Phase stability and magnetic properties of B2 and L10 PtMn1-xFeX alloys: a cluster expansion and ab initio approach

Ramogoho Diale1*, Phuti Ngoepe2, Joseph Moema1, Maje Phasha1 and Hasani Chauke2

1Advanced Materials Division, MINTEK, South Africa
2Materials Modelling Centre, University of Limpopo, South Africa

Abstract. MnPt-based alloys are promising new materials for magnetic recording and spintronic applications due to their interesting magnetic properties. The underlying thermodynamic properties are still unclear, despite numerous efforts to improve ferromagnetic stability through alloying. In this work, the phase stability of B2 and L10 PtMn1-xFeX alloys is investigated using a combination of density functional theory (DFT) and Cluster Expansion (CE). CE model accuracy is evaluated against DFT data, where cross-validation scores were found to be reasonable. The CE generated 16 and 27 new structures on B2 and L10 PtMn1-xFeX, respectively. The ground state line predicted 6 stable structures with negative formation energies for both B2 and L10 PtMn1-xFeX alloys, suggesting thermodynamic stability. Furthermore, the magnetic strength of the ground state structures is evaluated using DFT.

1 Introduction

The MnPt alloy is useful for magnetic recording and spintronic applications because its magnetization direction can be easily manipulated through external magnetic fields [1]. It consists of the B2-type (CsCl)-type (Pm3m) ordered paramagnetic (PM) cubic structure, which transforms into the collinear antiferromagnetic L10 type (CuAu)-type ordered tetragonal structure at 970 K, regarded as the Neel temperature (TN) [2]. Experimental research on MnPt has revealed that antiferromagnetic (AFM) order results from the AFM coupling between adjacent Mn atoms in the (100) plane at distance whilst the ferromagnetic (FM) coupling occurs between adjacent Mn atoms in the [001] direction [1, 3]. Furthermore, the formation of ferromagnetic phases occurs in quenched MnPt samples with disordered and partially ordered Mn atoms, and also in sputtered disordered samples [3]. A practical approach to using MnPt alloys has been extensively investigated due to their high ferromagnetism. MnPt alloys have been reported to have magnetic susceptibility and electrical resistivity at 1220 K [4, 5]. Previously, the effect of antiferromagnetic (Cr) and ferromagnetic (Fe, Co) elements on MnPt alloy was investigated by the first-principles calculation based on density functional theory (DFT) [6, 7]. It was found that the magnetism is improved when c/a is 1.10 for Pt50Mn43.75Cr6.25, whilst the magnetic moment drops to below

* Corresponding author: ram@mintek.co.za

© The Authors, published by EDP Sciences. This is an open access article distributed under the terms of the Creative Commons Attribution License 4.0 (https://creativecommons.org/licenses/by/4.0/).
that of Pt$_{50}$Mn$_{50}$ on the addition of Fe. The thermodynamic and mechanical stability also showed that both Fe and Cr on Mn-site favoured the L1$_0$ phase compared to the B2 phase. Although the uses of this alloy for data storage is becoming increasingly popular, not much research has been done on it theoretically with the addition of Fe, especially its phase stability.

In this paper, the ground-state structures and phase stability of B2 and L1$_0$ PtMn$_{1-x}$Fe$_x$ alloys were investigated using a combination of DFT and Cluster expansion methods. Furthermore, Monte-Carlo (MC) simulations were used to determine the high temperature properties of mixed B2 and L1$_0$ PtMn$_{1-x}$Fe$_x$ alloys for a concentration of 0.5.

# 2 Methodology

## 2.1 Cluster expansion and Monte Carlo simulation

The computation of phase equilibrium and ground-state structure of the B2 and L1$_0$ PtMn$_{1-x}$Fe$_x$ alloys require the calculation of total energy for all possible configurations. The cluster expansion (CE) method [8, 9] was used to represent the configurational total energy of these alloys. This method constructs an Ising-like Hamiltonian for the energies of the different atomic configurations. The CE method was performed with the UNCLE code [10] which can automate most of the tasks associated with the construction of the CE Hamiltonian and the calculation of thermodynamic properties. UNCLE proceeds by gradually increasing the number of clusters included in the cluster expansion until the desired accuracy is achieved. This code is capable of performing a complete CE fit that contains two or more elements. During fitting the CE was allowed to run until the maximum number of iterations is reached while adding a maximum of four or more structures on each iteration and starting from the initial training set of those four or more structures. This process continues until the energies of all structures are predicted by the CE at each concentration.

