Thermodynamic and magnetic properties of Pt$_{50}$Mn$_{50-x}$M$_x$ (M= Cr, Fe) alloys: A first-principles study

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Abstract. More recently, the L1$_0$ MnPt alloy has received massive attention in data storage applications such as spintronics due to its high ferromagnetic stability and very high Néel temperature. It was found that L1$_0$ MnPt alloy showed ferromagnetic behaviour at room temperature. In this study, the effect of introducing antiferromagnetic (Cr) and ferromagnetic (Fe) elements on MnPt alloy is being investigated using density functional theory (DFT). The thermodynamic stability was determined from the heats of formation to check the formability of Pt$_{50}$Mn$_{50-x}$M$_x$ (M= Cr, Fe; x=6.25, 12.5, 18.75, 25) alloys. These Pt$_{50}$Mn$_{50-x}$M$_x$ alloys were found to be thermodynamically stable although with lower heats of formation. Overall magnetic moments decrease slightly with an increase in Cr and Fe compositions, only at 6.25 at. % Cr the ferromagnetic state is improved when the c/a ratio is 1.10. The current work revealed that the DFT-based first-principle approach can be used to design new possible compositions for the development of PGM-bearing magnetic materials.

1 Introduction

Recently, manganese (Mn) based intermetallic compounds have attracted a great deal of attention due to their interesting hard magnetic properties and low cost [1]. Among intermetallic alloys containing platinum group metals (PGMs), the MnPt exhibits ferromagnetic exchange interactions. This material is useful for magnetic recording and spintronic applications, such as magnetic random-access memory, since it can serve as a pinning layer in giant magnetoresistive devices [2, 3]. It has L1$_0$ crystal structure with tetragonal distortions at low temperatures and shows high stability with very high Néel temperature. Previously, MnPt alloy has been reported to have magnetic susceptibility and electrical resistivity at 1220 K [4, 5]. Furthermore, the equiatomic MnPt also forms the CsCl (B2)-type ordered paramagnetic cubic structure, which, at 970 K, transforms into the L1$_0$-type (CuAu-I)-type ordered paramagnetic tetragonal structure. In recent years, there has been considerable interest in Mn-Pt alloys, since the type of magnetic interaction can be studied based on the degree of order, the separation and distribution of atoms and even the effects of environmental factors [6]. Unfortunately, there have been no much theoretical studies done

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previously on this material (MnPt), especially on its ferromagnetic behaviour, despite the emerging quest to use it in electronic devices for data storage.

In this work, the effect of antiferromagnetic (Cr) and ferromagnetic (Fe) elements on MnPt alloy was investigated by the first-principles calculation based on density functional theory (DFT). The aim is to study the effect of Fe and Cr on the phase stability, magnetic and elastic properties of B2 and L1₀ MnPt phases, introduced substitutionally on Mn-site.

2 Methodology

The calculations were performed using the Vienna ab initio simulation package (VASP) code [7, 8] based on the density functional theory (DFT). The ion-electron interaction is described by the projector-augmented wave (PAW) pseudopotential [9]. The exchange-correlation interaction is treated with the generalized gradient approximation (GGA) [10] of Perdew-Burke-Ernzerhof (PBE) [11]. A plane wave energy cutoff of 500 eV was used to converge the total energy of the systems. A k-spacing of 0.2 was used for the unit cells and supercells. The spin-orbit coupling was taken into account only for the calculation using the force theorem. A supercell of 2x2x2 was constructed on Pt₀.₅₀Mn₀.₅₀. The substitutional search tool embedded within the Medea software platform was used to substitute Mn with Fe and Cr, which provided the most stable composition at the desired symmetry. The elastic constants were calculated for a small strain of 0.005.

