Magnetism: the driving force of order in CoPt, a first-principles study

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Abstract
CoPt equiatomic alloy orders according to the tetragonal L1₀ structure which favors strong magnetic anisotropy. Conversely, magnetism can influence the chemical ordering. We present here ab initio calculations of the stability of the L1₀ and L1₂ structures of Co–Pt alloys in their paramagnetic and ferromagnetic states. They show that magnetism strongly reinforces the ordering tendencies in this system. A simple tight-binding analysis allows us to account for this behavior in terms of some pertinent parameters.

1. Introduction
Magnetism and chemical ordering are frequently coupled in alloys. On the one hand, the strong magnetocrystalline anisotropy characteristic of equiatomic binary alloys like FePt or CoPt is known to be due to an L1₀ order that alternates pure planes along the [001] direction [1–7]. On the other hand, magnetism can influence the phase stability and chemical ordering [8, 9]. Typical examples include the stability of the bcc α phase of iron [10] and the phase diagram of FeCo [11, 12]. In the case of NiFe alloys involving neighboring late transition elements, magnetism plays an important role in the stability of the ordered phases in a rather notable fashion [13, 14]. It is suspected that this should also be true for FePt and CoPt alloys and, in the case of CoPt, diffuse scattering as well as nuclear magnetic resonance experiments have established a clear relationship between magnetism and short range order [15].

Furthermore, these alloys, in the form of nanometer-sized grains, are ideal candidates for high density magnetic storage applications (provided that the L1₀ ordered state is preserved). The systematic modeling of their thermodynamic properties, and of the critical ordering temperature in particular [2], necessitates the development of multi-scale methods involving effective interatomic potentials. These potentials should include all the relevant physics of the alloy, while remaining simple enough to allow simulation of real life situations with hundreds or even thousands of atoms [16, 17, 19, 18, 20, 21]. It then becomes imperative to determine whether magnetism governs the energetic properties of bulk alloys and nano-alloys. Should this prove to be true, all interatomic potentials would need to include a magnetic term. Clearly, this is not the case for the potentials in current use [22–26]. We focus here on questions of importance in the field of material science that have far reaching consequences for thermodynamic properties of alloys. The challenge is to emphasize the requirement and possibility to develop a tight-binding potential including a magnetic term to undertake appropriate large scale simulations.

The purpose of this study is to quantify the role of magnetism in the formation energies of Co–Pt alloys through non-magnetic and magnetic ab initio electronic structure calculations. In the bulk form, three ordered phases are known to exist in the Co–Pt system at low temperature, corresponding to the stoichiometric concentrations of Co₃Pt, CoPt, and CoPt₃ [27–29]. The ordered phase of CoPt is of the tetragonal L1₀ type. Co₃Pt and CoPt₃ are both L1₂ ordered phases of cubic symmetry. Using ab initio calculations, we show that magnetism influences chemical ordering in the Co–Pt system by studying the stability of previous structures. Moreover, a tight-binding analysis allows us to explain and understand why magnetism strongly reinforces the ordering tendencies in this system. Interestingly, the role of magnetism is illustrated...
in a relatively simple manner in this scheme, thus providing tangible grounds for a magnetic interatomic potential.

2. Methodology

We carried out non-spin polarized and spin polarized calculations in the framework of the density functional theory (DFT) using the ABINIT code [30] with generalized gradient approximation (GGA) exchange correlation functionals. Core and valence electrons were represented by a plane wave basis and projector augmented wave (PAW) potentials [31]. The adopted valence electronic configurations for Co and Pt were $3d^84s^1$ and $5d^96s^1$ respectively. All plane waves with energies below the cut-off energy were included in the basis set. The cut-off energies (16 eV, 22 eV and 22 eV for Co, Pt and CoPt respectively) were chosen 25% larger than the largest default cut-offs of the element-specific potentials. Integrations over the Brillouin zone were based on a $20 \times 20 \times 20$ Monkhorst–Pack 2D grid, which is sufficiently fine to ensure numerical convergence of all the calculated properties. All the structures were fully relaxed using the Broyden–Fletcher–Goldfarb–Shannon minimization. The cold smearing method was used for the Brillouin zone integration with a smearing parameter of $7 \times 10^{-2}$ Ha, leading to formation energies converged to within $10^{-3}$ eV/at. The calculations were performed at zero pressure; the relaxation of the atoms and the shape of the simulation cell were considered using the conjugate gradient minimization scheme.

