Long-Range Order in Binary Late-Transition-Metal Alloys

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A ground-state search of a generalized, many-body Ising Hamiltonian whose interaction energies are determined from first-principles local-density calculations reveals that PtX intermetallics for X=Ni, Cu, Rh, and Pd will form stable *ordered* structures at low temperatures. In contrast, d-band tight-binding models universally predict phase separation in all late-transition-metal alloys. It is shown that the previously neglected s-electron cohesion is responsible for this phase stability.

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Voluminous catalogs of phase diagrams of binary transition-metal (TM) alloys[1,2] have instigated many attempts to identify global phenomenological trends and explain them in terms of microscopic constructs.[3-7] One such well-known[4-7] regularity is that systems where both constituents have nearly filled d shells ("late TM's"), have *positive* mixing enthalpies ΔH, and should show, at low temperatures, phase separation rather than long-range ordering. This has been explained in terms of tight-binding d-band-filling arguments:[4-7] It was found that even in the absence of size mismatch between the constituents,[6] occupation of the upper "antibonding" part of the d band leads universally to $\Delta H > 0$ for all late TM's with an average d-electron count $\bar{N} \geq 8$.

The actual situation appears to be more complex, as illustrated, for example, by the phase behavior of binary alloys of Pt with its neighboring elements in the periodic table.[1,2] First, even discarding for a moment "special cases" such as the ordering Pt-Cu and Pt-Ag intermetallics[1] that contain a noble metal, or the ordering[1,2] Pt-Co system which is complicated by a magnetic behavior over a wide composition range, the fact that even the nonmagnetic $Pt_{0.5}Ni_{0.5}$ alloy orders defies all current d-band theories.[5,7] While it is certainly possible to fit the observed Pt-Ni phase diagram with an Ising model,[8] attempts to explain even the *sign* of the Ising interaction energies required to produce the fit have all failed.[7] Second, while Pt-Rh and Pt-Pd were surmised[1,4] to phase separate, examination of the original data[9] shows that no evidence exists to this effect (they were measured only at very high temperatures where solid solutions exist[1]), except for a suggestive extrapolation from the known behavior of Pd-Rh and Pd-Ir. In fact, measurements on Pt-Pd have shown *negative* mixing enthalpies[10] and clear evidence in x-ray diffuse scattering[11] for a substantial degree of short-range order which remains unexplained. Such structural preferences in intermetallic compounds can be addressed by highly precise total-energy calculations based on the local-density approximation (LDA).[12,13] There, one selects for each intermetallic compound a few intuitively appealing candidate crystal structures and computes for each the equilibrium total energy, selecting the lowest. However, one is left to wonder whether other structures, not included in the trial set, might lead to yet lower energies, or if a combination of two (ordered or disordered) structures could be stabler than a single structure of the same average composition. Addressing such possibilities requires a "ground-state search"[14,15] among the astronomically large number (e.g., 2^N for a binary lattice with N sites) of possible configurations on a given lattice.

Recently, "first-principles statistical-mechanics" approaches have been developed,[16,17] combining a construction of an Ising-like cluster expansion whose multisite interaction energies are calculated from the LDA, with a systematic ground-state search among many possible structures. We apply this approach here to a number of binary late-TM alloys. We select Pt-Pd and Pt-Rh (which were expected[1,4,6,9] to phase separate, but at least Pt-Pd does not[10,11]), Pd-Rh (which is *known* both experimentally[9,18] and theoretically[15] to phase separate), Pt-Ni (which is expected theoretically[5,7] to phase separate, but is known[1] to order), and Pt-Cu (known experimentally[1,2] to order but was not treated previously theoretically). We find that (i) the rule[4-7] of "phase separation among the late-TM alloys" is broken not only in Pt-Ni and Pt-Cu, but also in Pt-Pd and Pt-Rh, while (ii) Pd-Rh is correctly shown elsewhere[4,6,15] and here to phase separate, (iii) $Pt_{0.5}Cu_{0.5}$ orders in the trigonal $L1_1$ structure[19] found experimentally,[1,2] and (iv) the ordered low-temperature ground-state structure of $Pt_{0.5}Pd_{0.5}$ is predicted to be $L1_0$, while that of $Pt_{0.5}Rh_{0.5}$ is predicted to be the $I4_1/amd$ structure (denoted previously[14] as "40"). We suggest, based on model calculations, that previously ignored[4-8] s-electron effects are responsible for ordering in these Pt-bearing intermetallics.