In order to evaluate the predictive power of the cluster expansion, the cross-validation (CVS) is introduced as a criterion. The CVS is defined as:

$$CV = \left( \frac{1}{N} \sum_{i=1}^{N} (E_i - \bar{E}_i)^2 \right)^{1/2}$$

(1)

where $E_i$ is the calculated energy of structure $i$, while $\bar{E}_i$ is the predicted value of the energy of structure $i$ obtained from a least-squares fit to the (N-1) other structural energies [9]. In contrast to the standard mean square error criterion, CVS aims only to minimize the fitting error. A cluster expansion can be considered accurate if the CVS is less than 5 meV/atom [11].

Having constructed the cluster-expansion Hamiltonian, it is used to perform Monte Carlo simulations in order to obtain the energy difference as a function of composition and temperature. The MC simulations were performed using the UNCLE [10] software for B2 and L1$_0$ PtMn$_{1-x}$Fe$_x$ alloys. It was used to check the mixing of the two phases (B2 and L1$_0$). In the current simulation, the averaging time was set to 0.1 % precision on the average alloy concentration. The MC moves consist of exchanging the position of the Mn and Fe atoms for B2 and L1$_0$ PtMn$_{1-x}$Fe$_x$ alloys. In an MC simulation, the energies of alloys were allowed to change in the calculation due to changes in the occupation (atom exchanges). High temperature properties were computed using the canonical ensemble as implemented in the UNCLE code. Using periodic boxes that contain 25x25x25 atoms was used. Both B2 and L1$_0$ PtMn$_{1-x}$Fe$_x$ alloys were tested at temperatures ranging from 100 to 3000 K.
2.2 Density functional theory calculation

The first-principles total energy of a given atomic configuration of the B2 and L10 PtMn1-xFex was calculated from the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [12, 13]. The interaction between the core and the valence electrons was described using the projector augmented wave (PAW) method [14]. As part of the expansion of wave functions, an energy cutoff of 500 eV was used for plane waves. Structural full optimization was achieved by allowing the cell volume, shape, and atomic positions to relax until stress was minimized and forces on any atom were below 0.02 eV/Å. Exchange correlation energy was described using the generalized gradient approximation (GGA) functional of Perdew-Burke-Ernzerhof (PBE) [15, 16]. UNCLE code [10] is used as a script interface to VASP which defines a parameter that automatically sets up the k-point mesh for similar systems which we used 0.2 k-spacing. The spin-orbit coupling was taken into account only for the calculation using the force theorem.

3 Results and discussion

3.1 Ground state structures

The obtained formation energies $\Delta E_f(\sigma)$ which were used to fit the cluster expansion Hamiltonians are shown in Figure 1. Once the ground states for a range of concentrations have been identified, the ones that are stable at $T=0$ K are determined by the convexity condition, that is the given structure at concentration $x$ is stable if it lies below any straight line connecting other compounds at concentrations. From Figure 1, it is noted that B2 Mn$_{1-x}$PtFe$_x$ structures have negative $\Delta E_f(\sigma)$ showing stability, while those close to the convex hull contribute to miscible constituents. Stable compounds are those that form the vertices on the lower boundary of this convex hull. The predicted ground state structures as shown by the ground state line are FePt (Pm-3m), MnFe$_2$Pt$_4$ (I4/mmm), MnFe$_2$Pt$_3$ (P-3m1), MnFePt$_2$ (Fm-3m), Mn$_3$FePt$_4$ (I4/mmm) and MnPt (Pm-3m). These results show that MnFePt$_2$ is the most thermodynamically stable structure due to the lowest $\Delta E_f(\sigma)$ (-24.3 meV/atom) compared to other compositions. Table 1 shows the predicted number of structures and their cross validation score (CVS). The fully optimized ternary ground state diagram produced 16 new structures. An evaluation of the cluster expansion’s predictive power was done using the CVS. A small CVS (<5) indicates the fitting accuracy of the cluster expansion in the study. A CVS is found to be 0.005 meV/pos., which is an indication of a good cluster expansion (since CVS<5 meV/pos.).