3. Results

We first verified that the face centered cubic (fcc), body centered cubic (bcc) and hexagonal close packed (hcp) structures were correctly reproduced in elemental Co and Pt. The relative stability of these various phases, as well as the influence of magnetism on the system can be determined from the energy versus atomic volume curves plotted in figure 1(a) for Pt and figure 1(b) for Co. Concerning Co, non-spin polarized calculations predict an fcc ground state while spin polarized calculations correct this and reproduce the experimentally stable hcp phase (see figure 1(b)). Such behavior of non-magnetic calculations has been highlighted in previous calculations [32]. Regarding the magnetic moment, as expected, it increases when the lattice is expanded and vanishes when it is reduced. The total energies of the ferromagnetically ordered bcc and fcc structures are slightly higher than the hcp ones, 0.12 eV/at. and 0.01 eV/at. excess energy per atom respectively. Since the energy difference between fcc and hcp is relatively small and since CoPt alloys are cubic or tetragonal according to the phase diagram, cobalt will be considered to be in its fcc phase in what follows.

### Table 1. The physical properties of Co and Pt in the fcc structure (GGA calculations). The lattice parameter ($a_0$) and magnetic moment per atom ($m_{tot}$) are given. DFT and experimental (in the case of Co, Pt, L1$_0$ and L1$_2$) values are presented in parentheses.

|          | $a_0$ (Å) | $m_{tot}$ (µB) |
|----------|-----------|----------------|
| Co       | 3.52 (3.53 [33]) | 1.64 (1.62 [34]) |
| Co$_3$Pt | 3.66 (3.66 [33]) | 1.43 (1.45 [35]) |
| CoPt (L1$_0$) | $a = 3.81 \ (3.81$ [33]) | 1.14 (1.20 [8]) |
|          | $c/a = 0.976 \ (0.973$ [33]) |             |
| CoPt (L1$_1$) | $a = 3.70 \ (3.80$ [36]) | 1.08 |
|          | $b/a = 1.016 \ (1.017$ [36]) |             |
| CoPt (A$_2$B$_2$) | 3.71 | 1.12 |
| CoPt$_3$ | 3.86 (3.83 [33]) | 0.73 (0.67 [8]) |
| Pt       | 3.97 (3.92 [37]) | 0 |

Figure 1. The total energy as a function of atomic volume for (a) Pt and (b) Co as predicted by GGA calculations (open markers: non-magnetic, full markers: ferromagnetic). For Co, the variation of the magnetic moment is also displayed.
As shown in table 1, our results for the physical and magnetic properties for the fcc structure are in agreement with both previous ab initio and, when relevant, experimental data. Although non-magnetic calculations have been performed, only values for magnetic calculations are listed in table 1 to keep it as simple as possible. We have calculated magnetic moments within the LDA and GGA equal to 1.54 $\mu_B$/at and 1.64 $\mu_B$/at, respectively. The LDA’s underestimation of the magnetic moment is clearly connected to the well-known underestimation of the lattice parameters generally obtained with the LDA. Conversely, the usual overestimation of the lattice parameter by the GGA is not observed in the case of Co, leading to good agreement between the experimental and GGA determinations of the magnetic moment. This leads us to prefer the use of the GGA to model the CoPt system, even though the structural properties of Pt are slightly better reproduced by the LDA. Regardless of the approximation, note that all structures for Pt are found to be non-magnetic (NM), the ground-state structure being NM fcc, as shown in figure 1(a).

We now focus on ordered L1$_0$ and L1$_2$ alloys, which are known to exist in the CoPt system. The L1$_0$ phase exhibits uniaxial anisotropy with lattice parameters $a$ and $c$ about 3.81 and 3.71 Å respectively. As was the case for elemental Co and Pt, the physical properties obtained for both alloyed structures are in excellent agreement with experimental data and other ab initio results, as shown in table 1. In the case of the L1$_0$ phase, the $c/a$ ratio has been optimized. Moreover, we have also considered a simplified geometry where $c = a$; the magnetic moment was found to differ by 2% and the total energy by 0.02 eV/at. This suggests that the precise value of the $c/a$ ratio is irrelevant when the focus is on the general physical properties of the structure. In particular, the magnetocrystalline anisotropy is principally governed by the (anisotropic) chemical ordering [38] more than by the deviation from unity of this ratio, in contrast to the case of FeCo [7, 39]. Therefore, in the following we assume that $c = a$.