We expand the excess energy $\Delta E(\sigma,V)$ of any configuration σ of A and B atoms on the fcc lattice

$$\Delta E(\sigma,V)=E(\sigma,V)-(1-x)E(A,V_A)-xE(B,V_B) \quad (1)$$

in terms of volume- (V-) dependent effective cluster interactions[16,20] as

$$\Delta E(\sigma,V)=\sum_k\sum_m[\bar{\Pi}_{k,m}(\sigma)-\eta]J_{k,m}(V)\,. \quad (2)$$

Here, $\Delta E(\sigma,V)$ is the energy with respect to equivalent amounts of solid A and B at their respective equilibrium

TABLE I. LAPW-calculated relaxed (except for Rh-Pt which is unrelaxed) formation enthalpies [Eq. (1)] of the $A_{1-x}B_x$ intermetallics in various structures defined in Ref. 19. Fitting these by Eq. (2) using eight interaction energies results in small standard deviation χ given here for both unrelaxed (U) and relaxed (R) configurations. Fitted values are illustrated for PdPt and PdRh (in parentheses). The last line gives the calculated high-temperature mixing enthalpies of the disordered alloys at $x=\frac{1}{2}$. All results are in meV/atom.

Structure	$\mathrm{Pd}_{1-x}\mathrm{Pt}_x$	$\mathrm{Pd}_{1-x}\mathrm{Rh}_x$	$\mathrm{Rh}_{1-x}\mathrm{Pt}_x$	$\mathrm{Cu}_{1-x}\mathrm{Pt}_x$
fcc (A)	0.0 (0.0)	0.0 (0.0)	0.0	0.0
$L1_2$ (A_3B)	−30.4 (−27.5)	66.8 (76.2)	−20.4	−115.8
DO_{22} (A_3B)	−22.1 (−23.1)	69.0 (65.9)	−25.2	−97.6
$\beta 1$ (A_2B)	−28.2 (−30.2)	72.5 (58.0)	−10.0	−66.4
$L1_0$ (AB)	−39.5 (−40.2)	82.4 (91.5)	−16.5	−98.9
$L1_1$ (AB)	−29.1 (−29.1)	79.0 (79.0)	−3.9	−128.9
40 (A_2B_2)	−32.1 (−31.4)	70.7 (70.9)	−29.5	−63.8
$Z2$ (A_2B_2)	−24.7 (−24.0)	35.1 (44.6)	−0.4	−43.0
$\beta 2$ (AB_2)	−30.4 (−29.8)	64.2 (59.7)	−4.3	−79.0
DO_{22} (AB_3)	−29.1 (−29.5)	63.8 (66.5)	−13.0	−65.9
$L1_2$ (AB_3)	−35.1 (−33.9)	85.0 (76.8)	−10.8	−96.3
fcc (B)	0.0 (0.0)	0.0 (0.0)	0.0	0.0
χ_U	1.0	5.3	2.1	4.1
χ_R	1.1	7.1	$\cdots$	7.0
$\Delta H_{\mathrm{mix}}(\frac{1}{2})$	−28.2	65.0	−11.6	−76.0

