Available online at www.sciencedirect.com
SCIENCE DIRECT®
Scripta Materialia 54 (2006) 1271–1276
Scripta MATERIALIA
www.actamat-journals.com

Ab initio calculation of the bcc Fe–Al phase diagram including magnetic interactions

Pablo Guillermo Gonzales-Ormeño [a,b,c], Helena Maria Petrilli [b], Cláudio Geraldo Schön [c,*]

[a] Facultad de Ciencias Naturales y Matemática, Universidad Nacional Federico Villarreal, Calle San Marcos 351, Pueblo Libre, Lima, Peru
[b] Departamento de Física dos Materiais e Mecânica, Instituto de Física da Universidade de São Paulo, CP 66318, CEP 05315-970 São Paulo-SP, Brazil
[c] Computational Materials Science Lab., Departamento de Engenharia Metalúrgica e de Materiais, Escola Politécnica da Universidade de São Paulo, Av. Prof. Mello Moraes, 2463, CEP 05508-900 São Paulo-SP, Brazil

Received 7 October 2005; received in revised form 6 December 2005; accepted 14 December 2005
Available online 19 January 2006

Abstract

The metastable phase diagram of the body-centered cubic-based ordering equilibria in the Fe–Al system has been calculated by the cluster expansion method, through the combination of the full potential-linear augmented plane wave and cluster variation methods. The results are discussed with reference to the effect of including the spin polarizations of Fe in the thermodynamic model.

Keywords: Intermetallic phases—iron aluminides; Ab initio electron theory; Full-potential, linear-augmented plane wave method (FP-LAPW); Cluster variation method; Magnetic interactions

---

1. Introduction

The iron-rich side of the Fe–Al system (up to 50 at.% Al) is dominated by a large stability field of the body-centered cubic (bcc) phase and its superlattices with B2 (CsCl-type) and $D0_3$ (BiF_3-type) structures [1]. This phase diagram topology is found with some additional complexities also in the Fe–Si, Fe–Ge and Fe–Ga systems, [1] as well as in several other binary and ternary systems (see e.g. Villars and Calvert [2]). It can be easily reproduced by the Ising model by setting an attractive interaction between dissimilar atoms for nearest and next-nearest neighbors pairs in the bcc lattice [3–6]. This made the Fe–Al system a natural choice as a prototype system to study ordering reactions in the bcc lattice, which has been done either experimentally [7,8] or theoretically [9–15]. It is, thus, surprising that no ab initio calculation of the bcc Fe–Al phase diagram has yet been published (at least to the knowledge of the authors).

In fact, several papers deal with ab initio calculations in Fe–Al alloys, e.g. in defect properties [16–19] or magnetism (see Ref. [20] and references therein). The reason for the lack of a published ab initio phase diagram lies, probably, in the controversial nature of the results concerning the magnetism of Fe–Al alloys in the frame of the present implementations of the density functional theory (DFT) [20–22]. In a previous work, however, the present authors demonstrated that, in spite of this controversy, the ab initio formation energies of the B2-FeAl and $D0_3$-Fe_3Al compounds based on full potential-linear augmented plane wave (FP-LAPW) [23] calculations agree quite well with experimental values taken from the literature using different experimental techniques, provided the ab initio calculations include spin polarization [24]. The aim of the present work is to present the implications of these findings for the calculation of the corresponding phase diagrams using the cluster variation method (CVM) [25]. The calculations will be presented only for the case in which the spin-polarized formation energies are used as input parameters for the

---

[*] Corresponding author. Tel.: +55 11 3091 5726; fax: +55 11 3091 5243.
E-mail addresses: hmpetril@macbeth.if.usp.br (H.M. Petrilli), schoen@usp.br (C.G. Schön).

1359-6462/$ - see front matter © 2006 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2005.12.024

CVM model. This will be also presented in two versions: without considering the spin degrees-of-freedom of iron in the thermodynamic model, as is usual in similar calculations [26] or, explicitly including these degrees-of-freedom in the thermodynamic model. These will be referred to as non-magnetic or magnetic modes, respectively. To our knowledge, this is the first time that such magnetic mode calculations have been performed in the context of ab initio phase diagram determination.

2. Methods

The procedure used for the Fe–Al phase diagram calculation is based on the so-called cluster expansion method [27]. It consists of the calculation of the total energies at the ground state ($T = 0$ K) of a set of stoichiometric ordered compounds (which are related to a common disordered lattice) by solving one particle's Schrödinger's equations. This set forms a basis for the truncated expansion of the internal energy of the lattice at all temperatures and compositions, which may then be used as input in a statistical mechanics method to calculate the phase diagram. The set used in the present work is formed by the A2-Al, A2-Fe, D0$_3$-Fe$_3$Al, D0$_3$-Al$_3$Fe, B2-FeAl and B32-FeAl compounds. The basis set is kept limited here on purpose since only a simplified thermodynamic description of the system based on the irregular tetrahedron approximation of the CVM is targeted and there is no necessity, therefore, to converge the cluster expansion, in the sense discussed by van de Walle and Ceder [28].