3 Results and discussion

3.1 Phase stability and magnetic properties at the ground state

The MnPt alloy is comprised of cubic B2 phase and tetragonal L1₀ crystal structures at high and low temperatures, respectively. The B2 phase consists of space group Pm-3m, No: 221 with Wyckoff atomic positions are Mn: 1a (0, 0, 0) and Pt: 1b (1/2, 1/2, 1/2) whereas the tetragonal structure belongs to space group P4/mmm, No: 123 with atomic positions are Mn: 1a (0, 0, 0) and Pt: 1d (0, 1/2, 1/2). The Bain paths for the Pt₀.₅₀Mn₀.₅₀₋ₓMₓ alloys (M= Cr and Fe, x=6.25, 12.5, 18.75, 25) are calculated and shown in Figure 1, where the atomic positions and volume are relaxed while the shape such as c/a ratio is fixed. The magnetic moment was calculated to check the magnetic strength of the systems at the ground state level.

The heats of formation and magnetic moments against the c/a ratio of Pt₀.₅₀Mn₀.₅₀₋ₓMₓ is shown in Figure 1 (a, b). The stability of Pt₀.₅₀Mn₀.₅₀₋ₓMₓ is discussed through the predicted heats of formation (ΔHᵢ) and can be approximated by:

\[
\Delta Hᵢ = Eᵢ - \sum xᵢ Eᵢ
\]

where \(Eᵢ\) is the determined total energy of the system and \(Eᵢ\) is the determined total energy of elements in the system. For a structure to be considered stable, the heat of formation value must have the lowest negative value because a positive value implies thermodynamic instability.

The results presented in Figure 1 (a) show that the binary L1₀ MnPt phase is slightly more thermodynamically stable than B2 when c/a is 1.2. Upon adding 6.25 at % Cr, the stability of B2 phase drastically drops while L1₀ phase remains thermodynamically favourable, presenting the latter with a be great possibility to form experimentally. Although with reduced stability, only the L1₀ phase is thermodynamically favourable as shown by the negative heat of formation compared to the unstable B2 phase at 12.50 and 18.75 at. % Cr compositions. Furthermore, the most stable structure is found when c/a = 1.10. However, an
opposite stability trend is observed for Pt$_{50}$Mn$_{25}$Cr$_{25}$ composition, wherein the B2 phase remains more than L1$_0$ phase over all c/a ratios considered. From Figure 1 (a), it is noted that B2 and L1$_0$ Mn$_{50}$Pt$_{50}$ structures maintain the same values of magnetic moments. However when 6.25 at. % Cr is added on Mn-site, L1$_0$ phase exhibits a significant increase with the highest magnetic moment when c/a is 1.10 compared to B2 phase, with a decreased magnetic moment, but drops gradually at higher c/a ratios. This suggests that the ferromagnetic behaviour is improved. Furthermore, despite depressed magnetism, it is observed that at 12.50 at. % Cr the magnetic moment increases at almost the same rate when the c/a is 1.10 and decreases with further increase in Cr content. In the cases of 18.75 and 25 at % Cr, the magnetic moment decreases when the c/a ratio is less than 1.2.

**Fig. 1.** Heats of formation and magnetic moments against c/a ratio for (a) Pt$_{50}$Mn$_{50-x}$Cr$_x$ and (b) Pt$_{50}$Mn$_{50-x}$Fe$_x$ alloys (x=6.25, 12.5, 18.75, 25).
Figure 1 (b) shows the heats of formation and magnetic moments against the c/a ratio of B2 and L1₀ Pt₅₀M₅₀₋ₓFeₓ compositions. It is noted that upon introducing 6.25 at % Fe, the structure is thermodynamically stable for L1₀, while B2 is completely unstable as shown in Figure 1 (b). At 12.50 at. % Fe, the heats of formation is negative for both the B2 and L1₀ phases but the tetragonal phase is the most favourable, suggesting a higher possibility to form experimentally, more so at c/a = 1.10. In the case of 18.75 at. % Fe, it was found that only the L1₀ phase is feasible, almost similar behaviour to 6.25 at. % Fe. This is due to the positive heats of formation found in the B2 phase. Lastly, at 25 at. % Fe the B2 and L1₀ phases are likely to form except when c/a is 1.20. Interestingly, much lower heats of formation are observed for L1₀ phase when c/a is 1.10 for considered compositions, i.e. 6.25, 12.50, 18.75, 25 at. % Fe. In Figure 1 (b), the ferromagnetism of Pt₅₀M₅₀₋ₓFeₓ increases sharply when c/a is 1.10, although still below that of unalloyed Pt₅₀M₅₀ which decreases at a higher c/a ratios. Interestingly, similar behaviour is also observed in 12.5, 18.75 and 25 at. % Fe compositions, where the L1₀ phase is more magnetic than the B2 phase. The results suggest that the addition of Fe does not increase the magnetic moment above that of Mn₅₀Pt₅₀ although the stability of the L1₀ phase is promoted at c/a = 1.10 over the B2 phase.

