First-principles studies on the structural, electronic and mechanical properties of L10 and L12 Fe\textsubscript{x}Pt\textsubscript{1-x} alloys

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Abstract. Bimetallic Fe\textsubscript{x}Pt\textsubscript{1-x} alloys with the L1\textsubscript{0} and L1\textsubscript{2} structures have recently gained a lot of consideration in practical applications for solid-state devices, storage of ultra-high density magnetic data and biomedicine. This is due to their high magnetic and magnetocrystalline anisotropy, density, and coercivity. In order to gain knowledge on the structural, electronic and mechanical properties of the cubic and tetragonal Fe\textsubscript{x}Pt\textsubscript{1-x} alloys, we have calculated their equilibrium lattice constants, density of states, and elastic constants at 0 K, employing first-principles calculations. The calculated equilibrium lattice constants were found to be in good agreement with the experimental data to within 3\%. All independent elastic constants satisfy the necessary stability conditions for both cubic and tetragonal systems, suggesting mechanical stability. The shear anisotropic factors predict that the tetragonal Fe\textsubscript{x}Pt\textsubscript{1-x} crystals are highly anisotropic along the \{001\} plane than \{100\}. Moreover, the percentage of bulk (A\textsubscript{B}) and shear (A\textsubscript{G}) anisotropies revealed completely isotropic systems in the bulk and slightly anisotropic in shear modulus.

1. Introduction

Nanocomposites of ferromagnetic alloys made of hard and soft nanoparticles have attracted a considerable amount of attention for the past few decades. This is due to their potential application as permanent magnets and new storage of ultra-high density magnetic data and in magnetic recording [1, 2, 3]. However, several experimental findings have reported that the density of magnetic recording is restricted by the “superparamagnetic limit” i.e. loss of data due to activated fluctuations of magnetisation. Amongst other possibilities, Wang et al. have suggested that superparamagnetic limit can be overcome by designing new magnetic storage, in which magnetic nanoparticle composite forms a patterned media and each bit (0 or 1) is stored in a single magnetic nanoparticle [4]. Hence, it is of great significance to understand how material’s properties such as electronic, elastic etc. relate with magnetic stability of magnetic nanoparticle.

Amongst other ferromagnetic alloys, the binary Fe\textsubscript{x}Pt\textsubscript{1-x} alloys are perceived to overcome the superparamagnetic limit, due to their high magnetocrystalline anisotropy (~6 \times 10\textsuperscript{6} \textit{J/m}\textsuperscript{3}) [5, 6] along \{001\} direction in their chemically ordered states. Fe\textsubscript{x}Pt\textsubscript{1-x} alloys exist in four chemically ordered phases categorised into two main crystal symmetry families (L1\textsubscript{0} and L1\textsubscript{2}) when in thermodynamic equilibrium (see Figure 1) [7, 8]. The L1\textsubscript{0} symmetry crystallises in the tetragonal distorted FePt (space group P4/mmm) in the equiatomic (50:50) composition. Antoniak et al. showed that the orbital magnetic moment of FePt nanoparticles is significantly influenced at the Fe site, whereas the spin magnetic moment remains largely unaffected at the Pt site [3]. Moreover, FePt possesses high magnetocrystalline...
anisotropy and high coercivity. On the other hand, the L1$_2$, existing between 25% - 75% Pt composition crystallises in three different space groups, namely; cubic Fe$_3$Pt (space group Pm-3m), tetragonal Fe$_3$Pt (space group I4/mmm) and cubic FePt$_3$ (space group Pm-3m).

In this work, we report preliminary studies on the structural, electronic and elastic properties of the bulk Fe$_x$Pt$_{1-x}$ alloys; in particular, we have calculated the lattice constants, density of states, elastic constants, moduli and anisotropy at 0 K. Moreover, we have determined thermodynamic stability by calculating heats of formation.

![Figure 1](image.png)

**Figure 1.** Schematic representation of (a) Pm-3m Fe$_3$Pt, (b) I4/mmm Fe$_3$Pt, (c) P4/mmm FePt and (d) Pm-3m FePt$_3$.

