Relativity and Magnetism in Ni-Pd and Ni-Pt Alloys

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Abstract

We show that the differences in the magnetic properties of Ni-Pd and Ni-Pt alloys arise mainly due to relativity. In particular, we find that the local magnetic moment of Ni increases with the addition of Pd in Ni-Pd while it decreases with the addition of Pt in Ni-Pt, as found experimentally, only if relativity is present. Our analysis is based on the effects of relativity on (i) the spin-polarized densities of states of Ni, (ii) the splitting of majority and minority spin d-band centers of Ni, and (iii) the separation between s-d band centers of Pd and Pt in Ni-Pd and Ni-Pt alloys.

1 Introduction

The magnetic properties of alloys of 3d transition metals Fe, Co and Ni with the nearly magnetic 4d Pd and 5d Pt show a wide range of behavior [1-4]. The variation in the magnetic properties of these alloys, as one goes from Fe-Pd(Pt) to Co-Pd(Pt) and then to Ni-Pd(Pt), can be attributed to the change in the number of valence electrons of one of the constituent atoms namely the 3d atoms. However, the change in the magnetic properties of these alloys, as one replaces Pd by Pt, is not obvious because both Pd and Pt have the same number of valence electrons. As an example, we show in Fig. 1 the experimentally determined average magnetic moments and the local magnetic moments of Ni, Pd and Pt in Ni-Pd [1,3] and Ni-Pt [1,4] alloys. From experiment [1,3] it is found that the addition of Pd to bulk Ni increases the magnetic moment of Ni (reaching a maximum at about 90% Pd), whereas the addition of Pt to bulk Ni decreases the magnetic moment of Ni.

Earlier work [1,2] on the magnetic properties of Ni-Pd and Ni-Pt alloys used parametrized local environment models to describe the magnetism in Ni-Pd and Ni-Pt alloys. The local environment models incorporated the changes induced due to the chemical environment as well as the magnetic environment.
Fig. 1. The experimental (a) average magnetic moment, (b) local magnetic moment at Ni site, plotted with respect to the bulk Ni magnetic moment of 0.616 $\mu_B$, and (c) local magnetic moment at Pd (Pt) site in Ni-Pd and Ni-Pt alloys.

Recent work \cite{7-10}, based on the local spin density functional method, have simply calculated the magnetic properties of Ni-Pd and Ni-Pt alloys without trying to understand the electronic mechanism responsible for the differences in their magnetic properties. The present study is, therefore, intended to improve our understanding of the reasons that lead to differences in the magnetic properties of Pd-based alloys and Pt-based alloys. In particular, using Ni-Pd and Ni-Pt alloys as examples, we explain the reasons for the differences in their magnetic properties.

The differences in the magnetic properties of Ni-Pd and Ni-Pt alloys are dictated by the electronic structure of 4$d$ Pd and 5$d$ Pt atoms and their sub-
sequent hybridization with Ni atoms. Since relativity is more important for heavier elements, the differences in the electronic structure of Pd and Pt atoms are mainly due to relativity. Thus it is possible that the magnetism in Ni-Pt alloys is of relativistic origin which, in turn, may explain its anomalous behavior vis-à-vis Ni-Pd alloys.

2 Computational Details

In this paper we examine the effects of relativity, by including the so-called mass-velocity and Darwin terms, on the electronic structure of ordered Ni-Pd ($L_1^2$Ni$_3$Pd, $L_1^0$NiPd and $L_1^2$NiPd$_3$) and Ni-Pt ($L_1^2$Ni$_3$Pt, $L_1^0$NiPt and $L_1^2$NiPt$_3$) alloys. The electronic structure of Ni-Pd and Ni-Pt alloys are obtained by carrying out spin-polarized, charge self-consistent calculations using the linear muffin-tin orbital (LMTO) method in the atomic-sphere approximation (ASA) [11,13], including the combined correction terms [11]. The calculations are carried out with the non relativistic Schrödinger equation as well as with the scalar-relativistic Dirac equation. In our calculations, the ratio of the atomic sphere radii, $R_{Ni}$, and the average Wigner-Seitz (WS) radii $R_{WS}$, in Ni-Pd and Ni-Pt alloys are chosen to make the respective atomic spheres charge neutral. We find that the charge neutrality is obtained for $R_{Ni}/R_{WS}$ = 0.98 (0.97), 0.97 (0.95) and 0.96 (0.93) for Ni$_3$Pd (Ni$_3$Pt), NiPd (NiPt) and NiPd$_3$ (NiPt$_3$) alloys, respectively. The $k$-space integrations are carried out with sufficient number of $k$ points in the irreducible wedge of the corresponding Brillouin zone to ensure the convergence of the magnetic moment [14]. The results, described below, correspond to the calculated equilibrium volume in each case.

