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# Relativity-Induced Ordering and Phase Separation in Intermetallic Compounds.

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**Abstract.** – The formation enthalpies of ordered compounds and the mixing enthalpies of random alloys were calculated for Ni-Au, Ni-Pt, and Au-Pt using an Ising-like cluster expansion based on the local-density formalism. We show that relativity i) induces long-range order in Ni-Pt due to a reduction in packing strain and enhancement of *s*-*d* coupling, but ii) it leads to phase separation in Au-Pt due to suppression of the $\mathrm{Au}(s,p) \rightarrow \mathrm{Pt}(d)$ charge transfer.

Despite their profound effects on atomic and molecular spectroscopy [1], relativistic effects have so far been implicated only in rather minor, quantitative corrections to the phase stability of compounds. Using a statistical-mechanics description of effective interatomic interactions deduced from first-principles local-density calculations, we illustrate here how relativistic mass velocity and Darwin effects are responsible for long-range crystallographic order in NiPt and for phase separation in AuPt. The general method of analysis presented here further permits a clear identification of the classic metallurgical stability factors in compounds (size mismatch, relaxation, and charge transfer) in terms of a first-principles electronic-structure theory.

The central energetic quantities used in the theoretical discussion of phase stability [2-5] are the formation enthalpy $\Delta H_{\mathrm{F}}(\sigma_x)$ of the ordered (ord) compound A/B in structure $\sigma$ and the mixing enthalpy $\Delta H_{\mathrm{mix}}(x)$ of a random (rand) alloy $\mathrm{A}_{1-x}\mathrm{B}_x$ of composition $x$. These are defined as the excess energies taken with respect to the equivalent amounts of the solid constituents A and B at their equilibrium volumes $V_{\mathrm{A}}$ and $V_{\mathrm{B}}$:

$$\Delta H_{\mathrm{F}}(\sigma_x) = E_\sigma(\mathrm{ord}) - [(1-x)E_{\mathrm{A}} + xE_{\mathrm{B}}], \tag{1}$$

$$\Delta H_{\mathrm{mix}}(x) = E_\sigma(\mathrm{rand}) - [(1-x)E_{\mathrm{A}} + xE_{\mathrm{B}}]. \tag{2}$$

The «ordering energy» is defined as the difference

$$\delta E_{\mathrm{ord}}(\sigma_x) = \Delta H_{\mathrm{F}}(\sigma_x) - \Delta H_{\mathrm{mix}}(x). \tag{3}$$

If $\delta E_{\mathrm{ord}} < 0$, the random alloy could develop short-range order of the type underlying the structure $\sigma$. When $\Delta H_{\mathrm{F}}(\sigma) < 0$, the long-range–ordered configuration $\sigma$ could become a stable «ground-state structure», whereas $\Delta H_{\mathrm{F}}(\sigma) > 0$ means that the ordered structure $\sigma$ is unstable with respect to phase separation into A and B.

Further insight into of the factors governing such stability trends can be obtained by decomposing the energies (1)-(3) into a sequential process (*e.g.*, ref. [6]), as follows:

*First*, deform hydrostatically pure A and B from their equilibrium volumes $V_A$ and $V_B$ to the volume $V_\sigma$ akin to the final compound $\sigma$ with composition $x$. In doing so we invest a «volume deformation» (VD) energy $\Delta E_{VD}$: it vanishes if the constituents are size-matched ($V_A = V_B \equiv V_\sigma$) and is *positive* (*i.e.* promotes phase separation) othervise. Since, to within a good approximation, the molar volumes of structures at the same composition are equal [6], $\Delta E_{VD}$ depends essentially on the composition $x$ but not on the atomic configuration $\sigma$.

*Second*, permit A($V_\sigma$) and B($V_\sigma$), both prepared at the final volume $V_\sigma$, to form the compound $\sigma(V_\sigma)$ in its ideal structure. In this constant-volume and constant-geometry reaction one permits charge-transfer, the formation of hybridized energy bands, etc.; the energy change will thus be called the «charge exchange» (CE) energy $\Delta E_{CE}$.