2. **Methodology**

First-principles DFT+$U$ calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP) [9] to determine the structural, electronic and elastic properties of bimetallic Fe$_x$Pt$_{1-x}$ alloys. We applied the spin-polarised local density approximation (LDA) exchange correlation energy functional [10]. Moreover, the Hubbard correction ($U$) necessary to treat strongly correlated transition metals was employed on the $d$ orbital of Fe; $U$=1 eV and $J$= 1 eV were found to correctly predict the lattice constants to within 3% in agreement with the experimental data. A plane-wave cut-off of 450 eV and suitable k-points spacing of 0.2 Å obtained by performing numerical convergence test to less than 0.01
eV/atom were employed for structure optimisation. The equilibrium values were achieved by performing full relaxation of cell volumes and atomic positions within the plane-wave pseudopotential method. The elastic properties were calculated employing a strain of 0.005, while the densities of states were calculated in the spin-polarised magnetism with the Methfessel–Paxton smearing width of 0.02 eV [11].

3. Results
3.1. Structural properties and thermodynamic stability
The equilibrium lattice constants and heats of formation for the considered FeₚₓPt₁₋ₓ alloys are shown in Table 1 and Figure 2, respectively. Our calculated DFT+U lattice constants are in good agreement with the experimental data to within 3 %, indicating the validity of the approach employed. The thermodynamic heats of formation were calculated according to equation 1.

\[
\Delta H_f (eV) = [E_{Fe_xPt_{1-x}} - (xE_{Fe} + 1 - xE_{Pt})]
\]

where \(E_{Fe_xPt_{1-x}}\) is the total energy of \(Fe_xPt_{1-x}\), while \(E_{Fe}\) and \(E_{Pt}\) are the total elemental energies of Fe and Pt in their respective ground-states. We note that the calculated heats of formation decrease with the Fe concentration (see Figure 2), indicating an increase in thermodynamic stability. This suggests that Pm-3m FePt₃ alloy is more thermodynamically favourable over P4/mmm FePt, I4/mmm Fe₃Pt and Pm-3m Fe₃Pt, respectively. Moreover, the heats of formation values of I4/mmm Fe₃Pt, P4/mmm FePt and Pm-3m FePt₃ are negative, suggesting that these structures can be formed experimentally.

| Structure     | a (Å) | c (Å) | V (Å³) | \(\Delta H_f\) (eV) |
|---------------|-------|-------|--------|---------------------|
| Fe₃Pt (Pm-3m) | 3.722 | -     | 51.58  | 0.060               |
| Exp.          | 3.73  |       | 51.90  | [12]                |
| Fe₃Pt (I4/mmm)| 5.282 | 7.416 | 206.85 | -0.080              |
| Exp.          | 5.73  | 6.34  | 208.16 | [13]                |
| FePt (P4/mmm) | 3.841 | 3.766 | 55.56  | -0.350              |
| Exp.          | 3.85  | 3.70  | 54.81  | [14]                |
| FePt₃ (Pm-3m) | 3.902 | -     | 59.41  | -0.679              |
| Exp.          | 3.86  |       | 57.78  | [15]                |

Figure 2. Plots of heats of formation at different Fe and Pt concentrations.
3.2. Electronic properties
In order to determine the electronic properties of Fe\textsubscript{\textit{x}}Pt\textsubscript{\textit{1-x}} alloys, we have calculated their densities of states (DOS) as presented in Figure 3. We note that the states in the up-spin bands are located below the Fermi level, while the down-spins overlap above the Fermi level. The analysis of electronic structure shows that the cubic Pm-3m Fe\textsubscript{3}Pt and FePt\textsubscript{3} systems are magnetic metals, characterised by the absence of energy band gaps (a continuous overlap of states) around the Fermi level. The tetragonal I4/mmmm FePt and P4/mmmm FePt systems are predicted to be strong half-metallic ferromagnets. This is in good agreement with the first principles calculations reported by MacLaren et al. [16]. Bands for spin up are semiconducting, while bands for spin down are metallic. Moreover, we note that the Pm-3m FePt\textsubscript{3} structure shows a trivial shallow pseudo gap around the Fermi level, suggesting stability, corresponding well with the heats of formation. The other Fe\textsubscript{\textit{x}}Pt\textsubscript{\textit{1-x}} alloys show much broader and flat peaks around the Fermi level.

![Figure 3](image-url)

**Figure 3.** Total density of states for FePt (P4/mmmm), Fe\textsubscript{3}Pt (Pm-3m), Fe\textsubscript{3}Pt (I4/mmmm) and FePt\textsubscript{3} (Pm-3m) alloys. The Fermi energy is used as the zero of the energy scale.