3 Results and Discussion

The most significant of our results are shown in Fig. 2, where we show the average as well as the local magnetic moments at the Ni and Pd (Pt) sites of Ni-Pd (Pt) alloys calculated non relativistically, Fig. 2(a)-(c), and scalar-relativistically, Fig. 2(d)-(f), as a function of Pd (Pt) concentration. The average magnetic moment calculated non relativistically, Fig. 2(a), for both Ni-Pd and Ni-Pt alloys are very similar, and they decrease as a function of Pd or Pt concentration, respectively. The magnetic moment at the Ni site, as shown in Fig. 2(b), increases substantially with increase in Pd or Pt concentration. The magnetic moment at the Pd or Pt site, Fig. 2(c), does not vary by much and is relatively small. Thus Figs. 2(a)-(c) clearly show that if we use the non relativistic Hamiltonian to describe the electronic structure then both Ni-Pd
and Ni-Pt alloys display similar magnetic behavior. However, as shown in Figs. 2(d)-(f), the calculated average as well as local magnetic moments are quite different for Ni-Pd and Ni-Pt alloys if we use the scalar-relativistic Hamiltonian to describe their electronic structure. In particular, we find from Fig. 2(e) that the magnetic moment at the Ni site in Ni-Pd alloys increases with Pd concentration, whereas it decreases with increasing Pt concentration in Ni-Pt alloys. As a function of concentration the change in the local magnetic moment at the Pd or Pt site, shown in Fig. 2(f), is small. Thus a comparison of our non relativistic and scalar-relativistic results clearly shows that the differences...
in the magnetic properties of Ni-Pd and Ni-Pt alloys are, to a large extent, determined by relativity. We next compare our calculated magnetic moments of Ni-Pd and Ni-Pt alloys with the calculations of others and the experimental values.

The calculated magnetic moment of fcc Ni, which changes from 0.59 $\mu_B$ to 0.62 $\mu_B$ with the inclusion of relativistic terms, compares very well with the experimental value of 0.616 $\mu_B$ and the non relativistic calculation of Ref. \[15\]. Note that our calculation ignores the orbital contribution to the magnetic moment of Ni which is expected to be around 0.05 $\mu_B$. The average magnetic moments, calculated scalar-relativistically, for Ni$_3$Pd, NiPd and NiPd$_3$ are 0.58 $\mu_B$, 0.50 $\mu_B$ and 0.37 $\mu_B$ respectively. Since we find that the substitutional disorder does not change the magnetic moment of Ni-Pd alloys at 25%, 50% and 75% concentrations of Pd by much \[16\], our calculated values can be compared with the experimental values \[3\], 0.59 $\mu_B$, 0.51 $\mu_B$ and 0.46 $\mu_B$, obtained for disordered Ni-Pd alloys at 25%, 50% and 71% concentrations of Pd respectively. The calculated local moments at the Ni (Pd) site in Ni-Pd alloys is somewhat smaller (larger) than the experimentally determined values, which can be due to uncertainty involved in site-decomposing the average magnetic moment. For Ni$_3$Pt the scalar-relativistic calculations show the average magnetic moment to be 0.50 $\mu_B$ with the local magnetic moments at the Ni and Pt sites being 0.58 $\mu_B$ and 0.27 $\mu_B$ respectively. The corresponding experimental values \[4,5,17\] are 0.43 $\mu_B$ (average), 0.49 $\mu_B$ (Ni) and 0.25 $\mu_B$ (Pt) respectively. The results of Refs.\[9,10\] on Ni$_3$Pt are based on self-consistent local spin density approximation using the LMTO method but the value of the local magnetic moment of Ni given in the two references are different.

