



Point defects and diffusion in ordered alloys: An ab initio study of the effect of vibrations



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ABSTRACT

We present a detailed investigation of the influence of atomic vibrations on the point defect and diffusion properties of ordered metallic alloys, by means of ab initio calculations with density-functional theory. Considering the case of Ni₂Al₃ which provides a rich panel of defect-related properties, our study reveals that the behaviour of this compound is largely monitored by self-interstitials, whereas such defects are usually ignored in metallic compounds. The vibration free energies are obtained for the full set of point defects of Ni₂Al₃, showing that these quantities are strongly defect-dependent, and significantly modify the free energy of the compound in an intricate composition-dependent manner. The second key-issue is the first ab initio full analysis of attempt frequencies, via the coupling of vibration analysis and saddle-point search for significant atomic jumps. This analysis indicates that attempt frequencies range over several orders of magnitude and exponentially increase with migration energies. We show the importance of these factors in reaching realistic composition-dependent diffusion coefficients.

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1. Introduction

The role of ordered metallic compounds in the elaboration processes of many complex materials is currently being realized with enhanced acuteness in materials science. Improving our knowledge of the fundamental properties of these compounds is therefore of primary importance, in order to understand the mechanisms underlying the formation of various phases and microstructures. The most efficient way to this aim is offered by atomic-scale investigations, but the difficulties inherent to experimental measurements at this scale turn theoretical approaches into valuable tools. The cornerstone of such tools being the design of reliable energy models, able to support thermodynamic and kinetic further developments, the best-known class of modelling is provided by cluster expansion (CE) methods, which allow a refined description of alloy energetics on wide composition ranges including various ordered structures. However, whereas CEs are relevant, in principle, for handling many situations (e.g. presence of interstitials and vacancies, complex crystallographies...), tractability

limits have often restricted their practical applications to vacancy-free substitutional disorders and higher symmetries. Conversely, experimental processes frequently imply ordered alloys with variously complex structures, including many so-called complex metallic alloys (CMAs) with giant unit cells, which highlights the interest of resorting, for these issues, to alternative modellings. The best one is based on point defects (PDs) within the independent point defect approximation (IPDA), an approach that presents noteworthy advantages, such as extensions towards diffusion properties, of high importance due to the intricate role of ordered compounds in solid-state processes. In particular, the recent interest for CMAs gave rise to IPDA applications in various cases of increasing complexity [1–4], and a general IPDA formulation applicable to arbitrary compounds was recently proposed [5].

In this context, the rapidly growing possibilities, during the last two decades, of ab initio simulations now allow to take into account accurately various physical phenomena that had been hitherto overlooked for feasibility reasons, allowing ab initio calculations of diffusion coefficients in solid solutions [6] and ordered compounds [7]. In particular, the role of vibration free energies should be paid special attention, since some early studies [8] exploring this issue in Ni–Al by means of empirical energy models [9]. Considering ab initio methods, a few works have pointed out the possible importance of vibrations, first in selected Al–Cu ordered compounds [10],

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and later in dilute Fe–Cu solid solutions [11]. The effect of lattice vibrations was also accounted for in a CE framework [12], in order to investigate the phase diagram of cubic BNC system. By contrast, ab initio investigations of PDs including atomic vibrations have almost never been carried out in non-stoichiometric ordered compounds, the only exception being a recent study of $Mg_{17}Al_{12}$, which reached the conclusion that vibrations should not have any significant influence [13]. Conversely, a work [14] concerned with this topic in $NiAl_3$ with cementite-type DO_{11} structure, led to conclude that vibrations do indeed modify significantly the properties. The interest of the issue was raised further by the fact that vibrations directly influence atomic diffusion, not only through the PD properties, but also via the attempt frequencies for atomic jumps, and EAM investigations of $NiAl_3$ [15] pointed out that attempt frequencies may be drastically dependent on the type of PD involved in the jump, in contrast with widespread assumptions underlying atomic-scale kinetic simulations. However, the limited reliability of EAM energy models left some doubt, and the question subsists to which extent these conclusions are really representative of ordered metallic compounds.

As a step towards elucidating these issues, the choice of the Al–Ni system is especially relevant, since, despite its utmost practical interest, this system remains largely unexplored as regards its ordered phases. Whereas Ni-rich phases with simple B2 and L_{12} structures have formed the subject of extensive works, more complicated Al-rich compounds are still overlooked in the literature. Nevertheless, these Al-rich Al–Ni intermetallics are known to form transiently in many complex situations that characterize current highly non equilibrium processes, for instance in syntheses involving reactive powders or as metastable compounds produced by severe thermomechanical treatments [16], and Ni_2Al_3 has been recently used as coating for high-temperature corrosion barriers in titanium alloys [17] or steels [18]. This emphasizes that better insight into the mechanisms underlying these complex processes depends on our knowledge of PD-mediated diffusion in relevant ordered compounds, among which Ni_2Al_3 will constitute our centre of interest below. As a key-issue, we will focus on the influence of vibrations on this ordered alloy, through detailed treatments of (i) PD properties and (ii) jump attempt frequencies. Combining these points with the energy barriers associated with the various atomic jumps will provide an ab initio-based picture of the influence of temperature and composition on the atomic diffusion in this compound.

