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# First-principles determination of low-temperature order and ground states of Fe-Ni, Fe-Pd, and Fe-Pt

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While the binary Fe-$X$ ($X$=Ni, Pd, Pt) alloys are among the most widely applied bimetallics, open questions remain regarding whether and which of their compounds are stable at low $T$. Based on density-functional theory and first-principles cluster expansions that are "filtered" against structural and magnetic bistabilities, we assess all three systems. We (i) review the stability of the known phases; (ii) predict phases unstable with respect to bcc-fcc *mixtures* but stable if restricted to fcc; and, (iii) remarkably, predict previously unknown stable phases. This pinpoints where more definitive low-$T$ experiments should find new stable compounds.

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Fe-Ni, Fe-Pd, and Fe-Pt are among the earliest transition-metal bimetallic systems to be studied, finding numerous applications at many important alloy compositions, including among others Invar (FeNi$_{36}$),[1] Permalloy (Fe$_{20}$Ni$_{80}$),[2] shape memory materials (FePd),[3] and high magnetic anisotropy materials for storage (FePt).[4–6] Knowledge of their atomic structure is the basis both for an improved understanding of experiments and for accurate future theoretical predictions. At high $T$, the thermodynamically stable phases can be found in standard phase diagram compilations;[7,8] but, surprisingly, significant questions remain in the intermediate- and low-$T$ regime ($T \lesssim 600$ K, in some cases even higher) for all three systems. Verifying the stability of low-$T$ structures in experiment is often hindered by the sluggish kinetics of the *bulk* thermal (quasi)equilibrium. Even seemingly basic questions, e.g., the existence and low-$T$ lattice stability of the simple ordered $L1_0$ compound FeNi, are still under debate.[7,9,10] However, modern experimental techniques can instead approach a suspected low-$T$ ordered phase in an epitaxial way[11,12] and/or at the nanoscale.[5] In these cases, slow bulk diffusion processes no longer limit the reaction pathway. Conversely, metastable structures are subject to fewer kinetic constraints and easily transform to more stable structures. Thus, the *actual* stability of a technologically desired atomic arrangement becomes much more important in order to guarantee its formation over any possible unsuspected different structures.[13]

Here, we present a comprehensive theoretical account of the low-$T$ ordered compounds of Fe-Ni, Fe-Pd, and Fe-Pt in the entire composition range of each alloy. Knowing the $T=0$ ordered structure is critical both in direct searches for future stable compounds, and because this controls the short-range order and thus the physics at higher $T$. As shown below, we predict the global stability of some simple as yet unknown compounds Fe$X_8$ ($X$=Ni,Pd,Pt) or Fe$X_2$ ($X$=Pd, Pt). We conclusively establish the low-$T$ phase stability of many known and suspected phases, but disprove others: for example, at the composition Fe$_3$Ni, the $L1_2$ structure is not even the preferred state of the metastable fcc alloy, contrary to what is often assumed. We predict a simple Fe$_3$Ni (100) superlattice (SL) known as $Z1$ instead. To reach our conclusions, we perform exhaustive "ground-state" structure searches based on the total energies of $\approx 10^6$ candidate structures for each alloy system, evaluated with the accuracy approaching that of density-functional theory (DFT) in the generalized-gradient approximation (GGA).[8,14] These total energies are derived from state-of-the-art cluster expansions (CEs) (Refs. 15–17) each parametrized from the DFT-GGA total energies of $O(100)$ fully relaxed ordered compounds,[8] computed using VASP program.[8,18]

Although the basic CE methodology is now well established, its use here is not straightforward: the application of a CE requires a *unique* total energy for a given configuration, but Fe-(Ni,Pd,Pt) alloys can show structural and magnetic *bistabilities*. This behavior is well known for pure Fe (Ref. 19) and is illustrated in Fig. 1 for one compound, the Fe$_3$Ni$_1$ (100) superlattice $Z1$. Its total-energy surface as a function of lattice distortion ($c/a$) and total magnetic moment shows three distinct minima, characterized as bcc, high spin (bcc,HS); fcc, high spin (fcc,HS); and fcc, low spin (fcc,LS). Similar fcc vs bcc and HS vs LS bistabilities must be expected for many more possible Fe-(Ni,Pd,Pt) compounds. This makes the corresponding input energy to a CE ambiguous. If first-principles total energies corresponding to local structure optima of very different lattice and electronic struc-