volumes V_A and V_B, $J_{k,m}(V)$ is the volume-dependent effective k-body interaction energy within a cluster of atoms separated by up to the mth neighbor distance, $\overline{\Pi}_{k,m}(\sigma)$ is the lattice-averaged spin products[17] for cluster (k,m) in configuration σ, and η equals $2x-1$ when k is odd and 1 when k is even. Rather than *define*[20] $\Delta E(\sigma,V)$ by the expansion of Eq. (2), we calculate $\Delta E(s,V)$ of Eq. (1) for N_s ordered structures s, using the LDA as implemented by the semirelativistic linearized augmented plane-wave (LAPW) method.[21] This set $\{\Delta E(s,V)\}$ is then mapped onto Eq. (2) thereby defining[16] a "renormalized" (volume-dependent) set $\{J_{k,m}(V)\}$. A recent test[22] of this approach for the case where $E(\sigma)$ equals the Madelung lattice energies (where exact results are available for comparison) showed that even in this extreme case where the *bare* interactions are long range, the *renormalized* energies $\{J_{k,m}\}$ obtained in the present way are rapidly decaying with distance. We use $N_s=12$ ordered configurations given in the first column of Table I and described in Ref. 19. In all cases we consider both "unrelaxed" configurations (where all atoms are assumed to be on the ideal fcc or bcc sites) and "relaxed" structures (all internal coordinates are optimized at each volume V). In the LAPW calculation we use the Wigner exchange-correlation potential, a basis set consisting of 100 LAPW's/atom, and a Brillouin-zone **k**-point sampling set consisting of 60–200 points (depending on the structures). The resulting LAPW error in *relative* energies is estimated at 10 meV/atom. These twelve equation of states are then used in a weighted least-squares fit by Eq. (2) to extract the first eight interaction energy functions $J_{k,m}(V)$. These include (i) the "empty figure" $(k,m)=(0,0)$ and single-site figure $(k,m)=(1,0)$, (ii) the first four pair ($k=2$) interactions $(k,m)=(2,1)$, (2,2), (2,3), and (2,4) between first through fourth fcc neighbors, respectively, and (iii) the lowest-order three-body (3,1) and four-body (4,1) terms. Table I gives the LAPW-calculated equilibrium values of $\Delta E(s,V_{\mathrm{eq}})$ (formation enthalpies ΔH) and shows that the fit by Eq. (2) is at least as accurate as the underlying LAPW calculations for both unrelaxed and fully relaxed structures. Hence, this set of $\{J_{k,m}\}$ represents the full informational content of the underlying total energies.

To test the transferability of $\{J_{k,m}\}$ we have recalculated these from a *subset* of $N_s=10$ (out of a total of 12) of our ordered structures, then used these new J's to *predict* through Eq. (2) the formation enthalpies of the *remaining* two structures, not included in the fit. Testing a number of different choices of 10 out of 12 structures gives an average "prediction error" (relative to direct LAPW calculations) that is comparable to the underlying error of LAPW itself. We can hence use these sets of $\{J_{k,m}\}$ to predict through Eq. (2) the energies of *arbitrary* fcc lattice configurations that are too numerous and often to complex to directly calculate by the LDA.

The effective interactions resulting from the full fits are depicted in Fig. 1. They show (i) rather rapid decay with interatomic distance; (ii) that the dominant interactions are "ferromagnetic" ($J<0$, i.e., repulsive) in Pd-Rh, indicating phase separation, but "antiferromagnetic" (attractive) in Pt-Cu, Pt-Pd, and Pt-Rh, indicating ordering; and (iii) significantly different $J_{2,1}/J_{2,m>1}$ ratios in Pt-Cu, Pt-Pd, and Pt-Rh, implying[14] different types of ordering vectors. We use these effective interaction energies to perform a ground-state search[17] comparing $2^{16}=65\,536$ structures. The resulting ground-state lines are

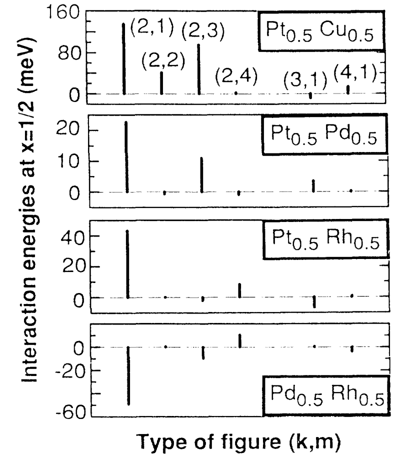

FIG. 1. Calculated k-body mth-neighbor cluster interaction energies $J_{k,m}$ at $x=\frac{1}{2}$.