In figure 2, we show the atom-projected electronic densities of states (PDOS) for the L1$_0$-non-magnetic (NM) and L1$_0$-ferromagnetic (FM) phases of CoPt. As expected, the Pt band is wider than the Co band, about 8 eV and 5 eV respectively. The bands above $-7$ eV are predominantly of $d$ character and also show a large hybridization, in this case between the Co 3d and Pt 5d states. In the paramagnetic phase, the Fermi level falls within a Van Hove peak, which, according to the Stoner criterion, suggests a possible instability towards a ferromagnetic state. Such is the case in figure 2(b), where a quasi-rigid shift between the majority (spin up) and minority (spin down) bands is observed. This alloy is a strong ferromagnet with a full majority spin band, as was the case for elemental fcc or hcp Co. About 1 eV above the Fermi level, we observe a hybridization between Co and Pt d states, leading to a small induced local magnetism on Pt, about 0.3 $\mu_B$/Pt atom. This value is based on a frequently used spatial decomposition of the electronic density. It is useful at this point to recall that one has to be very careful with the cutoffs of the spatial decomposition when performing such calculations. To balance the observed loss of electrons, we have normalized our results to a d band containing 10 electrons. Furthermore, the PDOS for the L1$_2$ phase shows roughly the same behavior with a small induced local magnetism on Pt. These calculations are consistent with previous works [40–43].

Similar studies were conducted in the alloyed phase at varying concentrations of Pt (Co$_{1-x}$Pt$_x$). The ordered phases L1$_2$ (Co$_3$Pt or CoPt$_3$) have been considered, as well as other equiatomic phases, L1$_1$ and the A$_2$B$_2$ phase [13]. Our results are presented in table 1. For the L1$_1$ structure in particular, the $b/a$ ratio, after relaxation, has been found to be equal to 1.016, closely comparable to the value of 1.017 from previous ab initio calculations [36]. The total magnetic moment expressed per atom in table 1 decreases as a function of the Pt concentration; this is due to the fact that the magnetic moment of Pt atoms is negligible, whereas the magnetic moment of Co atoms is almost independent of the Pt concentration, and even increases slightly with it, as already noticed [35].

Finally the enthalpies of formation ($\Delta H$, at $T = 0$ K) of these alloys were determined,

$$\Delta H = \left[ E_{tot}^{Alloy}(nCo, mPt) - nE_{fccc}^{Co} - mE_{fccc}^{Pt} \right] / (n + m),$$

where $E_{tot}^{Alloy}(nCo, mPt)$ is the total energy of the mixed Co + Pt system containing $n$ Co atoms and $m$ Pt atoms, and $E^X$ represents the energy per atom of the elemental form $X$ ($X = Co$ or Pt) in the appropriate reference state. Thus,
for the non-spin polarized calculations, the reference states for the two elements are the non-magnetic structures, whereas for the spin polarized calculations we consider the ferromagnetic state for Co and the non-magnetic state for Pt.

Figure 3 illustrates the importance of magnetism in assessing the stability of the ordered phases of the Co–Pt system. In non-spin polarized calculations, $\Delta H$ is found to be very weak for any concentration. This result is incompatible with experimental observations of ordered structures having critical temperatures above 1000 K. In the spin polarized calculations, $\Delta H$ takes negative values between $-0.07$ and $-0.10$ eV/atom, for the L1$_2$ and L1$_0$ phases. The same order of magnitude has been observed with the LDA, showing the intrinsic key role played by magnetism to stabilize Co–Pt alloys. The L1$_1$ and A$_2$B$_2$ equiatomic structures are also clearly stabilized by magnetic effects but are less stable than the L1$_0$ phase. The effect of magnetism is more pronounced for the L1$_1$ phase than for the A$_2$B$_2$ and L1$_0$ phases, but not sufficiently to modify the relative stability of the phases in comparison with the non-spin polarized calculations. The energy differences between these three phases show that effective pair interactions beyond first neighbors are not negligible [13] and that our $ab$ initio calculations are successful in predicting L1$_0$ to be the most stable phase. According to our calculations, the relative stability of the considered Co–Pt phases is found to be the same for both magnetic and nonmagnetic calculations. Indeed the L1$_0$ phase is the most stable and the L1$_1$ the least stable. The qualitative difference is the positive formation enthalpy for the non-magnetic L1$_1$.

Our results for the L1$_0$ phase also agree with those obtained by Alam et al [44]; these authors (who did not consider other equiatomic structures) found a formation enthalpy of about $-0.09$ eV/atom for the ferromagnetic state, to be compared to our value of about $-0.10$ eV/atom, and the experimental value of about $-0.13$ eV/atom [45]. Their value for the paramagnetic state is slightly smaller than ours, $-0.03$ eV/atom, instead of $\sim -0.02$ eV/atom. It should be mentioned that the uncertainties due the approximations made (LDA or GGA, pseudopotentials, KKR-CPA in the case of disordered states) are probably much larger. Recent calculations [46] also agree on the order of magnitude of the formation enthalpy (about $-0.1$ eV/atom for L1$_0$ ferromagnetic CoPt), but the role of magnetism is not discussed.

