The origins of phase stability in ordered and disordered Ni–Pt alloys

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Abstract. Using the atomic-sphere approximation formulation of the Korringa–Kohn–Rostoker coherent potential approximation (KKR CPA) method, we have studied the effects of relativity on the electronic structure of ordered and substitutionally disordered Ni–Pt alloys. The inclusion of mass-velocity and Darwin terms are found to be essential for describing the experimentally observed ground-state properties. For the stability of disordered Ni–Pt alloys we find that, in addition to relativity, the minimization of charge-transfer effects are important. We also find that the treatment of ordering tendencies based on the band energy term alone is not sufficiently accurate for alloys with charge-transfer effects. Further analysis, in terms of basis functions, densities of states and non-spherically averaged charge densities, indicate the importance of s- and d-electrons of Pt for the stability of both ordered and disordered Ni–Pt alloys.

1. Introduction

Recent studies [1–4] of ordered NiPt and AuNi, and substitutionally disordered $Ni_{0.5}Pt_{0.5}$ have clearly shown the importance of including the relativistic terms, the so-called mass-velocity and Darwin terms, in the Hamiltonian for describing accurately their phase stability properties. For those alloy-systems where phase stability is relativity-induced, studies based on inclusion or non-inclusion of relativistic terms provide an opportunity to pinpoint unambiguously the electronic mechanism responsible for their phase stability. In the process one also gains a better understanding of the electronic properties of these alloys.

In this paper we examine the effects of the mass-velocity and Darwin terms, referred to as R-terms in the following, on the electronic structure of ordered Ni_3Pt in $L1_2$, NiPt in $L1_0$, and $NiPt_3$ in $L1_2$ phases, and substitutionally disordered $Ni_{0.75}Pt_{0.25}$, $Ni_{0.5}Pt_{0.5}$ and $Ni_{0.25}Pt_{0.75}$ on fcc lattices using our formulation [5] of Korringa–Kohn–Rostoker coherent potential approximation (KKR CPA) method [6,7] in the atomic-sphere approximation [8]. We have chosen the Ni–Pt system primarily because it demonstrates the improvements, outlined below, of our approach over previous methods, and answers some of the questions raised by recent works on the Ni–Pt system [2–4].

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Our formulation of the KKR CPA in the atomic-sphere approximation (ASA) allows us to calculate the electronic structure of ordered as well as disordered alloys within the same framework, and is based on the screening transformations of the linear muffin-tin orbitals (LMTO) developed by Andersen *et al* [9, 10] and the KKR CPA approach as described in [6]. The advantages of our formulation include (a) an efficient calculation of electronic structure of ordered and disordered alloys with the same set of approximations for the Hamiltonians in each case, (b) minimization of charge-transfer effects by employing charge-neutral spheres [11], (c) a probable improvement over the MT formulation for those alloys where the potential in the interstitial region is not constant, and (d) the calculation of non-spherically averaged charge density [12]. Of course, the ASA leads to overlapping atomic spheres, but the error introduced due to such overlaps in the ordered alloys can be minimized with the use of combined correction (CC) terms [8]. A similar formalism that corrects for the overlap in the disordered alloys has also been developed and we are in the process of implementing it in our calculations.

Experimentally, at temperatures above 950 K, the Ni–Pt system is found to be stable in the form of face-centered-cubic (fcc) solid solution over the whole concentration range. At lower temperatures the fcc solid solution, depending on concentration, transforms into ordered Ni_3Pt $(L1_2)$, NiPt $(L1_0)$ and $NiPt_3$ $(L1_2)$, respectively.

Based on our calculations described below, we believe that relativistic effects are critical for the stability of ordered as well as disordered Ni–Pt alloys. The changes induced by relativity mainly affect the s- and d- (especially t_{2g}) electrons of Pt. Our results for ordered Ni–Pt alloys are in qualitative agreement with that given in [2, 13]. For disordered Ni–Pt alloys we find that an accurate electronic structure description within the single-site approach requires not only the inclusion of relativistic terms, in disagreement with [3], but also the minimization of charge-transfer effects.