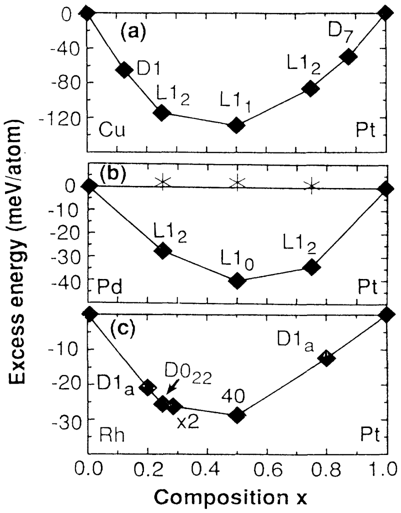

FIG. 2. Predicted $T=0$ ground states (diamondlike symbols) as a function of composition. The structures are defined in Ref. 19. Crosses in part (b) show nonrelativistic results that indicate instability.

shown in Fig. 2. These show that (i) Pd-Rh phase separates, as found experimentally[9,18] and by other calculations[15] (the trivial horizontal ground-state line at $E=0$ is not shown in Fig. 2), but (ii) Pt-Cu, Pt-Pd, and Pt-Rh are found to order in [111]-, [001]-, and $[10\frac{1}{2}]$-ordering vectors, respectively,[19] in conflict with expectations based on the d-band tight-binding model.[4,5] For $\mathrm{Pt_{0.5}Cu_{0.5}}$ we correctly[1,2] find trigonal $L1_1$ ordering showing that our expansion captures the delicate competition between trigonal ($L1_1$) and tetragonal ($L1_0$) structures (we find, however, that $L1_0$ is stabler than $L1_1$ within the nearest-neighbor approximation of Ref. 16). No low-temperature data exist for Pt-Rh. For $\mathrm{Pt_{0.51}Pd_{0.49}}$, x-ray diffuse-scattering experiments[11] revealed significant short-range order in the nominally disordered alloy; while the crystal structure (or phase diagram) was not determined, the average number of Pt first neighbors to Pd is consistent with tendencies to order in the structure predicted here. (iii) An analogous but less extensive non-spin-polarized calculation for Pt-Ni found a clear ordering behavior of the $L1_0$ type, in conflict with previous tight-binding based theories,[7] but in agreement with experiment.[1,2] Clearly, the simple rule predicting phase separation for nearly filled d-electron alloys is not general. It is interesting to note that our ground-state search also identifies new structures that were *not used* to determine the interaction energies, e.g.,[19] $D1$ and $D7$ for Cu-Pt, and $D1_a$ and $X2$ for Rh-Pt.

Using the set of interaction energies $\{J_{k,m}\}$, we have solved the spin-$\frac{1}{2}$ fcc generalized Ising model in the cluster-variation method[17] (CVM), evaluating the configurational entropy by folding interactions within figures that are larger than the tetrahedron (this method agrees closely with Monte Carlo simulations; see Fig. 15 in Ref. 17). Of the systems studied here in detail we display finite-temperature results only in the cases where experimental data are available for comparison. Figure 3(a) compares for Pd-Rh the calculated phase diagram with experiment.[18] The agreement is reasonable, given that no empirical data or parameter adjustment is used and that vibrational and coherency effects are neglected. This figure also shows that the calculated phase diagram can be brought into *perfect* agreement with experiment if our reduced excess enthalpy ΔH is lowered by a reasonable error margin of 12%. Figure 3(b) depicts for Pt-Pd the calculated mixing enthalpy and the excess free energy, showing good agreement with experimental data.[10].