4. Discussion

Even though $ab$ initio calculations are efficient in determining a quantitative description of an alloy with relatively high precision, general trends are best understood using simple models such as those provided by the tight-binding approximation [13, 44]. In the simplest model, the main alloy parameter is the diagonal disorder parameter, i.e., the difference in atomic d levels $\delta_{d} = \epsilon_{d}^{B} - \epsilon_{d}^{A}$ compared to an average bandwidth. In this context, the main outcome of tight-binding studies is the justification of an Ising Hamiltonian for order phenomena in transition metals [47]. In addition, effective pair interaction between first neighbors (V) which dominates this Hamiltonian can be calculated through the coherent potential approximation (CPA) for disordered alloys [13].

Figure 4(a) illustrates a typical variation of V as a function of the average number of d electrons $\overline{N}_{d}$ present in the system for an equiatomic alloy. Although for a real alloy $\overline{N}_{d}$ and the atomic concentration are related through $\overline{N}_{d} = cN_{d}^{A} + (1 - c)N_{d}^{B}$ for an $A_{x}B_{1-x}$ alloy, where $N_{d}^{A}$ is the number of d electrons ($X = A$ or B), it is convenient here to consider them as independent variables. Ordering of paramagnetic alloys occurs then when $\overline{N}_{d}$ is between 2.5 and 7.5. However, several alloys, notably CoPt with an $\overline{N}_{d}$ of 8.3, order rather than phase separate for higher values of $\overline{N}_{d}$ [9].

Off-diagonal disorder, defined as the difference between the band widths of the two constituents, $\delta_{nd} = W_{d}^{A} - W_{d}^{B}$, could be relevant here because of its importance when mixing 3d and 5d elements. Indeed, recently Los et al have shown that the variation of V with $\overline{N}_{d}$ is extremely sensitive to $\delta_{nd}$ [48]. Therefore for values of $\overline{N}_{d}$ and $\delta_{nd}$ adapted to CoPt, the region of ordered alloys can be shown to shift towards higher values of $\overline{N}_{d}$, and can include CoPt. Thus, contrary to what is usually argued [13], off-diagonal disorder can favor ordering instead of phase separation. However, the main reason for the ordering of CoPt and several other L1$_0$ structures seems to be the occurrence of ferromagnetism which modifies the relevant number of d electrons [9].

The role of magnetism can indeed be illustrated in a relatively simple manner in this scheme, by taking into account the strong ferromagnetic character of Co–Pt (figures 4(c) and (d)). The majority spin up band is completely full (5 out of the total 8.3 d electrons of the equiatomic CoPt are occupied) and does not participate in the cohesion of the system. This results in considering a new effective average $\overline{N}_{d}$ equal to 3.3 d electrons for a band normalized to 5 electrons or 6.6 electrons for a 10 electron band. This shift in the effective value of $\overline{N}_{d}$ due to magnetic considerations pushes the system fully into the area of $V > 0$, which in turn explains the stability of ordered structures and the negative heats of formation present in this system.

Actually, it is certainly the presence of magnetic moments on Co that matters, more than the type (ferromagnetic,
antiferromagnetic) of long range order that is stabilized at low temperature. This is clear when using the disordered local moment (DLM) picture, where local moments interact through effective pair interactions [9, 49, 12].

To summarize, from the analysis of our ab initio calculations within a simple tight-binding model, we have shown that the order in CoPt alloys, in particular at the equiatomic concentration, is principally driven by magnetic effects. Off-diagonal disorder plays a role by shifting the range of band fillings where order is stabilized towards high values. Magnetism, more precisely the presence of local moments, strongly reinforces this tendency. This should equally apply to other similar alloys, antiferromagnetic coupling becoming competitive at lower band filling, as in the case of FePt [50]. The present tight-binding analysis allows us to explain and understand why magnetism strongly reinforces the ordering tendencies in this system. Since this can be carried out in terms of some simple and relevant parameters, tight-binding potentials can account for all the relevant physics of this alloy. In the light of our conclusions, to go beyond the simplified empirical models present in the literature, it is necessary and possible to develop tight-binding potentials including magnetic terms to undertake appropriate large scale simulations. By inserting such an energetic model within Monte Carlo simulations, the thermodynamic properties of nano-alloys could be investigated.

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Figure 4. The typical variation of V as a function of the band filling N_d for an equiatomic composition. V > 0 means an ordering tendency.
(a) δ_d = 2 eV, δ_nd = 0 eV and (b) δ_d = 2 eV, δ_nd = 3 eV. (c), (d) Schematic representations of the band filling for (c) non-magnetic and (d) ferromagnetic CoPt.
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