2. Computational details

The self-consistent electronic structure of ordered phases, Ni, Pt, and Ni_3Pt, NiPt and $NiPt_3$ is calculated with the LMTO–ASA method [8, 9]. To find the best possible combination of various approximations that are usually made in the ASA, we have carried out an extensive set of calculations involving (i) equal atomic spheres, (ii) charge-neutral atomic spheres, (iii) combined corrections (CC) with (i), and (iv) CC with (ii). The calculations (i)–(iv) are performed using the non-relativistic (NR) Schrödinger equation as well as the scalar-relativistic (SR) Dirac equation as a function of volume. The k-space integration is carried out using more than 200 k-points in the irreducible wedges of the Brillouin zones (IBZ).

The KKR–ASA CPA method [5] is used for calculating the self-consistent electronic structure of substitutionally disordered $Ni_{0.75}Pt_{0.25}$, $Ni_{0.5}Pt_{0.5}$ and $Ni_{0.25}Pt_{0.75}$ on fcc lattices. The SR and NR calculations in this case are carried out for (v) equal atomic spheres and (vi) charge-neutral atomic spheres. During the CPA self-consistency cycle, 505 k-points are used in the IBZ. For both ordered and disordered calculations the exchange-correlation potential was parametrized as suggested by von Barth and Hedin [14]. The effective pair interactions (EPI) are calculated using generalized perturbation method (GPM) in ASA [15].
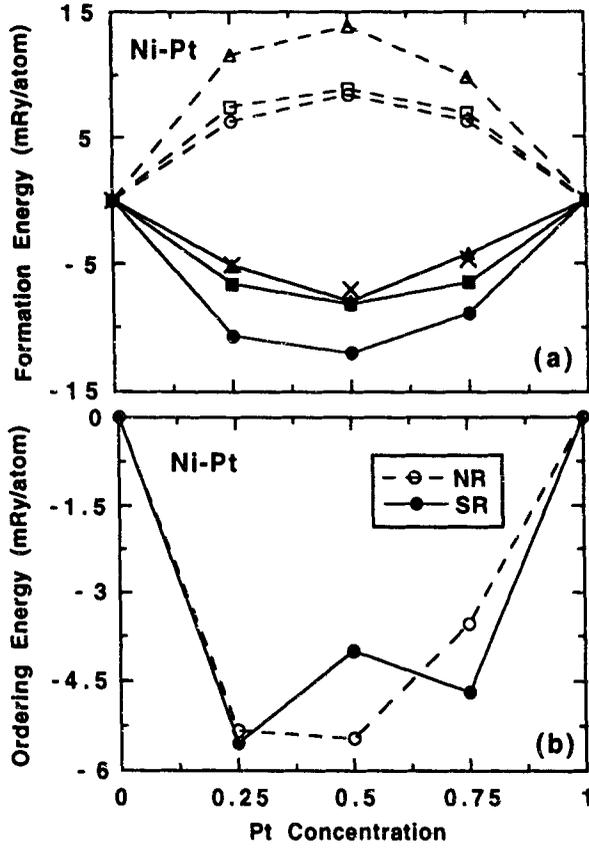
Figure 1. (a) The scalar-relativistic (filled symbols) and the non-relativistic (open symbols) formation energies of Ni–Pt alloys obtained with charge-neutral calculations as described in the text. The circles, the squares and the triangles represent the results of ordered, ordered with combined correction and the disordered calculations, respectively. The experimental heats of formation [16] are shown by crosses. (b) The scalar-relativistic (filled circles) and the non-relativistic (open circles) ordering energies of Ni–Pt alloys obtained with charge-neutral calculations for both ordered and disordered alloys.