*Finally*, permit the atoms in configuration $\sigma$ to relax to their energy-minimizing positions. Such strain-relieving relaxations (REL) change the energy by $\Delta E_{REL}(\sigma)$. This includes both cell-internal displacements as well as cell-external deformation (*e.g.*, changing the $c/a$ ratio in the $L1_0$ structure). Like the volume deformation, the energy $\Delta E_{REL}(\sigma)$ too tends to vanish for size-matched systems. In contrast to $\Delta E_{VD}$, however, relaxations depend on the atomic configuration $\sigma$ and are energy lowering (*i.e.* promote ordering).

We will compute the above-mentioned components of $\Delta H$

$$\Delta H_F(\sigma) = \Delta E_{VD}(x) + \Delta E_{CE}(\sigma) + \Delta E_{REL}(\sigma) \tag{4}$$

*directly from their definitions* as differences in the appropriate total energies, thus quantitatively isolating various factors governing phase stability. We will further repeat the calculations using a constrained Hamiltonian (*e.g.*, relativistic *vs.* nonrelativistic) finding how certain electronic interactions affect phase stability.

To calculate the mixing enthalpy $\Delta H_{mix}(x)$ of the random alloy, we use an Ising-like cluster expansion [7]. The alloy is treated as a lattice problem whereby configuration $\sigma$ is defined by specifying the occupation of each of the $N$ lattice sites $i$ by an A atom (where the spin variable is $\hat{S}_i = -1$) or a B atom ($\hat{S}_i = 1$). The energy of any of the $2^N$ configurations can be [8] mapped into an Ising Hamiltonian

$$E_{Ising}(\sigma) = J_0 + \sum_i J_i \hat{S}_i(\sigma) + \sum_{j<i} J_{ij}\hat{S}_i(\sigma)\hat{S}_j(\sigma) + \sum_{k<j<i} J_{ijk}\hat{S}_i(\sigma)\hat{S}_j(\sigma)\hat{S}_k(\sigma) + \dots, \tag{5}$$

where the $J$'s are effective interaction energies for sites, pairs and three-body (first, second, and third sums, respectively), etc. The interaction energies are found by mapping eq. (5) onto a set of *directly calculated* formation energies $\Delta H_F(\sigma)$ for $N_\sigma$ structures

$$\sum_\sigma^{N_\sigma} \omega_\sigma [\Delta H_F(\sigma) - E_{Ising}(\sigma)]^2 = \min. \tag{6}$$

Here, $\Delta H_F(\sigma)$ is calculated from eq. (1) using the local-density formalism, and $\omega_\sigma$ is the symmetry-mandated weight [9] of structure $\sigma$. We include in eq. (5) $N_F$ trial «figures» $F$ (pairs, three-body, four-body) and $N_\sigma$ structures. Solving eq. (6) we find a set of interactions $\{J_F\}$. Their transferability is then examined by using them to predict via eq. (5) the energy of a *new* set of structures $\{\sigma'\}$ (not included in eq. (6)). Convergence is tested by comparing these predictions with the directly calculated $\Delta H_F(\sigma')$ values of eq. (1). Lattice relaxation slows down the convergence of the Ising expansion. Reference [10] showed how a $k$-space representation leads to a better convergence. The energy of the perfectly random alloy is then found by taking the configurational average of eq. (5), *i.e.* $\Delta H_{mix}(x) = \langle \Delta E_{Ising}(\sigma)\rangle$. To calculate $\Delta H_{mix}(x, T)$ at finite temperature we solve eq. (5) using the tetrahedron cluster variation method as described in ref. [9].

