

First Principles Calculations of the Electronic Structure of $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$

J. M. MacLaren, S. D. Willoughby, M. E. McHenry, B. Ramalingam, and S. G. Sankar

Abstract—The L1_0 alloys CoPt and FePt have strong uniaxial magneto-crystalline anisotropy as a consequence of the layering of Co or Fe and Pt planes. This makes these compounds of interest in permanent magnet applications. In this work we present the results of a study of the magnetic properties of the L1_0 alloys $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$ for the range of compositions from FePt to CoPt . Local spin density calculations using the coherent potential approximation are used to follow trends in the magneto-crystalline anisotropy and magnetic moments across the composition range. Total energy calculations of ordered and disordered alloys are used to develop a pseudo-binary phase diagram of the Fe/Co layer predicting regions of phase separation in this layer at temperatures below 650°C .

Keywords—Local spin density calculations, coherent potential approximation, magneto-crystalline anisotropy, binary phase diagram.

I. INTRODUCTION

THE L1_0 $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$ alloys have technologically important magnetic properties. In particular the large uniaxial magneto-crystalline anisotropy that results from the intrinsic layering of the crystal is desirable for potential permanent magnet applications. The L1_0 structure is a natural superlattice and just like many of the artificially grown superlattices the interfaces produce a large uniaxial anisotropy. In the paper we will study the electronic and magnetic properties of $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$ alloys using first principles local spin density electronic structure calculations. The alloys are assumed to have a substitutionally disordered Fe/Co plane. The technique used in our study is the layer Korringa Kohn Rostoker method (LKRR) [1]. The disorder is treated within the coherent potential approximation [2]. This approach has been used previously to calculate the electronic structure of disordered magnetic alloys [3]. One benefit of the method is that it is able to handle both ordered and disorder compounds within the same set of approximations which facilitates a comparison of trends. The lattice parameters (a , and c/a) as a function

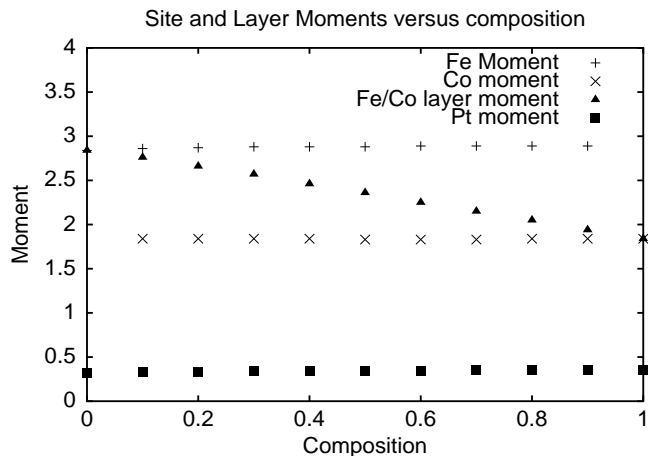


Fig. 1. Site moments for Fe, Co, and Pt as a function of the alloy composition. $x=0$ corresponds to FePt and $x=1$ to CoPt .

of composition were taken from published experiment data [4].

II. RESULTS

In the first part of this work, we have focussed on the variation of magnetic moments as a function of composition. The individual site moments for Fe, Co and Pt, as well as the composition weighted Fe/Co layer moments are shown in Figure. 1. The magnetizations for FePt and CoPt compare favorably to measured values. We find for FePt a magnetization of 1170 emu/cm^3 with a measured magnetization of 1140 emu/cm^3 [5], while for CoPt calculated and measured values are 750 emu/cm^3 and 800 emu/cm^3 [6] respectively. The Co and Fe moments in the $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$ alloy have enhanced local moments as compared with elemental Co and Fe. BCC Fe has a moment of about $2.2 \mu_B$ while the Fe moment in the L1_0 alloy lies between 2.8 and $2.9 \mu_B$. The enhancement of the Co site moment is not so dramatic, showing an increase from about $1.6 \mu_B$ for HCP Co to around $1.8 \mu_B$ in the alloy. Going from FePt to CoPt we find a slow increase in the Fe moment while the Co site moment is approximately constant. The variation in the Fe moment is consistent with typical behavior of Fe as a function of the effective number of Fe neighbors. The moment at an Fe surface has been predicted to be as large as $3 \mu_B$ [7]. Pt, while non-magnetic is readily polarized when in proximity to a ferromagnetic atom and a moment of about $0.3 \mu_B$ is induced by the ferromagnetic Fe/Co layer. Since the Fe and Co moments are roughly independent of composition, we see a reasonably linear variation in the layer