3. Results and discussion

The most important results of our calculations are shown in figure 1, where we plot the formation energies of ordered and disordered Ni–Pt alloys given by

$$E_{\text{ord(dis)}}^{\text{form}} = E_{\text{ord(dis)}}^{\text{total}} - E_{\langle\rangle}, \tag{1}$$

where $E_{\text{ord(dis)}}^{\text{total}}$ is the total energy of the ordered (disordered) Ni–Pt alloy calculated with the LMTO–ASA (KKR–ASA CPA) method, and the quantity $E_{\langle\rangle} = cE_{\text{Ni}} + (1-c)E_{\text{Pt}}$ with c being the concentration of Ni, is the average energy of the two pure elemental solids, Ni and Pt. A negative (positive) formation energy indicates that the compound is stable (unstable) with respect to phase separation. In our calculations we find that the

formation energies for ordered Ni–Pt alloys are positive for all sets of NR calculations, indicating phase separation. The results for NR charge-neutral calculations for ordered Ni–Pt alloys are shown in figure 1. The SR calculations predict Ni–Pt alloys to be stable, in agreement with experiment [16]. As for the ordered structures, the calculations carried out in (iv) are expected to be the most accurate, and it is not surprising that the corresponding formation energies are closest to the experimental values as well as to the full-potential calculations of [2].
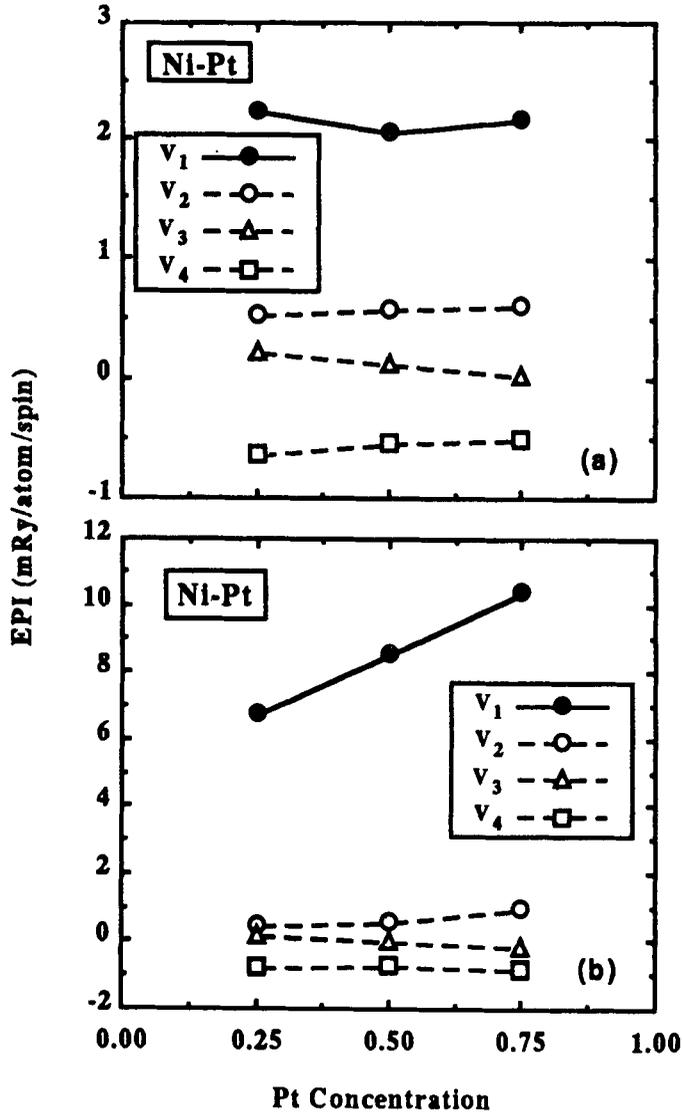

Figure 2. The scalar-relativistic effective pair interactions up to the fourth nearest neighbour obtained with (a) equal atomic spheres and (b) charge-neutral atomic spheres.