Figure 2 shows the ground state structure of L10 PtMn$_{1-x}$Fe$_x$ alloy compositions. Note that the ground state structures are those in the highlighted red line and are considered thermodynamically stable. The ground state line predicted six (6) stable structures relative to the predicted enthalpies of formation. The circles represent energies for a specific configuration as calculated by DFT and predicted by the CE. It can be noted that all the formation energies are negative for all ordered structures which indicates that the predicted structures are thermodynamically stable. The CE predicted stable structures with different compositions, space groups, lattice parameters, and different formation energies. The predicted ground state structures are MnPt, MnFe$_2$Pt$_3$, MnFePt$_2$, Mn$_2$FePt$_3$, Mn$_3$FePt$_4$ and FePt with different space groups. Thus, the results show that the MnFePt$_2$ (I4/mmm) is the most thermodynamically stable structure since it gave the lowest formation energy ($\Delta E_f = -20.0$ meV/atom) compared to other compositions. These results are reliable since a proper CE convergence was attained. The predicted number of new structures and cross validation
score (CVS) for L10 PtMn1-xFex are also shown in Table 1. The cluster expansion generated 27 new structures of the L10 PtMn1-xFex system. The CE truncated at iteration 8 since the proper convergence was revealed. This is evident from the corresponding CVS. It is noted that CVS is 0.077 meV/pos., which is also acceptable as prescribed above since CVS< 5 meV/pos. suggesting good cluster expansion prediction.

Fig. 1. Ground state line of the ternary B2 PtMn1-xFex system constructed from plotting formation energy against Fe concentration. The grey and green crosses predicted structures by CE and the red line is the DFT ground-state line. Binaries are used as a reference point, such that their energies are normalized.

Fig. 2. Ground state line of the ternary L10 PtMn1-xFex system constructed from plotting formation energy against Fe concentration. The grey and green crosses predicted structures by CE and the red line is the DFT ground-state line. Binaries are used as a reference point, such that their energies are normalized.
### 3.2 Optimized ground-state Structures from Cluster Expansion

The equilibrium lattice parameters and magnetic properties for B2 and L10 PtMn$_{1-x}$Fe$_x$ alloy compositions are evaluated and shown in Table 2. This is to determine the effect of Fe addition on both B2 and L10 phases on the Mn sub-lattices. The structures were subjected to full geometry optimization by alloying both the lattice constant and shape to change. The calculated lattice parameters were compared with theoretical values to validate a binary model (Mn$_{50}$Pt$_{50}$). The equilibrium lattice parameter of binary B2 Pt$_{50}$Mn$_{50}$ is predicted to be 3.12 Å (3.01 Å) [17] which agrees very well with theoretical data (in parenthesis) to within 5%.

#### Table 1. Characteristics of the calculated cluster expansions.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>B2 PtMn$_{1-x}$Fe$_x$</th>
<th>L10 PtMn$_{1-x}$Fe$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of new structures</td>
<td>16</td>
<td>27</td>
</tr>
<tr>
<td>Number of ground-state structures</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Cross-validation scores (meV/pos.)</td>
<td>0.005</td>
<td>0.077</td>
</tr>
</tbody>
</table>

#### Table 2. The predicted lattice parameters and magnetic moments of B2 and L10 PtMn$_{1-x}$Fe$_x$ alloys.

<table>
<thead>
<tr>
<th>Structures</th>
<th>Space group</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Magnetic moment (μB/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2 Mn$_{1-x}$PtFe$_x$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnPt</td>
<td>(Pm-3m)</td>
<td>3.122</td>
<td>3.122</td>
<td>3.122</td>
<td>4.439</td>
</tr>
<tr>
<td>Mn$_3$FePt$_4$</td>
<td>(I4/mmm)</td>
<td>2.272</td>
<td>2.272</td>
<td>2.867</td>
<td>1.154</td>
</tr>
<tr>
<td>MnFePt$_2$</td>
<td>(Fm-3m)</td>
<td>2.993</td>
<td>2.993</td>
<td>2.993</td>
<td>0.000</td>
</tr>
<tr>
<td>MnFe$_2$Pt$_3$</td>
<td>(P-3m1)</td>
<td>2.178</td>
<td>2.178</td>
<td>2.639</td>
<td>0.856</td>
</tr>
<tr>
<td>MnFe$_3$Pt$_4$</td>
<td>(I4/mmm)</td>
<td>3.838</td>
<td>3.838</td>
<td>3.765</td>
<td>1.324</td>
</tr>
<tr>
<td>FePt</td>
<td>(Pm-3m)</td>
<td>3.057</td>
<td>3.057</td>
<td>3.057</td>
<td>3.430</td>
</tr>
<tr>
<td>L10 Mn$_{1-x}$PtFe$_x$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnPt</td>
<td>(P4/mmm)</td>
<td>2.942</td>
<td>2.942</td>
<td>3.490</td>
<td>4.414</td>
</tr>
<tr>
<td>Mn$_3$FePt$_4$</td>
<td>(I4/mmm)</td>
<td>3.775</td>
<td>3.775</td>
<td>3.013</td>
<td>3.754</td>
</tr>
<tr>
<td>Mn$_2$FePt$_3$</td>
<td>(C2/m)</td>
<td>4.183</td>
<td>3.741</td>
<td>5.293</td>
<td>0.003</td>
</tr>
<tr>
<td>MnFePt$_2$</td>
<td>(I4/mmm)</td>
<td>3.750</td>
<td>3.750</td>
<td>3.720</td>
<td>0.000</td>
</tr>
<tr>
<td>MnFe$_2$Pt$_3$</td>
<td>(C2/m)</td>
<td>4.217</td>
<td>3.880</td>
<td>5.404</td>
<td>2.493</td>
</tr>
<tr>
<td>FePt</td>
<td>(P4/mmm)</td>
<td>2.728</td>
<td>2.728</td>
<td>3.763</td>
<td>3.293</td>
</tr>
</tbody>
</table>