To understand why Pt forms ordered compounds with other late TM's despite a large-d-band filling, recall that Pt is also distinguished by having one of the deepest s-state energies among all TM's: Its measured[23] atomic s ionization potential (9.0 eV) is smaller only relative to Ir (9.1 eV) and Au (9.2 eV) (the only elements with which Pt *does not* form ordered compounds, hence, the method of Ref. 6 is appropriate in these two cases). The occurrence of such a deep s state in Pt could lead to stabilization of its compounds both due to s charge transfer[3] into Pt (an ionic effect) and due to stronger s-d hybridization[12] (a covalent effect). Both effects were neglected in previous d-band tight-binding theories of alloy stability,[4-7] as s orbitals were viewed as extended, nearly spherical objects that act only to counter the attractive d-electron contribution but do not promote directional ordering.[6] We examine the significance of s electrons to phase stability by repeating the calculations of $\Delta E(\sigma,V)$ but artificially raising the Pt s orbital energy away from the d band. Such a manipulation is afforded by removing the relativistic mass-velocity and Darwin terms from the Hamiltonian. These relativistic terms act to deepen s-orbital energies and to raise the d-orbital energy (e.g., the relativistic 0.3-eV s-d separation in the Pt atom is in-

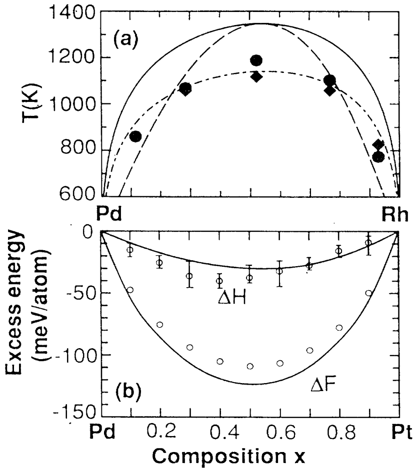

FIG. 3. (a) CVM calculated (lines) and measured [circles from Ref. 18(a) and diamonds from Ref. 18(b)] phase diagram of $Pd_{1-x}Rh_x$. The solid line is the binodal, the dashed line is the spinodal, and the dash-dotted line is the calculated binodal corresponding to a ~12% reduction in ΔH (see text). (b) Calculated and measured (Ref. 10) excess enthalpy ΔH (at $T=300$ K) and free energy ΔF (at $T=1600$ K) for Pt_xPd_{1-x}.

creased to 2.9 eV when these relativistic terms are omitted; the changes are smaller in Ni, Pd, and Rh, i.e., 0.5, 0.6, and 0.7 eV, respectively). We found that a *nonrelativistic* calculation for the stablest $L1_0$ structure of $Pt_{0.5}Ni_{0.5}$ raises its s-band energy and changes the negative ("ordering") formation enthalpy ΔH from -93.6 meV/atom (compared to the measured value[24] of -96 meV/atom) to a large *positive* value of $+143.9$ meV/atom ("phase separation") obtained for the calculated equilibrium lattice constants ($+96$ meV at the experimental lattice constants). Part of the effect arises from the fact that the relativistic s-orbital contraction reduces the calculated Pt lattice constant by 4.3% (from 4.106 to 3.935 Å, close to the experimental value of 3.920 Å), thus leading to a much better lattice match with Ni and a concomitant reduction in the elastic energy. Hence, nonrelativistic calculations,[25] either at the calculated or at the observed lattice parameters, cannot produce ordering in Ni-Pt. A similar trend (but with smaller magnitude) of loss in stability upon increasing the Pt s-d separation is observed in Pt-Pd as shown by the crosses in Fig. 2(b), representing nonrelativistic calculations. These effects are less important in the lighter $4d$-$4d$ alloy Pd-Rh. Interestingly, while mass-velocity and Darwin terms act to stabilize ordering, the spin-orbit interaction, which has no effect on the s orbital, leads to a (small) *destabilization* (by 3.2 meV/atom), in qualitative conflict with the suggestion of Ref. 7 that spin-orbit effects are the reason for ordering in PtNi.

We conclude that mapping of LDA energies onto a multisite Ising Hamiltonian[16,17] provides an effective means for systematically identifying ground-state structures and analyzing both regularities and irregularities in terms of the electronic structure.