An interesting picture emerges if we consider the disordered-alloy formation energies also shown in figure 1. Within the usual applications of KKR–ASA CPA, where we use equal atomic spheres, the substitutionally disordered alloy is unstable even in the SR case. One of the reasons that make disordered Ni–Pt alloys unstable is the neglect of Madelung-type contribution to the total energy in the single-site CPA. The choice of charge-neutral spheres renders the Madelung-type contribution negligible as well as improves the ASA description of the charge density as in the ordered case. This improvement is reflected by the fact that the SR calculations done with (vi) indicate disordered Ni–Pt alloys to be stable, as can be seen from figure 1. Thus in our opinion, for metallic alloys with essentially no charge-transfer the choice of charge-neutral spheres improves the accuracy over the conventional choice of equal spheres by minimizing the error due to the neglect of Madelung-type contribution within the single-site CPA. This has been examined in some detail in [11]. The other approaches for including the Madelung-type contribution are described in [17, 18].
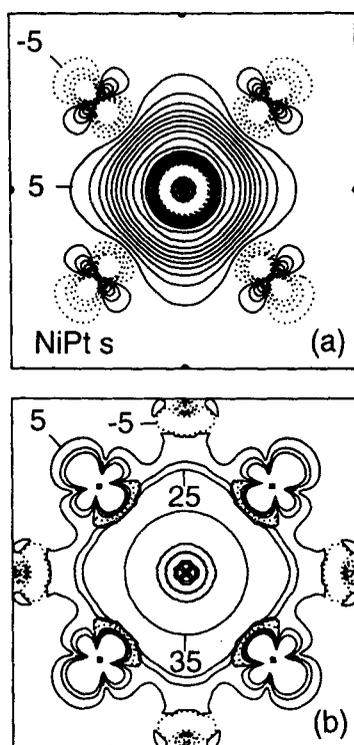
Figure 3. (a) The s-TB LMTO of $L1_0$ NiPt in (100) plane calculated scalar-relativistically at $a = 7.1$ a.u. with charge-neutral spheres. The contours are plotted at intervals of 10, and the values have been multiplied by 10^3. The filled (open) circles indicate the positions of Pt(Ni) atoms. (b) The difference in magnitude of scalar-relativistic and non-relativistic s-TB LMTOs calculated as in (a). The full (dashed) lines denote increase in SR (NR) values. The contours are plotted at an interval of 10, and the values have been multiplied by 10^4.

Surprisingly, we find that the ordering energy ΔE given by

$$\Delta E = E^{\text{form}}_{\text{ord}} - E^{\text{form}}_{\text{dis}}, \tag{2}$$

and shown in figure 1(b), is negative in all cases which implies that ordering is favoured over disordering. The point to note is that a negative ordering energy does not guarantee a stable ordered state, as can be clearly seen from figures 1(a) and (b). Hence, reliable predictions about the ordering tendencies based on methods that probe only ΔE, such as $S^2(\mathbf{k})$ [3] and generalized perturbation methods [19], can only be made in conjunction with the disordered-alloy formation energy $E^{\text{form}}_{\text{dis}}$.

The effective pair interactions up to the fourth nearest neighbour for both equal atomic spheres and charge-neutral atomic spheres are shown in figure 2. The calculated EPIs predict the stable structure in agreement with the experiments but the ordering energies as well as the ordering temperatures are much higher than that observed experimentally. These results clearly demonstrate the inadequacy of perturbative expansions such as GPM, which are based on band energy term only, for alloys with charge-transfer effects. We also like to note that the overlap effects of ASA may have undesirable effects on GPM which includes only the band energy.

Further insight into the effects of relativity on Ni–Pt system can be obtained by examining the changes in the individual terms that make up the electronic charge density, $\rho(\mathbf{r})$, namely the basis functions and the various elements of the density matrix. As shown in [10, 12] we can calculate the non-spherically averaged charge density $\rho(\mathbf{r})$ for ordered as well as disordered alloys from

$$\rho(\mathbf{r}) = \sum_{RL,R'L'} \chi^{\beta}_{RL}(\mathbf{r}_R) n^{\beta}_{RL,R'L'}(E) \chi^{\beta,*}_{R'L'}(\mathbf{r}_R), \tag{3}$$

where $\chi^{\beta}_{RL}(\mathbf{r}_R)$, $n^{\beta}_{RL,R'L'}(E)$, R and L are the LMTOs, the density matrix, site and angular momentum indices, respectively. The superscript β denotes the most-localized tight-binding (TB) representation of [10]. In the case of disordered alloys the density matrix is given by the imaginary part of the ensemble-averaged Green functions [12].