The magnetic moment was calculated to check the magnetic strength of the ground state systems. From Table 2, it is noted that the magnetic moments reduce with the addition of Fe. This suggests that the ferromagnetic behaviour is not enhanced when Fe is introduced on the Mn-site. At 25 at. % Fe, it is observed that the magnetic moment is zero which might suggest antiferromagnetic behaviour.

It is unfortunate that there is no experimental or theoretical value of the lattice parameters (a=2.942 Å, c=3.490 Å) of L10 MnPt (c/a=1.18) according to our knowledge to compare with the current results. In Table 2, the magnetism of L10 Mn$_{1-x}$PtFe$_x$ alloys decreases when Fe is
introduced on Mn-site. Amongst the ground state structures, it is observed that Mn$_3$FePt$_4$ has higher magnetic moment as compared to others. The results showed MnFePt$_2$ have antiferromagnetic behaviour due to zero magnetic moments. This suggests that indeed Fe is not good at enhancing the magnetism on the Mn-site. This is in good agreement with the results obtained using the supercell approach from our previous findings [6].

3.3 Monte Carlo Simulation

The Monte Carlo profiles of B2 and L1$_0$ PtMn$_{1-x}$Fe$_x$Mn$_{1-x}$PtFe$_x$ alloys at 0.5 concentration are computed and shown in Figures 3 and 4, respectively. Note that the plots are shown for the most thermodynamic stable structures (MnFePt$_2$) from the ground state line for both B2 and L1$_0$ phases. In Figure 3, we see that the energy difference between atoms increases with temperature. The energy difference increases minimally above 400 K which indicates that the system mixes very well. Furthermore, the findings indicate that Mn$_{0.5}$PtFe$_{0.5}$ mix well very at low temperatures below 400 K.

As shown in Figure 4, at low temperature, for example, at 200 K phase separation between MnPt and FePt can be observed in L1$_0$ PtMn$_{0.5}$Fe$_{0.5}$ alloy. Above 500 K, the energy differences increase minimally suggesting the mixing of the system has occurred. This suggests that the system becomes more and more homogeneous above 500 K.

![Monte Carlo frames and profile](image)

**Fig. 3.** Energy difference against temperature of B2 Mn-Pt-Fe at 0.5 concentration (Pt-Mn$_{0.5}$Fe$_{0.5}$).
4 Conclusion

The phase stability of B2 and L10 PtMn1-xFe_x alloys was studied using a combination of DFT, Cluster expansion and Monte Carlo simulation approaches. The cluster expansion method has successfully generated 16 new structures on B2 PtMn1-xFe_x and 27 new structures for L10 PtMn1-xFe_x (Mn-site). All formation energies were found negative, indicating a phase stability for PtMn1-xFe_x alloys. The most thermodynamically stable structure for both B2 and L10 Mn1-xPtFe_x is found to be MnPt2Fe with the lowest heats of formation. It was also found these structures (the most thermodynamic stable) showed antiferromagnetic behaviour due to zero magnetic moments. Furthermore, Monte Carlo simulations was used to check the mixing of PtMn1-xFe_x on the Mn-site. The findings revealed that Mn0.5PtFe0.5 remains thermodynamically stable at low temperatures for B2 and above 500 K for L10 phase. This suggests that a possible ferromagnetic material cannot be achieved when Fe is introduced on the Mn-site. Therefore, this work showed that CE can be used to understand the phase stability for future magnets.

5 Acknowledgements

The calculations were carried out using computer resources at the Materials Modelling Centre, the University of Limpopo and the Centre for High Performance Computing (CHPC) in Cape Town. The authors acknowledge the Advanced Materials Initiative (AMI) of the Department of Science and Innovation (DSI) through Mintek for their financial support. The support of the South African Research Chair Initiative of the Department of Science and Innovation is highly appreciated.

References