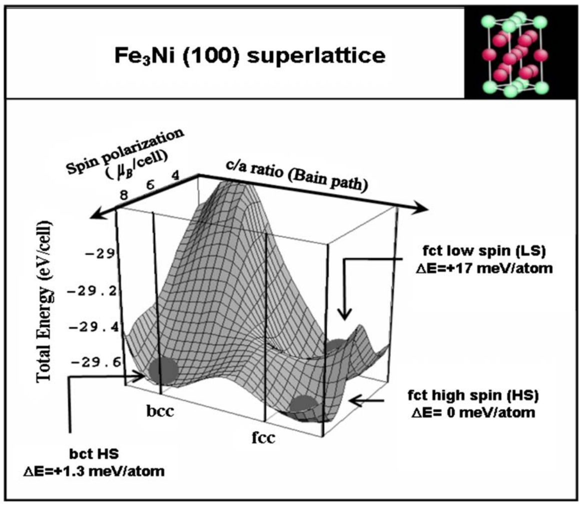


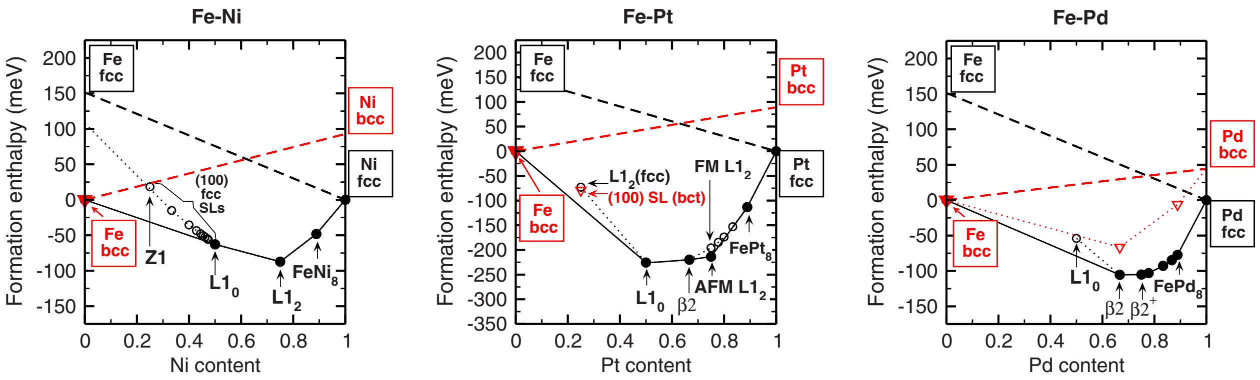
FIG. 1. (Color online) Total energy of the ferromagnetic Fe$_3$Ni (100) SL upon varying the $c/a$ ratio and the net magnetic moment (spin polarization). All the internal degrees of freedom are relaxed for each point. The minima are strictly tetragonal (labeled as fct and bct) but referred to as bcc and fcc for simplicity throughout the text.

ture types were indiscriminately mixed as input to the same CE, this would result in a handicapped CE with poor predictive power.[20] We resolve this conceptual difficulty by "filtering" the DFT input structures to create separate CEs according to their unit-cell relaxation and moment. Based on its atomic pair distribution function, each structure is first characterized as fcc- or bcc-like and then based on the observed total magnetic moments, as HS or LS [see EPAPS (Ref. 8) for details]. Remarkably, both "filter" criteria turn out to yield a distinct separation into different structure and magnetism "classes." We then perform separate CEs for structures that belong to different classes: specifically, (fcc,HS) for Fe-Ni and Fe-Pt, and both (fcc,HS) and (bcc,HS) for Fe-Pd. Based on the total magnetic moments per unit cell of the HS structures, all the performed CEs correspond to ferromagnetic (FM) ordering. As for the remaining classes, by sampling the energies of $O(100)$ structures belonging to (fcc,HS), (bcc,HS), and (fcc,LS) for each Fe-$X$ alloy system, we conclude that in Fe-Ni and Fe-Pt only (fcc,HS) compounds have sufficiently low energies to appear as *global* ground states. We find no evidence of any structure being stable in (bcc,LS) state (as Fig. 1 illustrates for one specific structure).