3.2 Structural properties

The structures which were able to form with the addition of both Fe and Cr as discussed in section 3.1 were subjected to full geometry optimization. During full optimization, both the lattice geometry and ionic positions were fully optimized. In Figure 2 and 3, the calculated equilibrium lattice parameters for Pt₅₀M₅₀₋ₓMₓ alloys (M= Fe, Cr) (0≤x≤25) are shown. The equilibrium lattice parameter of binary B2-Paramagnetic (PM) Pt₅₀M₅₀ is predicted to be 3.00 Å (3.01 Å) [12] which agrees very well with theoretical data (in parenthesis) to within 2 %. Unfortunately, there are no theoretical or experimental values of lattice parameters (3.12 Å) of Ferromagnetic (FM)-B2 to compare with current results. In addition, not much has been done to understand the influence alloying on the structural properties such as c/a ratio in the range 1.10 - 1.30 for the L1₀ phase. As expected, it is noted that the equilibrium lattice parameter of the B2 Pt₅₀M₅₀₋ₓFeₓ decrease as Fe content is increased (see Figure 2 (a)). This is attributed to the difference in the atomic radius, for which Mn (1.79 Å) is larger than Fe (1.72 Å). On the other hand, lattice parameter a decreases while the c lattice parameter increases with an increase in Fe content for the L1₀ phases with compositions that were able to form when c/a is 1.10. A similar trend is noticed when c/a is 1.20 and 1.30 as shown in Figure 2 (b). This trend suggests that upon Fe introduction the lattice contracts along a and expands along the c direction in accordance with Bain path transformation [13] observed in Fe.

The equilibrium lattice parameters for both B2 and L1₀ Pt₅₀M₅₀₋ₓCrₓ alloys (0≤x≤25) are shown in Figure 3 (a, b). In Figure 3 (a), it is observed that the partial substitution of Mn with Cr reduces the lattice parameter at 6.25 at. % but increases at about 25 at. % of the B2 Pt₅₀M₅₀₋ₓCrₓ. This may be attributed to the large atomic radius (1.85 Å) of Cr. The lattice parameter a of the L1₀ Pt₅₀M₅₀₋ₓCrₓ system (c/a = 1.10) decreases slightly as Cr content is increased with the c lattice parameter increasing almost at the same rate. This behaviour may suggest that the structure also contracts along a direction while it expands along the c direction with the addition of Cr. A similar trend is observed for L1₀ compositions with c/a = 1.20 and 1.30, as shown in Figure 3 (b).
Fig. 2. Equilibrium lattice parameter against atomic percent (at. % Fe) for (a) B2 and L1₀ (c/a = 1.10) and (b) L1₀ (c/a = 1.20 and 1.30) when 0 ≤ x ≤ 25 composition range.

Fig. 3. Equilibrium lattice parameter against atomic percent (at. % Cr) for (a) B2 and L1₀ (c/a = 1.10) and (b) L1₀ (c/a = 1.20 and 1.30) when 0 ≤ x ≤ 25 composition range.