3.3. Mechanical properties
In Table 2, we present the calculated elastic constants, moduli, anisotropy factors and Pugh ration for the Fe\textsubscript{\textit{x}}Pt\textsubscript{\textit{1-x}} alloys under study. Calculation of elastic constants is essential in gaining insights of mechanical stability and elastic properties of solids. The Taylor expansion of the total energy of a strained system [17, 18] (see equation 2) was used in the calculations of stress tensors on strains applied to the equilibrium structure to obtain the elastic constants C\textsubscript{\textit{ij}}.

\[
U(V, \varepsilon) = U(V_0, 0) + V_0 \left[ \sum_i \tau_i \xi_i + \frac{1}{2} \sum_{ij} C_{ij} \xi_i \xi_j \right],
\]

where \(U(V_0, 0)\) is the energy of the unstrained system with equilibrium volume \(V_0\); \(\tau_i\) and \(\xi_i\) are elements in the stress tensor and a factor taking care of the Voigt index, respectively. Cubic and tetragonal crystal systems contain three (\(c_{11}, c_{12}, c_{44}\)) and six (\(c_{11}, c_{33}, c_{44}, c_{66}, c_{12}, c_{13}\)) independent elastic constants, respectively. For cubic crystals (Pm-3m Fe\textsubscript{3}Pt and FePt\textsubscript{3}) to be considered mechanically stable, the following necessary Born stability criterion must be satisfied [19, 20].
We note that our LDA+U elastic constants values satisfy the necessary stability conditions, suggesting mechanical stability on the Pm-3m Fe₃Pt and FePt₃ cubic systems. On the other hand, the mechanical stability criterion of tetragonal P4/mmm FePt and I4/mmm Fe₃Pt are outlined according to equation 4 [21]. Similarly to cubic crystals, we note that the stability criterion are satisfied for tetragonal systems, suggesting mechanical stability. Furthermore, we observe a positive $C'$ value, also indicating the mechanical stability for all the crystal systems.

$$C_{11} - C_{12} > 0; \quad C_{11} + C_{33} - 2C_{13} > 0; \quad C_{ii} > 0 \ (i = 1,3,4,6); \quad 2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0$$

### Table 2. Elastic constants ($C_{ij}$), moduli, anisotropy factors ($A$) and Pugh ration ($K$) for FePt (P4/mmm), Fe₃Pt (Pm-3m), Fe₃Pt (I4/mmm) and FePt₃ (Pm-3m) alloys.

| $C_{ij}$ (GPa) | Pm-3m Fe₃Pt | P4/mmm FePt | I4/mmm Fe₃Pt | Pm-3m FePt₃ |
|---------------|-------------|-------------|--------------|------------|
| $C_{11}$      | 207.97      | 297.67      | 277.26       | 316.01     |
| $C_{12}$      | 174.75      | 170.90      | 95.43        | 180.81     |
| $C_{13}$      | -           | 158.95      | 172.27       | -          |
| $C_{33}$      | -           | 308.99      | 204.53       | -          |
| $C_{44}$      | 97.25       | 117.08      | 94.91        | 106.53     |
| $C_{66}$      | -           | 162.74      | 19.59        | -          |
| $C'$          | 16.61       | 63.39       | 90.91        | 67.60      |
| B             | 185.82      | 209.11      | 182.09       | 225.87     |
| G             | 49.02       | 101.33      | 48.48        | 88.77      |
| B/G           | 3.790       | 2.063       | 3.756        | 2.5445     |

| $A_1$         | -           | 1.6218      | 2.766        | -          |
| $A_2$         | -           | 2.567       | 0.21         | -          |
| $A$           | 5.855       | -           | -            | 1.576      |
| $A_B$ (%)     | 0           | 0           | 0            | 0          |
| $A_G$ (%)     | 32.57       | 5.67        | 30.25        | 2.467      |