The total energies of the ordered compounds have been calculated using the FP-LAPW method as embodied in the WIEN97 code [23]. The FP-LAPW method is developed in the framework of the DFT and allows the computation of very precise total energies and charge densities in metallic compounds due to its full potential feature and is, at the moment, one of the most accurate methods for electronic structure ab initio calculations in solids. In the present work the generalized gradient approximation (GGA) [29] has been adopted to perform spin-polarized ab initio calculations (as the system is known to be magnetic). The equilibrium lattice constants at the ground states have been optimized through the calculation of the minimum value of the total energy. The optimization of static lattice relaxations is not necessary in the present case, since the six compounds investigated here are symmetric (i.e. there are no internal site position variables in their crystallographic models). Details of the total energy calculation have been published in a previous work by the present authors [24] and will not be reproduced here.

The formation energies per mole of atoms of the four compounds, $\Delta^f U^{\Phi}_{\mathrm{Fe}_x\mathrm{Al}_y}$, with $\Phi = \mathrm{B2}$, B32 or D0$_3$ and Fe$_x$Al$_y$ stoichiometry, are used as input parameters in the statistical mechanics formalism (CVM) adopted for the calculation of the phase diagram. The CVM is based on the concept of a "basic cluster": a geometric figure contained in the reference lattice which represents the maximum correlation length explicitly considered in the approximation. In the present work, the irregular tetrahedron (IT) cluster approximation for the bcc lattice has been employed (see Fig. 1). The CVM formalism in the IT cluster approximation has been throughly outlined in several previous publications by one of the present authors (see e.g. Ref. [30]) and this shall not be reproduced here. For the sake of completeness only details of the magnetic mode calculation and the procedure for obtaining the respective interaction parameters of the model will be briefly described.

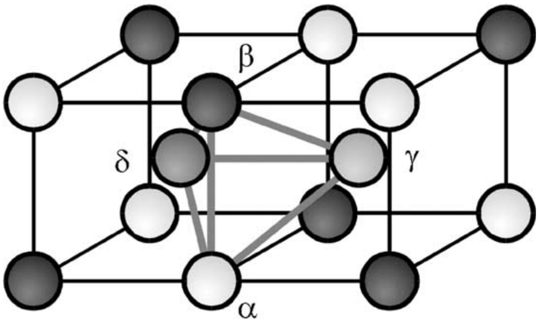

Fig. 1. The irregular tetrahedron (IT) cluster in the bcc lattice.

The internal energy (U) of a bcc lattice with N sites (containing $6N$ irregular tetrahedra) is written as [11]

$$U = 6N \sum_{i,j,k,l=\mathrm{Fe,Al}} \varepsilon^{\alpha\beta\gamma\delta}_{ijkl}\, \rho^{\alpha\beta\gamma\delta}_{ijkl} \tag{1}$$

In this expression, $\rho^{\alpha\beta\gamma\delta}_{ijkl}$ represents the probability of finding an $\{\alpha\beta\gamma\delta\}$ IT cluster with a configuration $\{ijkl\}$ (i.e. species i occupying cluster position α, j in cluster position β and so on) among the $6N$ tetrahedra of the system and $\varepsilon^{\alpha\beta\gamma\delta}_{ijkl}$ represents the eigen-energy associated with this configuration.

In the non-magnetic mode calculation the variables i, j, k, l are directly associated with the two components of the alloy (Fe or Al). In the magnetic mode calculation, however, iron atoms will be modeled as spin $s = 1$ particles, according to the experimental value of saturation magnetic moment of pure iron, $2.22\mu_{\mathrm{B}}$ [31]. The magnetic mode calculations, therefore, are in fact calculations in the quaternary Fe$^+$–Fe^0–Fe$^-$–Al system, where the three species of iron atoms correspond to the cases where the spin projection along the z-axis take values $s_i = +\mu_{\mathrm{B}}$, 0 or $-\mu_{\mathrm{B}}$ (+1, 0 and −1), respectively. In order to stress the distinction between species and components in the magnetic mode calculation, it is necessary to introduce a prime in the index to designate the latter, i.e., indices $i = 1$, 2 and 3 refer to iron ($i' = \mathrm{Fe}$, with spin orientations $s_i = +1$, 0 and −1, respectively), index $i = 4$, on the other hand, refers to aluminum ($i' = \mathrm{Al}$ and $s_i = 0$). This notation will be used even in the non-magnetic mode calculations, for the sake of compatibility.

The configuration eigen-energies are rewritten as

$$\varepsilon^{\alpha\beta\gamma\delta}_{i,j,k,l} = \left(\varepsilon^{\alpha\beta\gamma\delta}_{i,j,k,l}\right)_{\mathrm{chem}} + \left(\varepsilon^{\alpha\beta\gamma\delta}_{i,j,k,l}\right)_{\mathrm{mag}} \tag{2}$$