To further understand the electronic mechanism responsible for the differences in the magnetic properties of Ni-Pd and Ni-Pt alloys, we examine (i) the spin-polarized densities of states (DOS) of Ni, (ii) the separation between majority and minority spin d-band centers $\Delta C_{d_{\uparrow}-d_{\downarrow}}$ of Ni, $\Delta C_{Pd/Pt}$, and (iii) the separation between s- and d- band centers of Pd and Pt, $\Delta C_{s_{\uparrow}-d_{\uparrow}}$ in Ni-Pd and Ni-Pt alloys.

3.1 Spin-Polarised Densities of States

In Fig. 8 we show the spin-polarized DOS at the Ni site in fcc Ni, L1$_2$ NiPd$_3$ and L1$_2$ NiPt$_3$ calculated with the non relativistic and the scalar-relativistic Hamiltonian. As expected, the relativistic effects on the DOS of the elemental Ni, shown in Fig. 8(a), are very small. Since relativity is more important for Pd than for Ni, its effect on the DOS at the Ni site in NiPd$_3$ is more pronounced than in fcc Ni as shown in Fig. 8(b). We find that in NiPd$_3$ the inclusion of relativity leads to a decrease in the magnetic moment at the Ni site by
Fig. 3. The spin-polarized densities of states of Ni, calculated non relativistically (NR) and scalar-relativistically (SR), in (a) fcc Ni, (b) $L_1^2$ NiPd$_3$, and (c) $L_1^2$ NiPt$_3$.

However, in the case of NiPt$_3$, as shown in Fig. 3(c), the effect on the magnetic moment is an order of magnitude larger than for NiPd$_3$. The relativity reduces the magnetic moment at the Ni site in NiPt$_3$ by 0.24 $\mu_B$, i.e., from 0.79 $\mu_B$ to 0.55 $\mu_B$. Once again the change in the magnetic moment at the Pt site is negligible in comparison.
Fig. 4. The non relativistic (NR) and scalar-relativistic (SR) exchange-induced splitting of majority spin and minority spin $d$-band centers of Ni in (a) Ni-Pd and (b) Ni-Pt alloys. Figures (c) and (d) show the separation between majority spin $s$ and $d$-band centers of (c) Pd in Ni-Pd and (d) Pt in Ni-Pt alloys.

### 3.2 Separation Between Majority and Minority Spin d-band Centers

A more quantitative explanation for the changes in the magnetic moments due to relativity can be obtained by examining the separation between majority spin and minority spin $d$-band centers of Ni ($\Delta C_{d_{\uparrow}-d_{\downarrow}}^{Ni}$) in Ni-Pd, shown in Fig. 4(a), and Ni-Pt, shown in Fig. 4(b), alloys. As can be seen from Fig. 4(a), the exchange-induced splitting of the $d$-band increases with the addition of Pd in Ni-Pd alloys for calculations done with or without relativity. The increased
splitting leads to an increase in the local magnetic moment at the Ni site, as observed experimentally. It is interesting to note that the inclusion of relativity produces no net change in the exchange-induced splitting at the Ni site in equiatomic NiPd. On the other hand, in Ni-Pt alloys we find that relativity substantially reduces the exchange-induced splitting at the Ni site leading to a decrease in the local magnetic moment of Ni. For example, in Ni$_3$Pt the separation between $d$-band centers reduces from 51 mRy to 44 mRy and the corresponding reduction in the local magnetic moment is from 0.68 $\mu_B$ to 0.58 $\mu_B$, in agreement with experiment. With increasing Pt concentration the relativistic effects become more dominant which further reduces the splitting, as is the case for NiPt$_3$.

3.3 Separation Between $s$ and $d$ Band Centers

It is clear that the differences in the magnetic properties of Ni-Pd and Ni-Pt alloys are brought about by relativity through its effect on Pd and Pt atoms. To see how relativity affects the electronic structure of Pd and Pt atoms, we show in Figs. 4(c)-(d) the separation between the majority spin $s$- and $d$-band centers of Pd and Pt atoms as a function of concentration. We know that the most dominant effect of relativity is to lower the $s$ potential. The lowering of $s$ potential causes (i) the $s$-wavefunction to contract leading to a contraction of the lattice [18–20], and (ii) increased $s$-$d$ hybridization which results in electron transfer from $d$ to $s$ [20]. We see from Figs. 4(c) and 4(d) that the change in $s$-$d$ separation is almost an order of magnitude more in Pt than in Pd. For example, the $s$-$d$ separation for Pd in NiPd$_3$ changes from +66 mRy to -15 mRy, whereas for Pt in Ni$_3$Pt it changes from +74 mRy to -206 mRy. Thus the contraction of the $s$ wavefunction of Pt and the subsequent $s$-$d$ hybridization must be responsible for reducing the local magnetic moment at the Ni site.