The resulting CEs cover the technologically important (fcc,HS) configurations and their global stability vs bcc Fe. Since they reflect the energetics of structural and electronic ground states, they are thus able to pinpoint low-$T$ stable structures. Conversely, the CEs by construction do *not* account for any nonconfigurational entropy contributions relevant at high $T$ (lattice instabilities and nonferromagnetic spin excitations), but this $T$ range is not the focus of this work.

The solid phases presently discussed in most experimental[7,9,10,21–23] and theoretical[24–34] literature on $Fe_{1-x}Ni_x$, $Fe_{1-x}Pt_x$, and $Fe_{1-x}Pd_x$ are summarized as follows. At sufficiently high $T$, fcc solid solutions span all compositions. Upon cooling, bcc solid solutions become stable at Fe-rich compositions. At some other compositions, ordered fcc compounds emerge. In the table of Fig. 2, we list (under "experiment") both the assessments of the conventional "global equilibrium structures" (the *perceived* lowest free-energy phases at given composition as $T \to 0$), and the "fcc-restricted equilibrium structures," i.e., the phases expected to exist if cooling the fcc solid solution were to kinetically limit the emerging ordered phases to the underlying fcc lattice. Figure 3 shows the crystal structures of the phases discussed here. The unambiguous experimental facts *at intermediate* $T$ are[8] (i) around $x=0.5$, the $L1_0$ phase is globally stable in FePt and in FePd. (ii) Around $x=0.25$, both Fe-Ni and Fe-Pd phase-separate. $Fe_3Pt$ forms a stable $L1_2$ phase. (iii) Around $x=0.75$, all three Fe-$X$ systems show the $L1_2$ structure. Beyond these facts, some experimental uncertainties remain: (a) it is not clear whether $L1_0$-ordered FeNi forms only under fcc restriction[7,10] or is globally stable;[9] (b) *under fcc restriction*, an ordered $Fe_3Ni$ structure of unclear order ($L1_2$ or $L1_0$ suggested[7,24,28–30]) may or may not exist; (c) as $T \to 0$, it is not clear whether $Fe_3Pt$ remains globally stable[7] or undergoes a phase separation into (bcc Fe+$L1_0$ FePt);[21] and (d) as $T \to 0$, it is not clear whether FePd $L1_0$ phase at $x=0.5$ remains stable.[8,23]

Figure 2 shows our predicted formation enthalpies and $T=0$ ground-state structures for Fe-Ni, Fe-Pt, and Fe-Pd, based on exhaustive structure searches ($\approx 10^6$ structures each). In each plot in Fig. 2, the filled symbols indicate the



| | | $Fe_3X$ | | $FeX$ | | $FeX_3$ | | new compounds |
|---|---|---|---|---|---|---|---|---|
| | | global | fcc | global | fcc | global | fcc | |
| Fe-Ni | experiment | (bcc+$L1_2$)? | $L1_2$? | (bcc+$L1_2$)? | $L1_0$ | $L1_2$ | $L1_2$ | — |
| | present work | bcc+$L1_0$ | Z1 | $L1_0$ | $L1_0$ | $L1_2$ | $L1_2$ | $FeNi_8$ |
| Fe-Pt | experiment | $L1_2$? | $L1_2$ | $L1_0$ | $L1_0$ | $L1_2$ | $L1_2$ | — |
| | present work | bcc+$L1_0$ | $L1_2$ | $L1_0$ | $L1_0$ | $L1_2$ | $L1_2$ | $FePt_2$ $\beta2$, $FePt_8$ |
| Fe-Pd | experiment | bcc+$L1_0$ | ? | $L1_0$? | $L1_0$ | $L1_2$ | $L1_2$ | — |
| | present work | bcc+$\beta2$ | none | bcc+$\beta2$ | $L1_0$ | $\beta2^+$ | $\beta2^+$ | $FePd_2$ $\beta2$, $FePd_8$,<br>shallow $\beta2$-based |

FIG. 2. (Color online) Viewgraphs: calculated formation energies of ground-state structures for Fe-Ni, Fe-Pt, and Fe-Pd. Triangles (red) and circles (black) denote bcc- and fcc-based structures, respectively. Filled (open) symbols and solid (dotted) lines designate globally stable (fcc- or bcc-restricted) structures and convex hulls, respectively. Long-dashed lines connect the pure elemental solids in high-spin fcc and bcc structures, as labeled. Table: comparison of existing experimental and present theoretical assessments of both global low-$T$ phase stability (single structures and two-phase fields) and low-$T$ expectations based on an underlying fcc lattice only.