3.3 Elastic properties

Based on the results and discussions above, it is of great importance to find out whether those structures which can form are mechanically stable. To our best knowledge, there is no experimental/ theoretical data about the elastic constants for Pt₅₀Mn₅₀₋ₓMₓ. Theoretical elastic constants were calculated from energy variation by applying small strains to equilibrium
lattice configuration. They depend on the type of lattice i.e. for the cubic and tetragonal crystals, there are three (c_{11}, c_{12}, c_{44}) and six (c_{11}, c_{12}, c_{13}, c_{33}, c_{44}, c_{66}) independent elastic constants, respectively. For example, applying two kinds of strains (c_1 and c_4) to the cubic system give stresses relating to three elastic coefficients, this is an efficient method for obtaining elastic constants. The mechanical stability condition for cubic system as outlined [14] is given as follows:

\[ c_{44} > 0; \ c_{11} > c_{12} \] and \( c_{11} + 2c_{12} > 0, \tag{2} \]

A tetragonal crystal has to obey the following restrictions of its elastic constants:

\[ c_{44} > 0; \ c_{66} > 0; \ c_{11} > |c_{12}| \] and \( c_{11} + c_{12} - \frac{2c_{13}^2}{c_{11}} > 0, \tag{3} \]

For the structure to be stable, the stability criterion for the elastic constants must be satisfied. The calculated elastic constants of the Pt_{50}Mn_{50-x}Fe_{x} alloys at different c/a ratios are shown in Figures 4 (a-c) and 5. The binary B2 Pt_{50}Mn_{50} alloy is found to be mechanically stable due to positive elastic shear modulus. So, the addition of a third element has been suggested to check their effect on elastic constants of the binary system. In Figure 4 (a), all the predicted C_{ij} does not satisfy the stability criteria for B2 Pt_{50}Mn_{37.5}Fe_{12.5} since c_{11} is less than c_{12} which resulted in negative elastic shear modulus (C'<0). Similar behaviour was noted for Pt_{50}Mn_{50}Fe_{25} as the C' decreased (C'<0). The C_{ij} for ternary addition is less than those for the binary Pt_{50}Mn_{50} structure, which indicates that the doping element Fe has no potential to improve the C_{ij} of the B2 phase.

Furthermore, the calculated elastic constant of the L1$_0$ Pt$_{50}$Mn$_{50-x}$Fe$_x$ alloys (0 ≤x≤25) when c/a is 1.10 is shown in Figure 4 (b). It is noted that all the independent elastic constants (c_{11}, c_{12}, c_{13}, c_{33}, c_{44} and c_{66}) are positive in the entire range of L1$_0$ Pt$_{50}$Mn$_{50-x}$Fe$_x$ alloys (0 ≤x≤25). The elastic shear modulus (C') is positive for the desired composition range and also meets the tetragonal stability criteria which indicate the structures are mechanically stable. Interestingly, L1$_0$ Pt$_{50}$Mn$_{31.25}$Fe$_{18.75}$ appears to have the highest values of elastic constants compared to other compositions. This suggests that at 18.75 at. % Fe the maximum value of elastic shear modulus is reached and the sharp increase in C' indicate that the tetragonal phase is the most mechanically stable structure and possess highest shear resistance which could be correlated to high magnetic moment at this composition. It is also observed that above 25 at. % Fe, the elastic constants decrease which suggests that the shear strength of this phase is reduced.

In the case of the L1$_0$ Pt$_{50}$Mn$_{50-x}$Fe$_x$ alloys (0 ≤x≤25) (c/a = 1.30), all elastic constants meet the tetragonal stability criterion for the entire composition range indicating mechanical stability. However, Pt$_{50}$Mn$_{31.25}$Fe$_{18.75}$ appears to have the highest values of elastic constants, which indicates that the structure becomes the most stable at that composition as shown in Figure 4 (c). It is also noted that the elastic constants reduce at 25 at. % Fe which suggests that the shear strength of the structures decreases.

