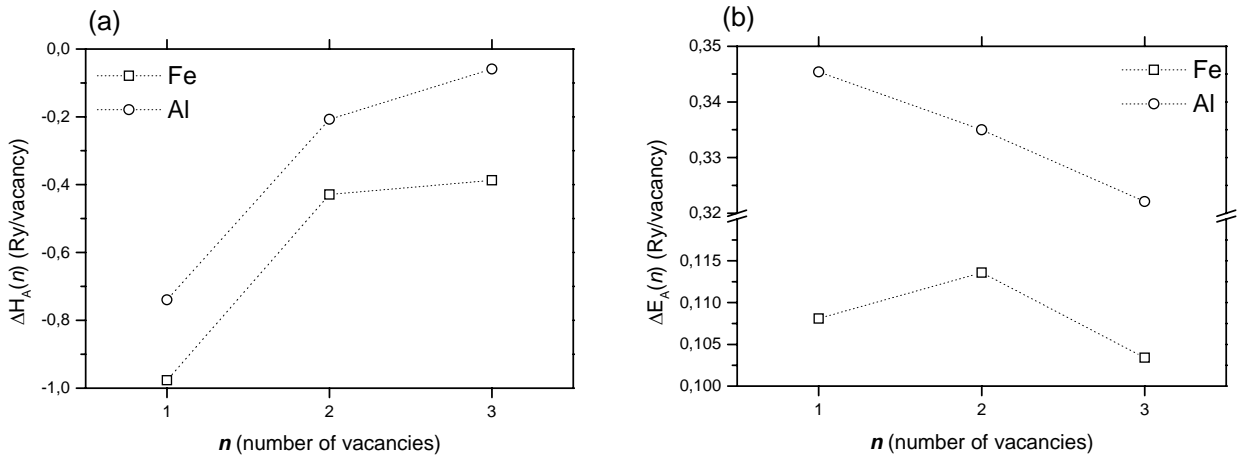


Fig. 2 (a) Enthalpy of formation of vacancies (Eq. 1) and (b) Formation energy as (Eq. 2)

Consequently, from these results and taking into account the fact that the calculated vacancy formation enthalpies for the Al sublattices are higher than that for the Fe in Fe₃Al and FeAl alloys⁴⁰, we may conclude that thermal vacancies do prefer the Fe sublattices than Al ones.

Anti-site of Fe and Al in FeAl matrix. In order to review the anti-site preference in the FeAl matrix, the heat of formation per atom is given as follows :

$$\Delta H_{Fe}(n, Al) = \frac{1}{n} [E(Fe_{8+n}Al_{8-n}) - [(8+n)E(Fe) + (8-n)E(Al)]] \quad (2.a)$$

$$\Delta H_{Al}(n, Al) = \frac{1}{n} [E(Fe_{8-n}Al_{8+n}) - [(8-n)E(Fe) + (8+n)E(Al)]] \quad (2.b)$$

In these equations, $E(Fe_{8+n}Al_{8-n})$ and $E(Fe_{8-n}Al_{8+n})$ are the total energies of the $Fe_{8+n}Al_{8-n}$ and $Fe_{8-n}Al_{8+n}$ systems, respectively. The heat of formation per atom is plotted in Fig. 3(a) as a function of the number of anti-sites n . It is characterized by comparable values for both Fe and Al anti-sites. While the heats of formation for one anti-site (either Fe or Al) and FeAl without defects are fairly close, there is a large gap in energy for forming multiple anti-sites. This suggests that alloys with small variation in stoichiometry around FeAl are quite stable. Further information can also be obtained from the formation energy defined as :

$$\Delta E_{Fe}(n, Al) = \frac{1}{n} [E(Fe_{8+n}Al_{8-n}) - E(Fe_8Al_8)] + [E(Al) - E(Fe)] \quad (3.a)$$

$$\Delta E_{Al}(n, Fe) = \frac{1}{n} [E(Fe_{8-n}Al_{8+n}) - E(Fe_8Al_8)] + [E(Fe) - E(Al)] \quad (3.b)$$

Here, $\Delta E_{Fe}(n, Al)$ ($\Delta E_{Al}(n, Fe)$) is the energy per atom needed to create n anti-sites of Fe (Al) in Al (Fe) sublattice. Fig. 3(b) shows the evolution of ΔE (Eq. 3.a and Eq. 3.b) with the number of anti-sites. A single Fe anti-site has a lower energy cost than an Al anti-site. This indicates that Fe-rich alloys are more stable than Al-rich alloys, as confirmed by the binary phase diagram. In contrast, two and three Al anti-sites are more favorable than two and three Fe anti-sites. These results also allow us to better understand the nature of triple defect in FeAl alloys by taking into account the favorable formation of both thermal vacancies in Fe sublattices (see Sec. 3.1) and Fe antisite (this section).