Table 1. The SR and NR lattice constants a for Ni–Pt system obtained with charge-neutral calculations. The numbers in the brackets correspond to calculations that included combined correction terms. The experimental lattice constants are also given.

|	NR	SR	Expt·
Ni	6·625 (6·576)	6·585 (6·536)	6·66
Ni$_3$Pt	7·001 (6·949)	6·849 (6·809)	
Ni$_{0.75}$Pt$_{0.25}$	7·010	6·856	
NiPt	7·392 (7·277)	7·117 (7·062)	
Ni$_{0.5}$Pt$_{0.5}$	7·366	7·122	
NiPt$_3$	7·653 (7·568)	7·364 (7·287)	
Ni$_{0.25}$Pt$_{0.75}$	7·655	7·374	
Pt	7·925 (7·816)	7·605 (7·501)	7·41

In figure 3(a) we show the s-TB LMTO in the (100) plane of $L1_0$ NiPt calculated with charge-neutral atomic spheres. Because of the contributions coming from the neighbouring sites, the orbital is spherical only close to its own site. To illustrate the effects of relativity on s-TB orbital, we have plotted in figure 3(b) the difference in magnitude of SR and NR $\chi_s^{\beta,NiPt}$. The decrease in magnitude of $\chi_s^{\beta,NiPt}$ due to relativistic effects around the nearest-neighbour (nn) Ni atoms and the second nn Pt atoms is obvious. The inclusion of relativity decreases the lattice constants of both ordered and
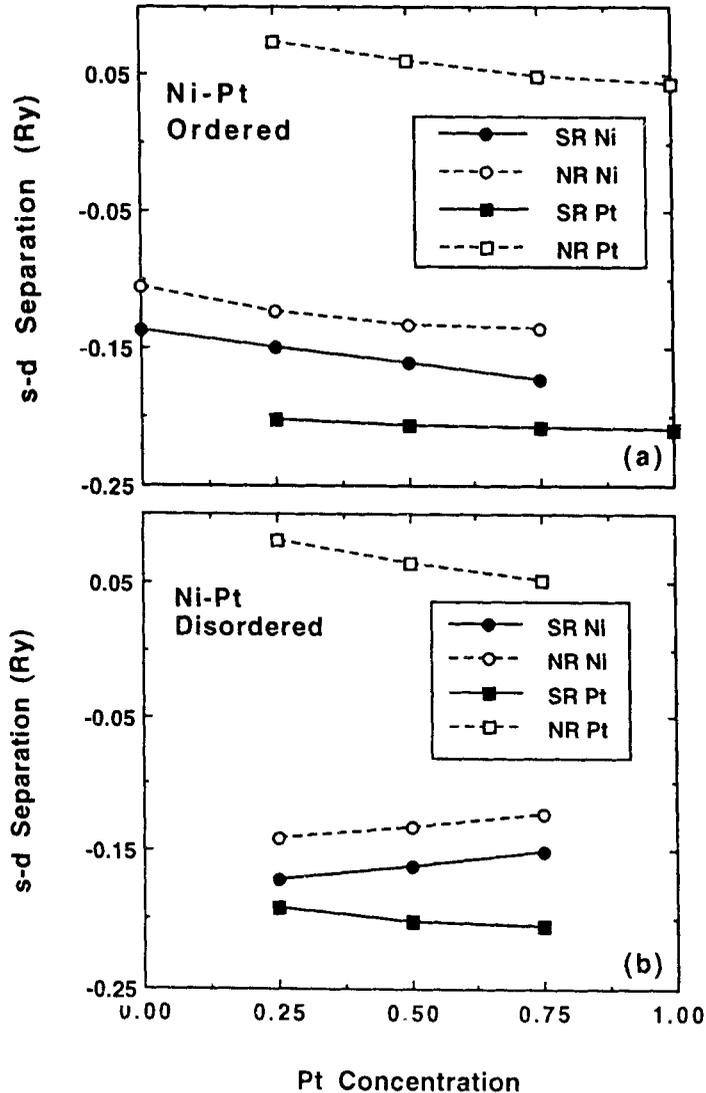
Figure 4. The scalar-relativistic and the non-relativistic separation between s and d band centres of (a) ordered and (b) disordered Ni–Pt alloys obtained with charge-neutral calculations.

disordered Ni–Pt alloys as shown in table 1. In general, the effects of R-terms on Ni are relatively small in comparison to Pt. For example, the lattice constant of bulk Pt contracts by about 4% due to relativity. Similar contractions take place for ordered and disordered Ni–Pt alloys. The contractions in the lattice constants are due to the fact that the R-terms make the potentials more attractive which pull the wave function inside, thereby reducing the overlap. The deepening of potentials is reflected in the downward movement of the centres of l-bands.