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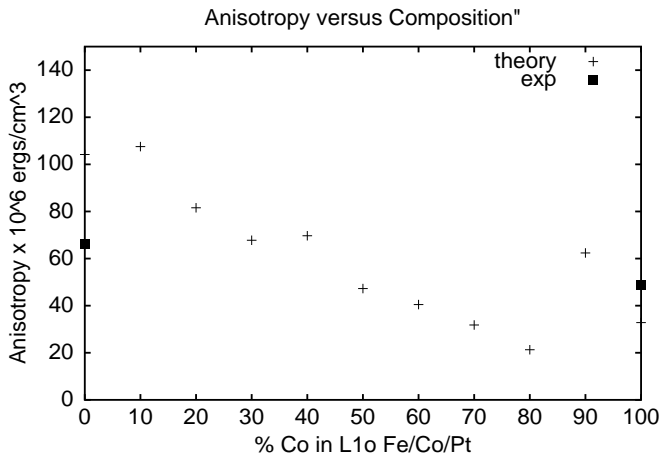


Fig. 2. Uniaxial anisotropy constant K_1 as a function of the percentage of Co in the alloy. Experimental data for the two ordered $L1_0$ alloys are marked by the filled boxes.

moment with composition, and it follows a simple rule of mixtures.

The spin resolved densities of states for the Fe, Co and Pt atoms, not shown due to space limitations, in the alloy show an almost completely filled majority spin band. Hybridization between minority Pt and minority Fe and Co states broadens broadens the Pt d-band by about 2 eV, and the Fermi energy passes through a local minimum. The alloy exhibits strong ferromagnetism with the Fermi energy states primarily of minority spin character.

The magneto-crystalline anisotropy as a function of alloy composition is shown in Figure 2. The anisotropy calculations were based upon the force theorem [8] in which the anisotropy energy, defined as the difference in total energy between systems with two different magnetization directions - easy and hard - is found using self-consistent potentials that did not include spin-orbit coupling. The force theorem connects the total energy difference to the difference in the one electron energy once spin-orbit coupling is included provided the same potential is used for both magnetization directions. Test calculations that included spin-orbit coupling in the self-consistent step results in anisotropies that differ by about 10%, consistent with our earlier experience [9]. The experimental results for the uniaxial anisotropy constant K_1 for CoPt, 49×10^6 ergs/cm³ [6], and FePt, 66×10^6 ergs/cm³ [5] are in reasonable agreement with our calculated values. Two possible origins of discrepancy are disorder on the Pt sublattice and choice of lattice constant. Calculations have shown that the anisotropy is quite sensitive to the a lattice constant. While the variation is on the whole monatomic, there are slight peaks in anisotropy close to the FePt and CoPt ends of the graph.

Previous work using the nearest neighbor Neel model [10] to describe the anisotropy of this alloy predicts a smooth change in anisotropy as a function of composition [11]. In previous studies the variation in anisotropy for Co/Pd and Co/Pt superlattices has been quantitatively described by

this model [9]. In comparing predictions of the Neel model to those of more detailed electronic structure calculations it was observed that the Neel model described trends on the average rather than any one particular system, and that there could be significant scatter between first principles work and the Neel model. This is not too surprising since the Neel picture, parameterized in terms of effective pair interactions, does not include subtle changes associated with specifics of the electronic structure. Nonetheless the model has use and in this system would show the overall trends in alloying.

The final part of this paper describes our use of first principles calculations in a study of the pseudo-binary phase diagram of the Fe/Co plane. Our total energy calculations show that Fe and Co obey a pseudo-binary regular solution model, predicting phase separation (in $\{100\}$ planes) at low temperatures, and random mixing above 650 °C. The calculated total energies for the $Fe_{1-x}Co_xPt$ ternary alloys are analyzed here within a quasi-chemical, Regular Solution Model (RSM) to study the possibility of Fe and Co partitioning. In this model we would write the alloy energy E as

$$E = P_{CC}E_{CC} + P_{FF}E_{FF} + P_{CF}E_{CF}, \quad (1)$$

where P_{CC} , P_{FF} , and P_{CF} , are the probability of finding Co-Co, Fe-Fe, and Co-Fe bonds, respectively, within the $\{100\}$ plane and E_{CC} , E_{FF} , and E_{CF} , are the energies of these bonds. In order to develop the phase diagram we only need the enthalpy of mixing which we determine from total energy calculations of the alloys as well as the two ordered $L1_0$ compounds FePt and CoPt. We have not extracted effective pair interactions from this data though we intend to investigate this in more detail in future. The change in total energy due to mixing, ΔE_m (enthalpy of mixing, ΔH_m) as follows:

$$\Delta E_m = \Delta H_m = E_{cpa}(\text{alloy}) - (1-x)E(\text{FePt}) - xE(\text{CoPt}), \quad (2)$$

where $E_{cpa}(\text{alloy})$ is the total energy of the disordered alloy found from the LKKR calculations within the coherent potential approximation, and the other two energies in equation (2) are the LKKR total energies of the ordered structures.