From the calculated independent elastic constants for cubic and tetragonal systems, the macroscopic elastic bulk and shear moduli were determined according to the Voigt [22] and Reuss [23] approximations of simple and linear relations between the isotropic bulk and shear moduli of polycrystalline constants. Moreover, Hill proved that the Voigt and Reuss equations represent upper and lower bounds and proposed an arithmetic average moduli value [24]. The bulk modulus is a measure of resistance to volume changes by applied pressure, while the shear defines resistance to plastic deformation. From the obtained values (Table 2), we note that $B > G$ for all the systems, indicating that the shear modulus is the parameter limiting mechanical stability for Fe-Pt alloys. Pugh proposed the B/G ratio to predict the ductility or brittleness [25] of solids: if B/G is greater than the critical value 1.75, the material is ductile, otherwise brittle. We obtained the ratio B/G values greater than 1.75 for all Fe-Pt alloys, indicating ductility.

$$B = \left( \frac{C_{11} + 2C_{12}}{3} \right); \quad G_v = \left( \frac{C_{11} - C_{12} + 3C_{44}}{5} \right); \quad G_r = \left( \frac{4C_{44}(C_{11} - C_{12})}{3(C_{11} - C_{12})} \right);$$

$$G_{II} = \left( \frac{G_v + G_r}{2} \right); \quad C' = \left( \frac{C_{11} - C_{12}}{2} \right)$$

$$B_v = \frac{1}{9} \left[ 2(C_{11} + C_{12}) + C_{33} + 4C_{13} \right];$$

5.

6.
\[ G_V = \frac{1}{30} (M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}); \]
\[ M = (C_{11} + C_{12}) + 2C_{33} - 4C_{13}; \]
\[ B = B_H = \left( \frac{B_V + B_R}{2} \right) \]
\[ B_R = \frac{C^2}{M}; \quad G_R = 15/(18B_V/C^2 + 6/(C_{11} - C_{12}) + 6/C_{44} + 3/C_{66}); \]
\[ C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^1; \]
\[ G = G_H = \left( \frac{G_V + G_R}{2} \right) \]

Moreover, we have calculated the elastic anisotropy factors, which are essential to determine the susceptibility of materials to cracks induced in alloys owing to the anisotropy of the coefficient of thermal expansion as well as elastic anisotropy [26, 27]. These parameters measure the degree of anisotropy in bonding between atoms in different planes: a material is considered completely isotropic if \( A = 1 \), while any divergence from unity shows a degree of elastic anisotropy. The anisotropy factor for cubic system defined as the ratio of the extreme values of the orientation-dependent shear moduli is given as follows [28]:
\[ A = \frac{2C_{44}}{C_{11} - C_{12}} \]

while the shear anisotropic factors along \{100\} and \{001\} shear planes is defined by [29].
\[ A_1 = A_{(100)} = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}; \quad A_2 = A_{(001)} = \frac{2C_{66}}{C_{11} - C_{12}} \]

We note that all Fe\(_x\)Pt\(_{1-x}\) systems show greater anisotropy behaviour, since anisotropy factors \( A, A_1 \) and \( A_2 \) are far from unity. In addition, the percentage elastic anisotropy proposed by Chung and Buessem for bulk modulus \( A_B \) and shear modulus \( A_G \) in polycrystalline materials was also calculated as follows [30]:
\[ A_B = \frac{B_V - B_R}{B_V + B_R}; \quad A_G = \frac{G_V - G_R}{G_V + G_R} \]

where, \( B \) and \( G \) are the bulk and shear modulus, whereas subscripts \( V \) and \( R \) represents the Voigt and Reuss bounds. For these two expressions, a value of zero represents elastic isotropy and a value of 100% is the largest possible anisotropy. We note that Fe\(_x\)Pt\(_{1-x}\) alloys are completely isotropic in the bulk \((A_B = 0)\) and anisotropic \((A_G > 0)\) in shear moduli.

4. Conclusion
First-principles calculations were performed to determine the structural, thermodynamic, electronic and mechanical properties of Fe\(_x\)Pt\(_{1-x}\) alloys at 0 K. The structural lattice constants obtained by full structure optimisation were in good agreement with the experimental data to within 3%. The heats of formation showed that thermodynamic stability improves with decreasing Fe concentration. Electronic structure analysis predicted that the cubic Fe\(_3\)Pt and FePt\(_3\) are magnetic metals, whereas the tetragonal FePt\(_3\) and Fe\(_3\)Pt are half-metallic ferromagnets. Lastly, the elastic properties showed that all Fe\(_x\)Pt\(_{1-x}\) alloys are mechanically stable and behave in a ductile manner.
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6. References
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