To show the effect that relativity has on the centres of l-bands, we show in figures 4(a) and (b) the separation between the centres of s and d levels of Ni and Pt atoms in the ordered and the disordered alloys, respectively. The change due to relativity in the s–d separation in the Pt sphere over the whole concentration range is ≈ 0.25 Ry, compared to ≈ 0.04 Ry in the Ni sphere. The lowering of the Pt s-band leads to increased s–d hybridization which contributes to the stability of Ni–Pt alloys.
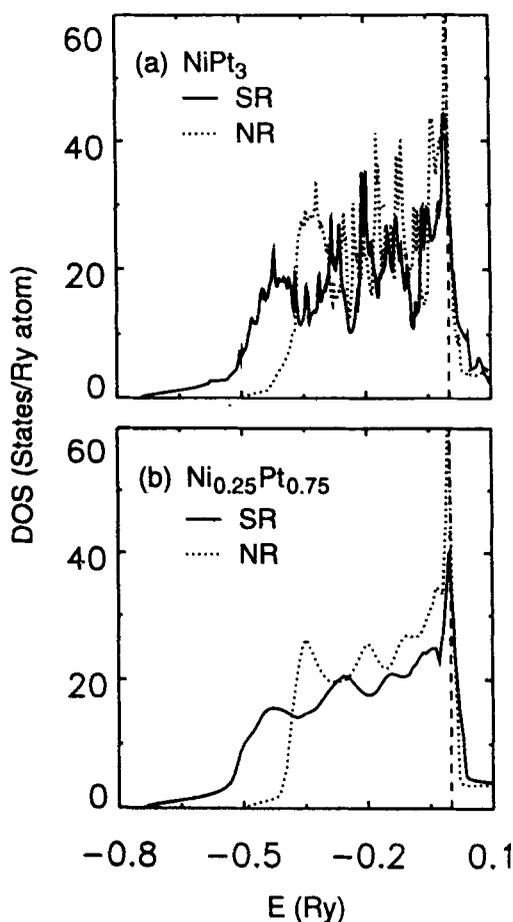
Figure 5. The scalar-relativistic (solid line) and the non-relativistic (dashed lines) total densities of states for (a) $L1_2$ NiPt$_3$ and (b) substitutionally disordered Ni$_{0.25}$Pt$_{0.75}$ calculated at their equilibrium lattice constants.

The changes in the densities of states (DOS) of ordered $NiPt_3$ and disordered $Ni_{0.25}Pt_{0.75}$ alloys due to relativity are shown in figure 5. Most of these differences arise due to the movement of the centres of l-bands due to relativistic effects and subsequent hybridizations. Not surprisingly, these effects get larger as the concentration of Pt is increased. The corresponding results for NiPt are given in [1]. Figure 5 demonstrates the importance of relativity for describing correctly the electronic structures of ordered as well as disordered Ni–Pt alloys.

We have discussed the effects of relativity on the basis functions and the densities of states of Ni–Pt alloys. The changes in the nonspherical charge density due to relativity incorporates changes in the basis functions and the densities of states as well as the changes in the off-diagonal matrix elements of the density matrix, thereby characterizing completely the effects of relativity on the system.

4. Conclusions

Based on our recently formulated approach that provides a consistent and unified framework for studying the electronic structure of ordered as well as disordered alloys, we have examined the effects of mass-velocity and Darwin terms on ordered Ni_3Pt, NiPt and $NiPt_3$ and substitutionally disordered $Ni_{0.75}Pt_{0.25}$, $Ni_{0.5}Pt_{0.5}$ and $Ni_{0.25}Pt_{0.75}$. For both ordered and disordered Ni–Pt alloys we find that (i) the inclusion of mass-velocity and Darwin terms is essential and (ii) the changes induced by these terms mainly affect the s- and d-electrons of Pt.

Acknowledgements

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