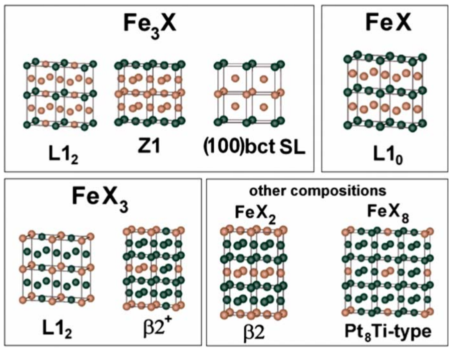


FIG. 3. (Color online) Ground-state structures of Fe-$X$ (dark green: $X$=Ni,Pd,Pt atoms; light red: Fe) in this work and earlier assessments (cf. Fig. 2). Note that based on $c/a$ ratio, we distinguish between crystallographically equivalent polymorphs [e.g., the fcc-based $Z1$ and the "(100) bct SL"].

globally stable structures (depicted in Fig. 3); the "convex hull" connecting those stable structures is shown with the solid lines. Black open circles connected by dotted lines indicate the HS fcc-restricted structures, and the open red triangles indicate hypothetical bcc-restricted structures where we find such structures to be noteworthy. The entry "present work" in the table presented in Fig. 2 summarizes our predictions for stable $T$=0 structures, *vis-à-vis* the experimental finite-$T$ assessments. Our main results are as follows.

*For all three alloys*, ordering universally includes 00$k$ vectors. Additionally, other ordering vectors may be present, and the specific ordered structures may be different for the three systems. For clarity, we discuss the similarities as we describe each of the three alloys consecutively:

*Fe-Ni*: (i) at $x$=0.5, we predict a *globally* stable $L1_0$ FeNi ground state, confirming the experimental assessment of Ref. 9 over other opinions.[7,10] Although the stabilization energy over (bcc Fe+$L1_2$ $FeNi_3$) is small, $L1_0$ appears to be the global ground state. (ii) At $x$=0.25, we find the globally stable state to be a two-phase field, in agreement with experiment.[7] *Under fcc restriction*, we predict a structure which is *not* $L1_2$, but a (001)$(Fe)_3/(Ni)_1$ superlattice ($Z1$ in Fig. 3). Throughout the Fe-rich composition region $x<0.5$, we predict further (001) superlattice structures as fcc-restricted ground states, including a structure noted earlier by Mishin *et al.*[35] (iii) At $x$=0.75, we predict a $L1_2$ $FeNi_3$ global ground state, in agreement with experiment.[7] (iv) In addition, we predict a *yet undetected* globally stable $FeNi_8$ ground state of $Pt_8Ti$-type[36] order.

*Fe-Pt*: (i) at $x$=0.5, we find a globally stable $L1_0$ phase, in agreement with experiment.[7] (ii) At $x$=0.25, the *two-phase* field (bcc Fe)+($L1_0$ FePt) is globally stable at $T$=0. Only under fcc restriction the ground state is indeed the experimentally observed phase $L1_2$ $Fe_3Pt$. We thus conclude that *ordered* $L1_2$ becomes metastable as $T\rightarrow 0$, as suggested by early experiments.[21] Further, we find that an ordered bcc-based structure labeled "(001) bct SL" in Figs. 2 and 3 (open red triangle in Fig. 2) has a lower energy than $L1_2$. Indeed, bcc structures could be expected to have lower energies than fcc structures at this composition since overcooled *disordered* $Fe_{0.75}Pt_{0.25}$ can undergo a martensitic fcc-bcc transformation. At the same time, we find that ordered $L1_2$ is not susceptible to a *direct* martensitic instability (it has 2.6 meV/atom lower energy that its direct bcc-based polymorph), again consistent with experiment. (iii) At $x$=0.75, we predict a globally stable $L1_2$ structure, in agreement with experiment.[7] This is similar to $FeNi_3$, except that $FePt_3$ $L1_2$ is antiferromagnetic (AFM), with (1/2 1/2 0) AFM order in both experiment and GGA. (iv) At Pt-rich compositions, we predict *two yet undetected* structures: $FePt_8$ (similar to $FeNi_8$) and $FePt_2$ $\beta2$(shown in Fig. 3).[37]