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[1] P. M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).

[2] T. B. Massalski, *Binary Alloy Phase Diagrams* (American Society for Metals, Metals Park, OH, 1986).

[3] A. R. Miedema, R. Boom, and F. R. DeBoer, J. Less Common Met. **41**, 283 (1975).

[4] A. Bieber and F. Gautier, Acta Metall. **34**, 2291 (1986).

[5] M. Cyrot and F. Cyrot-Lackmann, J. Phys. F **6**, 2257 (1976); M. Sluiter, P. Turchi, and D. de Fontaine, *ibid.* **17**, 2163 (1987); J. Van Der Rest, F. Gautier, and F. Brouers *ibid.* **5**, 2283 (1975)..

[6] D. G. Pettifor, Phys. Rev. Lett. **42**, 846 (1979).

[7] G. Treglia and F. Ducastelle, J. Phys. F **17**, 1935 (1987).

[8] C. E. Dahmani *et al.*, Phys. Rev. Lett. **55**, 1208 (1985).

[9] E. Raub, J. Less Common Met. **1**, 3 (1959).

[10] J. B. Darby and K. M. Myles, Metall. Trans. **3**, 653 (1972).

[11] A. Kidron, Phys. Lett. **25A**, 112 (1967).

[12] C. D. Gelatt, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **27**, 2005 (1983).

[13] R. E. Watson, J. W. Davenport, and M. Weinert, Phys. Rev. B **35**, 508 (1987).

[14] J. Kanamori and Y. Kakehashi, J. Phys. (Paris), Colloq. **38**, C7-274 (1977).

[15] P. E. A. Turchi *et al.*, Phys. Rev. B **37**, 5982 (1988).

[16] J. W. D. Connolly and A. R. Williams, Phys. Rev. B **27**, 5169 (1983).

[17] S.-H. Wei, L. G. Ferreira, and A. Zunger, Phys. Rev. B **41**, 8240 (1990).

[18] (a) J. E. Shield and R. K. Williams, Scr. Metall. **21**, 1475 (1987); (b) E. Raub, H. Beeskow, and D. Menzel, Z. Metallkd. **50**, 428 (1959).

[19] Most of these structures can be described as A_pB_q superlattices along direction **G**: $L1_0$ and $L1_1$ correspond to $p=q=1$ and $\mathbf{G}=[001]$ and $[111]$, respectively, "40" and "$Z2$" correspond to $p=q=2$ and $\mathbf{G}=[201]$ and $[001]$, respectively, and $\beta 1$ and $\beta 2$ are $p=1$, $q=2$ and $p=2$, $q=1$, respectively, for $\mathbf{G}=[001]$. The DO_{22} structure is $p=1$, $q=3$ (or $p=3$, $q=1$) with $\mathbf{G}=[201]$. $L1_2$ is the Cu_3Au-type structure. $D1_a$ corresponds to $p=4$, $q=1$ and $\mathbf{G}=[201]$. $X2$ corresponds to $p=5$, $q=2$ and $\mathbf{G}=[201]$. $D1$ (A_7B) and $D7$ (AB_7) are fcc-like structures with the unit-cell vectors double that of the underlying fcc unit vectors.

[20] J. M. Sanchez, F. Ducastelle, and D. Gratias, Physica (Amsterdam) **128A**, 334 (1984).

[21] S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985), and references therein.

[22] R. Magri, S.-H. Wei, and A. Zunger, Phys. Rev. B **42**, 11388 (1990).

[23] L. H. Ahrens, *Ionization Potentials* (Pergamon, Oxford, 1983).

[24] R. A. Walker and J. B. Darby, Acta Metall. **18**, 1761 (1970).

[25] F. J. Pinski *et al.*, Phys. Rev. Lett. **66**, 766 (1991), suggested $L1_0$-ordering tendencies in Pt-Ni on the basis of nonrelativistic calculation. Since we demonstrated that $\Delta H_{NR}(L1_0) > 0$, this cannot be the case.