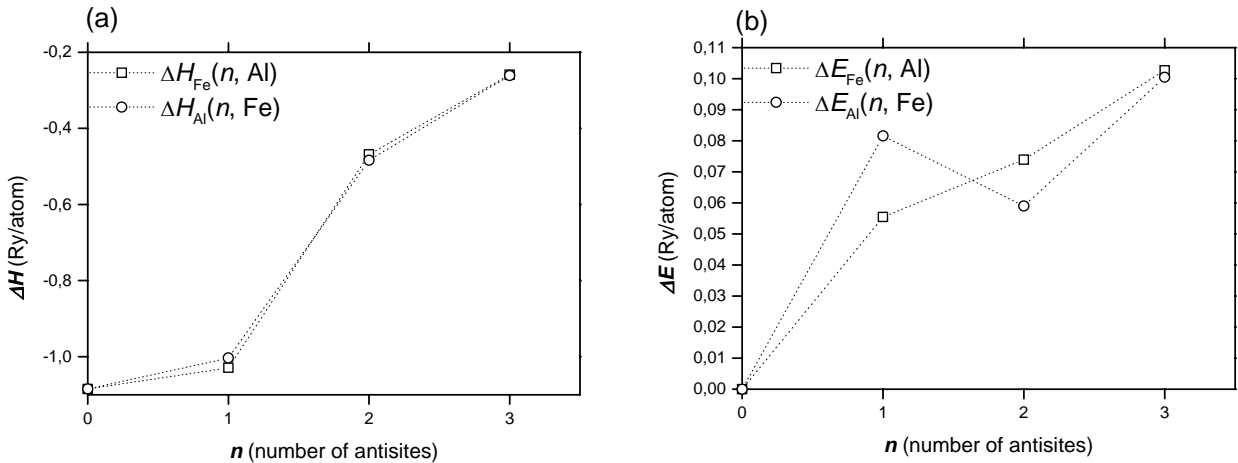


Fig. 3 (a) Enthalpy of formation of anti-sites and (b) Formation energy.

According to these two types of defects, a triple defect can be potentially created as: (i) one vacant site on Fe and two Fe anti-sites (1 ν , 2Fe), (ii) two vacant sites in Fe and one anti-site (2 ν , 1Fe). It is established from experiments that the triple defect actually consists of an Fe atom on an Al site and two vacancies, each on Fe sites [38]. In order to confirm if this triple defect is stable from an energetic point of view in FeAl matrix, the following difference in energy formation is calculated:

$$\Delta E = \Delta E(\nu, 2Fe) - \Delta E(2\nu, 1Fe) = \frac{1}{2}[Fe_7Al_8 + Fe_{10}Al_6 - Fe_6Al_8 - Fe_9Al_7] + \frac{1}{2}[E(Al) - 2E(Fe)]. \quad (4)$$

In this equation, $\Delta E(\nu, 2Fe)$ and $\Delta E(2\nu, 1Fe)$ are the formation energies of one vacancy and two Fe anti-sites and two vacancies and one Fe anti-site, respectively. The calculated value is positive at about $\sim +0.89$ Ry. This again confirms that the triple defect (two Fe vacancies with one Fe anti-sites) is energetically favored and not associated to any other side effect.