The thermodynamics of mixing are addressed through examination of the Gibbs free energy of mixing

$$\Delta G_m = \Delta E_m - T\Delta S_m, \quad (3)$$

where we use a simple configurational entropy term ΔS_m given by

$$\Delta S_m = -k_B (x \ln(x) + (1-x) \ln(1-x)) \quad (4)$$

Figure 3 illustrates the energy (enthalpy) of mixing difference as a function of alloy composition (x) for all of the $Fe_{1-x}Co_xPt$ ternary alloys studied. This energy difference is seen to deviate only slightly from the $x(1-x)$ dependence predicted for an ideal regular solution. Also shown

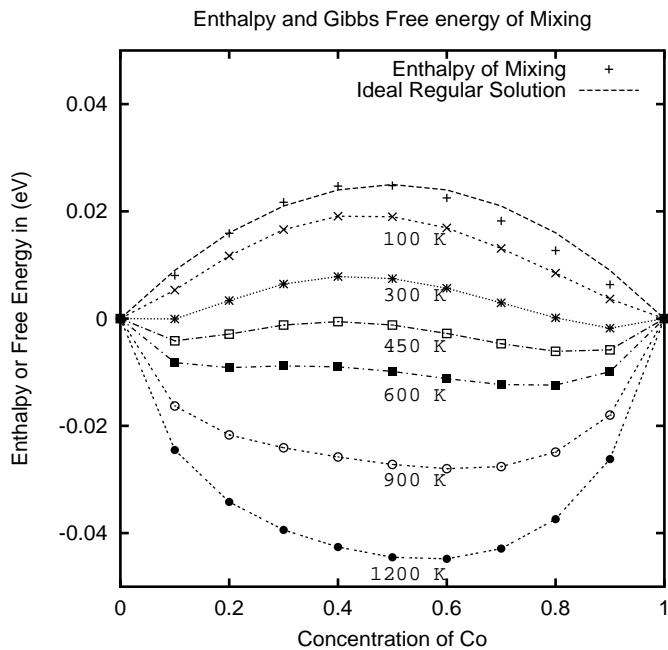


Fig. 3. Comparison of Enthalpy of mixing obtained from first principles calculations compared with predictions of the ideal regular solution. Calculated Gibbs Free energy curves at various temperatures as function of alloy composition.

are Gibbs Free energies of mixing constructed at different temperatures between 100 K and 1200 K, respectively. A common tangent construction can be used to determine points on a pseudo-binary phase diagram for $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$. Figure 4 illustrates an $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$ pseudo-binary phase diagram constructed from the data of Figure 3. It can be seen that Fe and Co obeys a pseudo-binary regular solution model predicting phase separation (in $\{100\}$ planes) at low temperatures into a Co rich α -phase and an Fe rich β -phase, respectively.

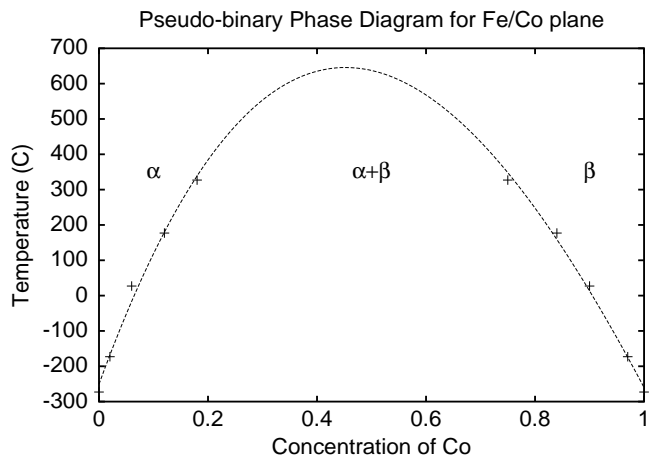


Fig. 4. Pseudo-binary Phase Diagram for $L1_0$ $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$ alloys. The curve is a third order polynomial fit through the data.

III. CONCLUSIONS

In this paper we have studied the variation in magnetic properties in the $L1_0$ alloys $\text{Fe}_{1-x}\text{Co}_x\text{Pt}$ as a function of composition. The atomic moments are almost constant across the series as a result of strong ferromagnetism, leading to magnetization variations that follow a simple rule of mixtures. The Fe and Co moments are both enhanced over respective bulk values and show behaviours typical of the atoms at interfaces where the number of like coordinating atoms is reduced. The uniaxial anisotropy constant K_1 follows the trends expected by the Neel model, though there some enhancement near the two ordered ends. Total energy calculations of both ordered and disordered alloys have been used to construct a pseudo-binary phase diagram for the Fe/Co layer. The enthalpy of mixing is close to that of the ideal regular solution, and the system shows phase separation below 650 °C.

IV. ACKNOWLEDGEMENTS

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