2. Methods

Ni_2Al_3 is an ordered compound (D_{519} hexagonal structure, P-3m1 space group, five-atom unit cell, Fig. 1) with three sublattices, two occupied by aluminium Al_{1a} and Al_{2d} and one occupied by Ni,

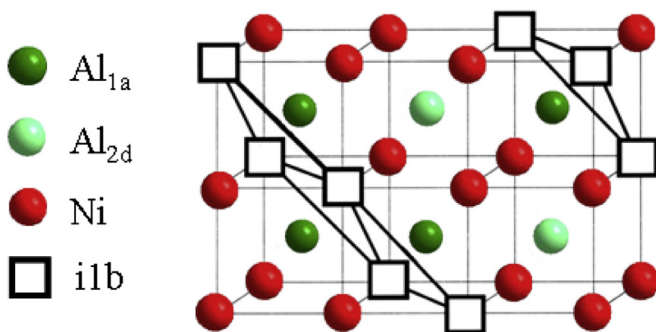


Fig. 1. Unit cell of Ni_2Al_3 with D_{519} structure, showing the three occupied sublattices as well as the interstitial one (i1b), in relation with the parent B2 structure.

each being possibly subject to the formation of vacancies ($V_{Al_{1a}}$, $V_{Al_{2d}}$, V_{Ni}) or antisite defects ($Ni_{Al_{1a}}$, $Ni_{Al_{2d}}$, Al_{Ni}). Moreover, as suggested by previous works [19], an additional 1b sublattice should be considered as possible location of interstitial defects, leading to a total number of 8 defects distributed on 4 sublattices. As indicated on Fig. 1, the relevance of i1b sites stems from the fact that the D_{519} structure can be regarded as a B2 structure where one third of the (111) planes of Ni are missing. The i1b sublattice exactly corresponds to these vacancy planes.

In this work, all ab initio calculations were performed using the VASP software [20,21], implementing density-functional theory with plane waves and ultrasoft pseudopotentials. Values of 360 eV energy cutoff for plane waves and $5 \times 5 \times 5$ k-mesh of the Brillouin zone were found to ensure sufficient convergence (<1 meV/atom) for all results, and PD energetics was investigated on $2 \times 2 \times 2$ Ni_2Al_3 unit cells, this size leading to reasonably accurate defect energies, as confirmed by tests with $3 \times 3 \times 3$ unit cells. For purpose of completeness, the PD study was initially conducted in LDA as well as GGA (Perdew–Wang form [22]) frameworks. Considering the formation energy and hexagonal lattice parameters of the perfect compound, the validity of both descriptions is shown from comparison with experiments (Table 1). The main part of the work (effect of vibrations, transition profiles) was carried out using GGA, which provides a slightly better agreement than LDA with the measured values.

The approach of independent PDs, underlying the present work, has already been described previously, firstly for binary cubic two-sublattice compounds [1], and then in more general situations [5]. This method, which remains the only tractable one for complex crystallographies, was used throughout this work, within the grand canonical (GC) formalism [2] which can be extended to include the effect of vibrations, as briefly recalled now. F_{ud} being the free energy of the reference, undefected system and $F(d)$ that for a single PD of type d , the key-quantities to be determined are the point defect GC free energies $F_{GC}(d) = F(d) - F_{ud}$, which can be decomposed as:

$$F_{GC} = E_{GC}^0 + F_{GC}^{vib}(T) \quad (1)$$

with E_{GC}^0 the ground-state energy, and the T -dependent vibration contribution given by:

$$F_{GC}^{vib} = E_{GC}^{vib}(T) - TS_{GC}^{vib}(T) \quad (2)$$

The ab initio determination of vibration free energies of point defects in ordered compounds (F_{GC}^{vib} term in Equation (1)) is still far from being an easy task. In fact, few works have tackled the question of investigating the effect of vibrations on alloy free energies, a deficiency mainly due to the requirement of obtaining a wide panel of force constants. Considering this issue for an ordered compound with a complex PD structure is thus an originality of the present work. To this aim, we used the “frozen phonon” method within the harmonic approximation, applying a full panel of finite displacements to the atoms of each system, either perfect or defected. Moreover, following previous conclusions pointing out the importance of careful convergence [24], we have checked that for a cutoff equal to 4 Å, the accuracy on GC free energies of PDs is roughly

Table 1

Experimental and calculated formation energies (eV/atom) and lattice parameters (Å) of Ni_2Al_3 .

	LDA	GGA	Exp.
Lattice parameters a;c	3.97;4.82	4.05;4.91	4.04;4.90
Formation energy	−0.67	−0.65	−0.61 [23]

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