X atoms (X = B, C, N, O) in Fe and Al sublattices. Concerning the site preference of X defects (X=B, C, N, O) in the FeAl matrix, the energy difference between the energies needed to create a defect in the Fe sublattice and Al sublattice (Eq.5) is proposed and given by the following formula:

$$\Delta E(pref) = [E(Fe_7Al_8X) - E(Fe_8Al_7X)] + [E(Fe) - E(Al)]. \quad (5)$$

Here, the $E(Fe_7Al_8X)$, $E(Fe_8Al_7X)$, $E(Fe)$, and $E(Al)$ are the total energies of the Fe_7Al_8X , Fe_8Al_7X , *bcc*-Fe, and *fcc*-Al systems, respectively. A negative value means that the X defect prefer to be located in a Fe site, whereas a positive value mean that the X defect prefers an Al site.

The obtained results for ΔE_{pref} are summarized in the last column of Table 1. It is found that one vacancy, C, N and O prefer to be localized in the Fe sites whereas the probability of finding B in Fe and Al sites is fairly similar. It is also interesting to note that O has a higher probability than C and N.

The stability of structural defects can also be estimated by comparing the number of the electronic states at the Fermi level. Indeed, in many cases and in particular for aluminum intermetallics, it is accepted that a large peak near the Fermi level indicates that the considered structure is unstable [41, 42]. Calculations of total densities of states (DOS) at the Fermi level ($N(E_F)$) for the FeAl structure and the different defects have been carried out and reported in the first two columns of Table1.

Table 1

	$N(E_F)$ [states/Ry]		ΔE_{pref} [Ry]
B2-FeAl	39.74 (31.1 [43]) (39.4 [44])		
Type of defect	Fe site	Al site	
Vacancy	42.32	54.85	-0.237
B atom	31.05	40.13	+0.000
C atom	38.08	38.47	-0.058
N atom	25.12	57.84	-0.154
O atom	29.82	43.59	-0.185

Table 1 Number of states at the Fermi level ($N(E_F)$) for various defects on Fe and Al sites. ΔE_{pref} characterises the site preference (negative values mean that the defect prefers Fe sites to Al ones).

The value obtained for the B2-FeAl structure without defects is 39.74 states/Ry. This value is slightly higher than the experimental value [43] and is very much consistent with the reported Tight-Binding value taken from [44]. Except for the case of C where substitution for Fe or Al leads to very similar values, the $N(E_F)$ values are always higher when defects are present in Al site. This confirms that single small radius atom defects tend to reside in the Fe sites when compared to the Al ones.

Compared to FeAl, the obtained values for vacancy or N substituting Al are very high indicating low probability of presence in Al sites. This is consistent with the large value of energy difference (ΔE_{pref}) given in for vacancy and N in Table 1. In contrast the presence of N in Fe site has a high probability. For the case B and C, the complementary information obtained from both the energetics calculations and the electronic properties is needed to elucidate the stability and the site preference for the defects in FeAl. Indeed, for the case of B, the difference in energy between the Fe and Al sites is extremely small ($\Delta E_{pref} = 0$), suggesting no significant preference for one site or the other. The values of the $N(E_F)$ reported in Table 1 indicates that B is more favorable in Fe site than in Al one. For the C atom, the $N(E_F)$ are very close but the ΔE_{pref} calculations show that the presence of C in Fe site is more favorable. Finally, the reported values of $N(E_F)$ for O show again that O prefers to be in Fe sites in agreement with the calculated preference energy.

Lattice parameters and bulk modulus. The effect of the selected defects for the different site occupancies on the lattice parameters is shown in Fig. 4(a). The general trend is that the atomic defects (B, C, N, and O) and vacancy induce a contraction of the FeAl crystallographic cell. Fig. 4 also shows that, although the probability of their presence is less likely on Al sites, defects residing in Al site have more effect on the lattice parameter than when they are present in Fe sites. For Al substitution, the results indicate that the C atomic defect, followed by B, has induced the lowest lattice parameter. The highest lattice parameter is obtained for O substituting Fe site. A very interesting result shown in Fig. 4(a) is the fact that the volume of the FeAl cell is decreased more when atomic defects like B, C, and N are present on Al or Fe vacancies than in the case of vacancies only. It is also visible from Fig. 4(a) that the shrinking in volume is more pronounced for C and B defects than for N. This indicates that the presence of these atomic defects in vacant site generates an attractive potential energy which leads to more compact structures. This effect should increase the rigidity of FeAl alloys when B- or C-doped. To confirm this possibility, bulk modulus calculations have been carried out. The determined values are reported in Fig 4(b). It can be seen that all atomic defects present in the Fe or in the Al sites increase the bulk modulus of the FeAl alloy.