Since the input to eq. (6) is a set $\{\Delta H_F(\sigma)\}$ of formation enthalpies for *ordered* compounds, and since each of these can be decomposed according to eq. (4), the final random alloy energy $\Delta H_{\text{mix}}(x)$ can also be represented in the form (5). Consequently, the «ordering energy» of eq. (3) can be expressed as

$$\delta E_{\text{ord}}(\sigma) = [\Delta E_{\text{CE}}(\text{ord}) - \Delta E_{\text{CE}}(\text{rand})] + [\Delta E_{\text{REL}}(\text{ord}) - \Delta E_{\text{REL}}(\text{rand})], \tag{7}$$

permitting its analysis in terms of *excess* relaxation and charge exchange relative to the random alloy. Note that $\delta E_{\text{ord}}(\sigma)$ does not depend on the volume deformation $\Delta E_{\text{VD}}$.

While the direct inversion cluster expansion formalism of eqs. (5), (6) has been previously used to predict ground-state structures and phase diagrams of semiconductor [11] and transition metal compounds [9], we use it here for the first time in the context of the microscopic decomposition (eqs. (4) and (7)), as a tool for analyzing the *electronic origins of phase stability* in intermetallic compounds. The binary structures formed in the Ni-Pt-Au group are particularly challenging in this respect: i) While $d$-band filling arguments [4] suggest that all alloys of late transition metals will phase-separate (rather than order) at low temperatures (since the antibonding part of the $d$ band is nearly filled), NiPt exhibits strong $L1_0$ ordering [12]. ii) While charge transfer and hybridization were predicted to lead to long-range ordering in NiPt [9], the NiAu system that has a 50% larger electronegativity difference is *known* to phase-separate [12]. iii) However, despite its phase separation at low temperatures [12], NiAu exhibits $L1_0$-type short-range order at high temperatures [13].

We have carried out the formalism described here using in eq. (6) the $N_\sigma = 8$ structures: f.c.c. (A and B), $L1_2$ ($A_3B$ and $AB_3$), $L1_0$, $L1_1$, the bilayer $A_2B_2$ (001) superlattice termed $Z2$, and bilayer $A_2B_2$ (012) superlattice. The $N_F$ figures used in eq. (5) are i) $J_0$ and $J_1$ («empty» and single site), ii) the first four pair interactions between first through fourth neighbors, and iii) the first three- and four-body terms. Total energies are calculated using the spin-restricted local-density scalar-relativistic theory, as implemented by the general potential linearized augmented plane wave (LAPW) method [14] with the Wigner exchange correlation potential. We include mass velocity and Darwin terms but neglect spin-orbit coupling which has a small effect (¹) on the formation energies. Inside the muffin-tin spheres, the nonspherical charge density and potential are expanded in terms of lattice harmonics of angular momentum up to $l \leq 8$. A basis set of about $\sim 90$ LAPWs/atom is used. The Brillouin-zone integrations are performed using equivalent $k$ points, thereby assuring equal sampling for the compounds and their f.c.c. constituents. These sets are equivalent to 60 special $k$ points in the f.c.c. structure. All structures are fully relaxed. The maximum convergence error in $\Delta H$ is estimated to be $\leq 10$ meV/atom. The reliability of the results is reflected in part by the agreement of the calculated $\Delta H_{\text{mix}}(1/2, T_m)$ with experiment (given in parentheses, measured at $T_m$). We find for NiPt at $T_m = 298$ K $\Delta H = -98.9$ meV/atom ($-96.1$ [15]), for NiAu at $T_m = 1150$ K $\Delta H = +85.9$ ($+78.4$ [12]), and for AuPt at $T_m = 1400$ K $\Delta H = +47.5$ ($+38.9$ [16]). The calculated $c/a$ ratio for the $L1_0$ structure of NiPt is 0.933, in close agreement with the experimental value of 0.939 [17]. Our results for $\Delta H_F$ differ in some cases from previous studies which used spherical potentials. Using a spherical approximation to the crystal potential, ref. [5] finds *negative* $\Delta H_F$ for the B2 form of AuPt ($-43$ meV/atom) and for $Au_3Pt$ in the $L1_2$ structure ($-22$ meV/atom). Our full potential calculation gives $+132.1$ and $+41.5$ meV/atom, respectively. Muffin-tin calculations using variable muffin-tin radii for different structures of the same compound

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(¹) The spin-orbit interaction has only a minor effect on the $T = 0$ formation energy, *i.e.* changing it for NiPt in the $L1_0$ structure from $-95.7$ to $-92.5$ meV/atom.

