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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 previ-
ously 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' have instigated many at-
tempts to identify global phenomenological trends and
explain them in terms of microscopic constructs. One
such well-known regularity is that systems where both
constituents have nearly filled d shells ("late TM's"),
have posi'tive mixing enthalpies AH, 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: It was found
that even in the absence of size mismatch between the

constituents, occupation of the upper "antibonding"

part of the d band leads universally to AH)0 for all late

TM's with an average d-electron count N ~ 8.
The actual situation appears to be more complex, as il-
lustrated, for example, by the phase behavior of binary
alloys of Pt with its neighboring elements in the periodic table.

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First, even discarding for a moment "special
cases" such as the ordering Pt-Cu and Pt-Ag intermetal-lics' that contain a noble metal, or the ordering' Pt-Co system which is complicated by a magnetic behavior over
a wide composition range, the fact that even the non-
magnetic Ptp sNip 5 alloy orders defies all current d-band
theories. While it is certainly possible to fit the ob-
served Pt-Ni phase diagram with an Ising model, at-
tempts to explain even the sign of the Ising interaction
energies required to produce the fit have all failed.
Second, while Pt-Rh and Pt-Pd were surmised' to
phase separate, examination of the original data shows
that no evidence exists to this effect (they were measured only at very high temperatures where solid solutions ex-
ist'), except for a suggestive extrapolation from the
known behavior of Pd-Rh and Pd-Ir. In fact, measure-
ments on Pt-Pd have shown negative mixing enthalpies'
and clear evidence in x-ray diffuse scattering" for a sub-stantial degree of short-range order which remains unex-
plained. Such structural preferences in inter metallic
compounds can be addressed by highly precise total-
energy calculations based on the local-density approxi-
mation (LDA). ' '

There, one selects for each interme-
tallic 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 sta-bler than a single structure of the same average composi-tion. Addressing such possibilities requires a "ground-- state search"'

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among the astronomically large num-
ber (e.g., 2 for a binary lattice with N sites) of possible
configurations on a given lattice.
Recently, "first-principles statistical-mechanics" ap-proaches have been

the

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(lattice)TT /Xi4 /Xi0 9.110 618.44 Td (deterseparate4 ET /Xi0 9.110 9 Tf 1511.56 549.67 Td (ionfiguBT /Xi0 /Xi0 9.11f 281.

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TABLE I. LAPW-calculated relaxed (except for Rh-Pt which is unrelaxed) formation enthalpies [Eq. (1)] of the A ~ „B„—intermetallics in various structures defined in Ref. 19. Fit-ting these by Eq. (2) using eight interaction energies results in small standard deviation Z given here for both unrelaxed (U) and relaxed (R) configurations. Fitted values are illustrated for PdPt and PdRh (in parentheses). The last line gives

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5 Pdp

5

Ptp

5 Rhp.

5

Pdp

5 Rhp

5

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