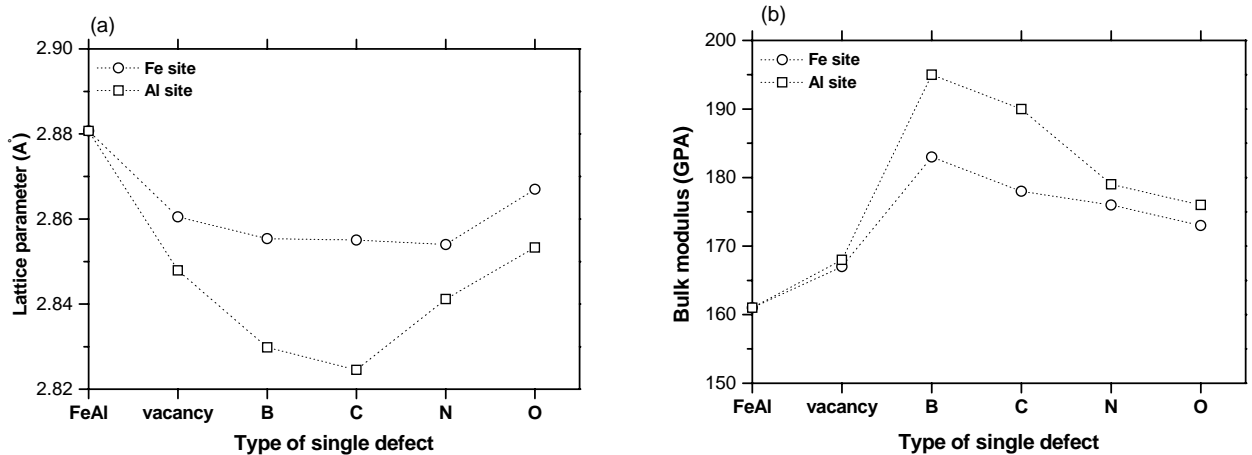


Fig. 4 Evolution of the (a) lattice parameter and (b) bulk moduli as a function of the nature of the structural defects present in FeAl.

The calculations also confirm that the addition of small radius atom in vacancy sites has more potential than single vacancies alone for hardening the FeAl matrix. The effect of B atom, followed by C, in both Al and Fe sites has the highest potential to enhance the compressibility of FeAl. Comparatively, the presences of N and O atomic defects have smaller effects on the bulk modulus.

4. Summary

The FeAl B2-structure is known to be highly sensitive to the presence of both vacancies and small radius atoms such as B, C, N and O. The aim of the present work was to gain new insights on the stability of structural defects associated to their presence and determine their effects (lattice parameter and bulk modulus modifications) on the FeAl structure properties. To this end, a systematic and comparative atomistic modeling study has been carried out using a supercell structure consisting of 16 atoms within which various defects were introduced successively. The site preference and stability were determined from the energetics and the electronic states at the Fermi level. The major results can be summarized as follows:

1. Vacancies prefer to reside in the Fe than in the Al sublattice. The Fe sublattice favors single and triple vacancies creation than double vacancies.
2. The triple defect in FeAl is predicted as one anti-site Fe and two vacancies in Fe sites.
3. B, C, N and O atoms prefer to reside in Fe site than in Al ones. The additions of B, C, N, and OFe defects increases the cohesion of the FeAl alloys, whereas the presence of O in Al site decreases the stability of FeAl alloys.
4. Although their presence is statistically less likely in Al sites than in Fe ones, structural defects (vacancies and small atoms) in Al sites would be more effective in modifying the lattice parameter and bulk modulus values.
5. The presence of atomic defects (B, C, N, and O) and single vacancy induce a contraction of the FeAl crystallographic cell. The highest lattice parameter is obtained for O substituting Fe site. The volume of the FeAl cell is decreased more when atomic defects like B and C are present than in the case of vacancies only.
6. The addition of small radius atom in vacancy sites has more potential than single vacancies alone for hardening the FeAl matrix. The effect of the B atom, followed by C, has the highest potential to enhance the compressibility of FeAl while, comparatively, the presence of N or O atomic defects has smaller effects on the bulk modulus.

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