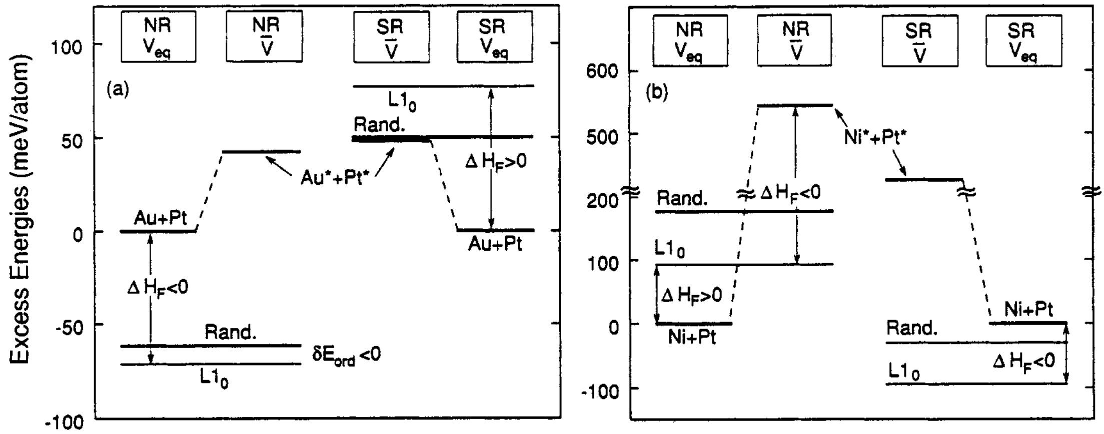

Fig. 1. – Calculated relaxed excess energies of *a*) $Au_{0.5}Pt_{0.5}$ and *b*) $Ni_{0.5}Pt_{0.5}$. We show separately nonrelativistic (NR) and scalar-relativistic (SR) results. The energies of the constituents are calculated both at their equilibrium volumes $V_{eq}$ (the energy zero) as well as at the 50%- 50% volume ($\bar{V}$). See eqs. (1)-(3).

produce large errors relative to a full potential calculation. For example, Amador *et al.* [18] find $\Delta H_F(L1_1) = -80.2$ and $\Delta H_F(Z2) = -53$ meV/atom for NiPt, while our full potential calculation gives $\Delta H_F(L1_1) = -29.5$ and $\Delta H_F(Z2) = +3.2$ meV/atom, respectively.

The main results of this work are illustrated in fig. 1. They show the excess energies of the random alloy and of ordered compounds as obtained in a nonrelativistic and scalar-relativistic calculations. The ordering energy can be read off as the difference (eq. (3)) between ordered and random energies. To isolate the effects of volume deformation, we show in each figure the energy of A + B before and after they are volume deformed. Table I gives the decomposition of eqs. (4) and (7) for ordered and disordered structures. Our analysis shows the following features:

i) A *nonrelativistic* description of NiPt predicts phase separation as the ground state, despite the fact that the ordering energy $\delta E_{ord}(L1_0)$ is negative. Neglecting $\Delta E_{VD}$ and $\Delta E_{REL}$, Pinski *et al.* [3] have previously calculated nonrelativistically the finite-temperature generalization of $\delta E_{ord}$ and from it the long-range order (LRO). They predict an ordering transition into the $L1_0$ structure at the temperature of $T_c \sim 1500$ K. However, since the nonrelativistic description used by them gives $\Delta H_F(L1_0) > 0$ (table I), the system must phase-separate rather than order. Hence, a correct nonrelativistic description does not produce LRO at any temperature. This illustrates the fact that neglect of relaxation [3] can lead to large errors in order-disorder transition temperatures, and that, in general, LRO cannot be predicted from a theory of $\delta E_{ord}$. A similar conclusion is apparent in the relativistic description of NiAu (table I): we find that $\Delta H_F(L1_0) > 0$ despite $\delta E_{ord}(L1_0) < 0$. This is consistent with the observation of (001) short-range order in high-temperature NiAu alloys which phase-separates at lower temperatures [13].

ii) The reason why the nonrelativistic ground state of NiPt is phase separation is the dominance of volume deformation over charge exchange and relaxation (table I). Indeed, the calculated nonrelativistic lattice constants of the f.c.c. constituents ($a_{Ni} = 3.479$ Å and $a_{Pt} = 4.107$ Å) show a large (16.6%) relative size mismatch leading to a large destabilizing $\Delta E_{VD}$. Relativity stabilizes NiPt for two reasons. First, it reduces the size mismatch to 12.9%: we find $a_{Ni} = 3.459$ Å and $a_{Pt} = 3.935$ Å (compared with measured values of 3.524 Å and 3.923 Å, respectively). The relativistic reduction in size mismatch leads to a reduction in $\Delta E_{VD}$, hence

TABLE I. - *Contributions of volume deformation* (VD), *charge exchange* (CE), *and relaxation* (REL) *to the excess enthalpies* (*eqs.* (4) *and* (7)). *Results are in* meV/atom.

| | Nonrelativistic | | Relativistic | |
|---|---|---|---|---|
| | $L1_0$ | Random | $L1_0$ | Random |
| $Ni_{0.5}Pt_{0.5}$ | | | | |
| $\Delta E_{VD}$ | + 543.6 | + 543.6 | + 426.8 | + 426.8 |
| $\Delta E_{CE}$ | − 398.4 | − 307.0 | − 504.5 | − 403.3 |
| $\Delta E_{REL}$ | − 51.6 | − 60.5 | − 18.0 | − 53.8 |
| $\Delta H$ | + 93.6 | + 176.1 | − 95.7 | − 30.3 |
| $\delta E_{ord}$ | − 82.5 | — | − 65.4 | — |
| $Au_{0.5}Pt_{0.5}$ | | | | |
| $\Delta E_{VD}$ | + 42.3 | + 42.3 | + 48.6 | + 48.6 |
| $\Delta E_{CE}$ | − 113.5 | − 103.5 | + 28.2 | + 1.5 |
| $\Delta E_{REL}$ | ~ 0 | ~ 0 | ~ 0 | ~ 0 |
| $\Delta H$ | − 71.2 | − 61.2 | + 76.8 | + 50.1 |
| $\delta E_{ord}$ | − 10.0 | — | + 26.7 | — |
| $Ni_{0.5}Au_{0.5}$ | | | | |
| $\Delta E_{VD}$ | + 722.2 | + 722.2 | + 561.8 | + 561.8 |
| $\Delta E_{CE}$ | − 337.8 | − 283.8 | − 464.8 | − 369.2 |
| $\Delta E_{REL}$ | − 11.9 | − 82.5 | − 20.2 | − 68.3 |
| $\Delta H$ | + 372.5 | + 355.9 | + 76.8 | + 124.3 |
| $\delta E_{ord}$ | + 16.6 | — | − 47.5 | — |

stabilization. The same effects exist in other compounds in which only *one* of the two elements is heavy; see, for example, $\Delta E_{VD}$ in NiAu, table I. Second, relativity leads to a significant lowering of $\Delta E_{CE}$. Examination of the density of states and charge transfer shows the reason: relativistic effects lower the Pt *s* band more than the Ni *s* band, leading to a more effective Ni → Pt charge transfer and *s*-*d* hybridization. The combined effect of reduced repulsiveness of $\Delta E_{VD}$ and increased attractiveness of $\Delta E_{CE}$ leads in a relativistic description to a negative $\Delta H_F(L1_0) = -95.7\,\text{meV/atom}$, *i.e.* ordering.