*Fe-Pd*: (i) at $x$=0.5, we predict the two-phase field (bcc Fe)+($\beta2$ $FePd_2$) to be globally stable. Under fcc restriction, we find the $L1_0$ structure, which is observed in the experimentally accessible $T$ range.[7,38] (ii) At $x$=0.25, the global ground state is again a two-phase field, consistent with experiment.[7] However, we predict *no* fcc-restricted state in $Fe_3Pd$ (unlike $Z1$ in $Fe_3Ni$ or $L1_2$ in $Fe_3Pt$). The reason is a direct martensitic instability: many structures at $x$=0.25, including those predicted to have the lowest energies, relax without a barrier into bcc-based structures in our first-principles structure optimization. Thus, it is impossible to impose an fcc restriction at this composition. Remarkably, the energies of the bcc-based structures resulting from this martensitic transformation are still above the bcc-restricted convex hull (shown in Fig. 2 by the red line connecting the red open triangles), which is found to contain no bcc $Fe_3Pd$ ground state. Thus, even under a hypothetical bcc restriction the low-$T$ stable form of $Fe_{0.75}Pd_{0.25}$ is a two-phase field (bcc Fe)+(bcc-based $FePd_2$), rather than a single ordered structure. (iii) At Fe-poor $x$=0.75, we predict that the globally stable structure at $T\rightarrow 0$ is $\beta2^+$ $Fe_3Pd_9$ (shown in Fig. 3). The $\beta2^+$-$L1_2$ energy difference is small ($\approx$5 meV/atom); still, this is in real conflict with experiment,[7] which clearly shows an $L1_2$ phase. We have not found the reason for this conflict. On one hand, its origin could simply be the accuracy limit of DFT-GGA. On the other hand, finite-$T$ entropic effects outside our current scope (spin excitations and lattice dynamics) could stabilize $L1_2$ over $\beta2^+$ in experiments. (iv) In addition, at Pd-rich compositions, we predict several *yet undetected* structures: $FePd_8$ and $FePd_2$ $\beta2$ (just like in Fe-Pt) and several other ordered structures. All these structures, as well as $Fe_3Pd_9$ $\beta2^+$, can be formed from $FePd_2$ $\beta2$ structure via a number of Fe$\rightarrow$Pd substitutions. Very similar structures would result in Fe-Pt if the AFM state were not stabilized[37] in $L1_2$ $FePt_3$.

As noted above (and discussed further in Ref. 8), our first-principles CEs do not account for high-$T$ spin and lattice entropy contributions, which are important in the present systems. Nonetheless, we use our CEs to obtain semiquantitative estimates of the order-disorder transition temperatures (using the configurational Monte Carlo method of Ref. 39) for some of our predicted compounds, yielding, e.g., $T_{\mathrm{ord}} \gtrsim 500$ K for $FeNi_8$, $FePd_8$, and $FePt_8$, and $T_{\mathrm{ord}} \gtrsim 600$ K for $FePt_2$, indicating that an experimental stabilization of these structures could be possible.[8]

To conclude, we (i) resolve the questions regarding fcc-restricted vs global phase stability, characterizing the two-phase fields with bcc Fe in the Fe-rich parts of the Fe-(Ni,Pd,Pt) phase diagrams, and (ii) identify phases that have not been observed experimentally but would be stable at low $T$, such as $FeNi_8$, $FePt_8$, and $FePd_8$ with $Pt_8Ti$-type order,[36] or $FePd_2$ and $FePt_2$ with $\beta 2$-type order. The stability of as yet unknown structurally simple phases in such widely investigated systems offers easy access points for quantitative verification by atomically controlled experimental research techniques.[11,12]

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[37] To ensure that the AFM order in $L1_2$ $FePt_3$ is an isolated case, we calculated the AFM energies of competing Fe-Pt structures, as well as of $L1_2$ $FeNi_3$ and $FePd_3$. We found that only $FePt_3$ $L1_2$ is AFM. Note that if $FePt_3$ $L1_2$ were FM rather than AFM, some of these competing HS Fe-Pt structures would have become stable, as indicated in Fig. 2 by the open circles; further, the $FePt_3$ $\beta 2^+$ structure would have become degenerate with $L1_2$.

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