Figure 5 depicts the calculated elastic constants of the L1$_0$ Pt$_{50}$Mn$_{50-x}$Fe$_x$ alloys (0 ≤x≤18.75) when c/a is 1.20. In this case, the addition of Fe shows that the elastic constants satisfy the tetragonal stability criteria for the entire desired concentration range (0≤x≤18.75). It is unfortunate that the structure at 25 at. % Fe does not form when the ratio is 1.20. The calculated elastic constants of the structures which can form for B2 and L1$_0$ Pt$_{50}$Mn$_{50-x}$Cr$_x$ alloys (0 ≤x≤25) are shown in Figure 6 (a-d). In Figure 6 (a), all the predicted C_{ij} does not satisfy the stability criteria for B2 Pt$_{50}$Mn$_{50-x}$Cr$_x$ since c_{11} is less than c_{12}, which resulted in a negative elastic shear modulus (C'<0). In the case of L1$_0$ Pt$_{50}$Mn$_{50-x}$Cr$_x$ (c/a = 1.10), the elastic constants satisfy the tetragonal stability condition for the desired concentration range (0 ≤x≤25) (see Figure 6 (b)). Interestingly, it is noted that the C_{ij} for ternary addition is greater than those for the binary L1$_0$ Mn$_{50}$Pt$_{50}$ structure, which indicates that the alloying element (Cr) has the potential to improve the C_{ij} of pure structure as it increases with an increase in compositions. Furthermore, the elastic constants of L1$_0$ Pt$_{50}$Mn$_{50-x}$Cr$_x$ when the c/a = 1.20 and 1.30 are shown in Figure 6 (c) and (d), respectively. As the composition of Cr is added,
the elastic constants \(c_{11}, c_{12}, c_{13}, c_{33}, c_{44}, c_{66}\) are positive, condition of stability. It is observed that the \(C'\) is positive for the desired composition range and also meets the tetragonal stability criteria which indicate the structures are mechanically stable. Interestingly, \(L_{10} Pt_{50}Mn_{31.25}Cr_{18.75}\) and \(Pt_{50}Mn_{43.75}Cr_{6.25}\) appear to have the highest values of elastic constants compared to other compositions when \(c/a\) is 1.20 and 1.30, respectively. This suggests that at 18.75 at. % Cr the maximum value of elastic shear modulus is reached, which is indicative of enhanced mechanical stability and increased shear resistance when \(c/a\) is 1.2.

Fig. 4. Elastic constants (GPa) of (a) B2, (b) \(L_{10}\) \((c/a=1.10)\) and (c) \(L_{10}\) \((c/a=1.30)\) for the \(Pt_{50}Mn_{50-x}Fe_{x}\) alloys \(0\leq x \leq 25\).

Fig. 5. Elastic constants (GPa) of \(L_{10} Pt_{50}Mn_{50-x}Fe_{x}\) alloys \(0\leq x \leq 18.75\) \((c/a = 1.20)\).
Fig. 6. Elastic constants (GPa) of (a) B2, (b) L1\textsubscript{0} (c/a=1.10), (c) L1\textsubscript{0} (c/a=1.20) and (d) L1\textsubscript{0} (c/a = 1.30) Pt\textsubscript{50}Mn\textsubscript{50-x}Cr\textsubscript{x} alloys (0≤x≤25).

4 Conclusion

DFT approach was used to study the thermodynamic and magnetic properties of Pt\textsubscript{50}Mn\textsubscript{50-x}M\textsubscript{x} (M= Cr, Fe; x=6.25, 12.5, 18.75, 25) alloys. The thermodynamic stability was deduced from the heats of formation analysis. The results suggested that the addition of Cr and Fe promoted thermodynamic stability of L1\textsubscript{0} phase over the B2 phase. It was found that the magnetism is improved when c/a is 1.10 for Pt\textsubscript{50}Mn\textsubscript{43.75}Cr\textsubscript{6.25}, whilst the magnetic moment drops to below that of Pt\textsubscript{50}Mn\textsubscript{50} on the addition of Fe. Based on mechanical stability criterion of crystals, current results reveal that B2 Pt\textsubscript{50}Mn\textsubscript{50-x}M\textsubscript{x} phase is unstable whereas L1\textsubscript{0} Pt\textsubscript{50}Mn\textsubscript{50-x}M\textsubscript{x} is stable. It is thus concluded from thermodynamic phase stability as well as
mechanical stability point of view that the addition of both Fe and Cr on Mn-site favours the L1₀ phase compared to the B2 phase.

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