The effects of the contraction of $s$ wavefunction in Ni-Pd and Ni-Pt alloys can be clearly seen in Figs. 5(a)-(b), where we show the equilibrium lattice constants calculated non relativistically and scalar-relativistically for these alloys. We find that the change in the lattice constant due to relativity is much more for Ni-Pt alloys than for Ni-Pd alloys. For example, in NiPt$_3$ relativity reduces the lattice constant by around 0.3 a.u., whereas the corresponding change in NiPd$_3$ is only about 0.1 a.u. Such a drastic reduction in the lattice constant due to relativity effectively put the Ni sublattice under strain in Ni-Pt alloys which, in turn, reduces the magnetic moment at the Ni site. To see how relativity-induced strain in Ni sublattice leads to a reduction in the local magnetic moment in Ni-Pt alloys, we have used the radii of the charge-neutral Ni atomic spheres ($R_{Ni}$) in these alloys as the average Wigner-Seitz radii ($R_{WS}$) to calculate, self-consistently, the electronic structure of fcc Ni.
Fig. 5. The non relativistically (NR) and scalar-relativistically (SR) calculated equilibrium lattice constants for (a) Ni-Pd and (b) Ni-Pt alloys. Figures (c) and (d) show the exchange-induced splitting between the majority and minority \textit{d} band centers in fcc Ni, calculated using the average Wigner-Seitz radii in bulk Ni equal to the radii of the charge neutral Ni atomic spheres in (c) Ni-Pd and (d) Ni-Pt alloys.

The corresponding results, in terms of the separation between majority and minority \textit{d}-band centers in fcc Ni, \((\Delta C^{N_i(Bulk)}_{d^\uparrow - d^\downarrow})\), are shown in Figs. (c)-(d). As shown in Fig. (c), the relativistic terms have a very small effect on the exchange splitting in Ni-Pd alloys. However, in Ni-Pt alloys the exchange splitting is \textit{reduced} with increasing Pt concentration, as can be seen from Fig. (d). The reduced exchange splitting leads to diminished local magnetic moment at the Ni site in Ni-Pt alloys, consistent with Fig. (b) and the experiments.
We like to point out that the present study can be further improved by including (i) the full-potential instead of spherically symmetric potential used in the ASA, and (ii) the spin-orbit terms. Also, as Ni and Pd form a ferromagnetic fcc solid solution throughout the concentration range while Ni and Pt form a ferromagnetic fcc solid solution for Pt concentration below 0.6, an approach based on the study of disordered alloys can lead to a more accurate description of the magnetic properties of these alloys. Thus one can use the Korringa-Kohn-Rostoker coherent-potential approximation in the ASA (KKR-ASA CPA) [18,21] to describe the electronic structure of disordered Ni-Pd and Ni-Pt alloys. However, for a reliable description of the magnetic properties of disordered Ni-Pd and Ni-Pt alloys, the overlap errors associated with the ASA must be corrected [14] which is not possible in the present implementation of the KKR-ASA CPA method [18]. We emphasize that the improvements outlined above are unlikely to change the main results of the present study because of the robustness of the relativistic effects.

4 Conclusions

In conclusion, we have shown that the differences in the magnetic properties of Ni-Pd and Ni-Pt alloys arise due to relativity. In particular, relativity ensures that the local magnetic moment of Ni increases with addition of Pd in Ni-Pd while it decreases with addition of Pt in Ni-Pt, consistent with experiment. We also find that the decrease in the local magnetic moment of Ni in Ni-Pt alloys is facilitated by relativity through lowering of the s potential of Pt, which leads to a contraction of the s wavefunction and an increase in s-d hybridization.

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