iii) A *nonrelativistic* description of AuPt leads to ordering, while a relativistic description leads to the observed [12] phase-separating behavior: the reason is again twofold. First, while relativity does not significantly change the lattice mismatch if both atoms are heavy, it raises significantly the bulk moduli $B$ of heavy elements: nonrelativistically $B_{Pt} = 1.79$ Mbar and $B_{Au} = 1.03$ Mbar, while relativistically $B_{Pt} = 2.87$ Mbar and $B_{Au} = 1.83$ Mbar. (The measured values are 2.78 Mbar and 1.73 Mbar, respectively.) This leads to a (small) relativistic *increase* in $\Delta E_{VD}$, hence destabilization. Second, relativity *diminishes* strongly the stabilizing effects of charge exchange in AuPt (indeed, it even changes the sign of $\Delta E_{CE}$; see table I). The reason is evident by inspecting the calculated electronic structure of f.c.c. Au, Pt and $L1_0$ AuPt (all evaluated at the same $L1_0$ atomic volume): Au has 11 valence electrons and exhibits *s*-like states at the Fermi surface, while Pt has only 10 valence electrons and exhibits *d* states at the Fermi surface. In a nonrelativistic description there is a significant stabilizing charge transfer from the higher Au *s*-*p* band into the Pt *d* band (the calculated excess charge $\Delta Q_l^\alpha = Q_l^\alpha(L1_0) - Q_l^\alpha(\text{f.c.c.})$ in the $\alpha$-th muffin-tin sphere is $\Delta Q_d^{Pt} = 0.13\,e$). However, relativity shifts the Au *s* band to deeper binding energies; this band is then less able to provide charge to the Pt *d* band (the Pt charge now comes predominantly from the Au *d* band). Hence, ordered AuPt is less stable in a relativistic description.

Considering the Au-Ni-Pt triangle, we conclude that when *both* elements are heavy (AuPt), relativity promotes phase separation through *increased* $\Delta E_{\mathrm{VD}}$ and *diminished* $\Delta E_{\mathrm{CE}}$, while when only one of the two elements is heavy (NiPt and NiAu), relativity *reduces* $\Delta E_{\mathrm{VD}}$ and *increases* $\Delta E_{\mathrm{CE}}$, thus contributing to ordering.

iv) Relaxation can have a profound effect both on the short-range order (underlying $\delta E_{\mathrm{ord}}$) and on the LRO. Table I shows for example that a nonrelativistic description of NiAu gives $\delta E_{\mathrm{ord}}(L1_0) = \Delta E_{\mathrm{CE}}(L1_0) - \Delta E_{\mathrm{CE}}(\mathrm{rand}) < 0$ in the absence of relaxation. In contrast, when relaxation is permitted one finds $\delta E_{\mathrm{ord}}(L1_0) > 0$ (since the random alloy relaxes more than the ordered $L1_0$ structure). In general the relaxation energy depends strongly on the symmetry of the structure: $\Delta E_{\mathrm{REL}}$ for the $L1_0$, $L1_1$, and the $Z2$ structures are $-20.2$, $-28.0$, and $-177.8$ meV/atom in NiAu, and $-18.0$, $-24.5$, and $-134.0$ meV/atom in NiPt. The neglect of relaxation effects by previous methods [2-4] can hence cloud the predictions of both formation energies and ordering energies.

The method illustrated here offers a general way of analyzing trends in phase stability in terms of electronic-structure constructs obtained from first-principles studies.

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