PHYSICAL REVIEW B **84**, 180202(R) (2011)

Ordering trends in transition metal alloys from tight-binding electronic structure calculations

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(Received 31 August 2011; published 10 November 2011)

Accurate prediction of the ordering behavior of transition metal alloys from the electronic structure is a challenging task, opening the way to build materials with unique properties in a controlled way. To this goal, we provide an accurate model based on the fourth-moment approximation of the tight-binding approach, which exhaustively gives ordering trends as a function of d-band filling, within maps where both the d-band positions and widths are used as parameters.

DOI: 10.1103/PhysRevB.84.180202 PACS number(s): 71.20.Be, 61.66.Dk, 61.50.Ah, 71.15.Nc

It has been a longstanding issue of modeling activity in material science to derive thermodynamic properties of transition metal alloys from the knowledge of the electronic structure of their pure constituents.[1–4] The goal was both to better understand the intimate coupling between electronic and chemical structures, and to use this understanding to build structures with unique properties (as it is the case with the recent development of nanoalloys[5]). Application domains are, e.g., metallurgy, catalysis, magnetism, and optics.

Many approaches have been proposed, based upon a more or less sophisticated description of the electronic structure, from *ab initio* density functional theory (DFT)-type methods,[6–10] through the tight-binding (TB) approximation,[11,12] up to semiempirical potential models.[13–18] Whereas the latter are too simple to establish a link between the electronic and chemical structure up to the desired level of accuracy, the TB method within a pure d-band description is known to capture the corresponding physics. In addition, it is more suited for a trend study than the DFT methods. It is therefore taken as the starting point for the present Rapid Communication.

The TB Hamiltonian for a binary alloy A_cB_{1-c} involves two types of matrix elements, respectively, *diagonal* and *off-diagonal* on the basis of d atomic orbitals. The first one ε_d^a is the atomic d orbital level for an atom of type a. The second one is the hopping integral between two orbitals on neighboring sites, which can be expressed in terms of the usual Slater parameters derived from the band structure using interpolation schemes,[19] and relates to the d bandwidth ($W_d^a \simeq -8dd\sigma^{aa}$ for the fcc structure[4]). In this framework, the first term gives rise to the so-called *diagonal disorder* effect coming from the difference $\delta_d = \varepsilon_d^A - \varepsilon_d^B$ between the d orbital levels of two elements, whereas the second one accounts for a possible effect of *off-diagonal disorder* due to the difference in d bandwidth W_d^a: $\delta_{nd} = W_d^A - W_d^B$. The parameters δ_d and δ_{nd} actually drive the redistribution of the electronic states with respect to those of pure elements and therefore both the properties of the alloy and its preference to order or phase separate at low temperature. The respective values of δ_d and δ_{nd} for all possible transition and noble metal alloys are shown in Fig. 1. Without any loss of generality, in this Rapid Communication the elements A and B are chosen such as $\delta_d = \varepsilon_d^A - \varepsilon_d^B > 0$.

As can be seen, δ_d and δ_{nd} follow a similar variation so that none of them prevails on the other. However, up to now, the only systematic study of the link between ordering tendency and electronic structure in transition metal alloys has been to completely neglect the off-diagonal disorder effect ($\delta_{nd} = 0$). In that case a generalized perturbation method [GPM (Ref. 20)] allows to derive effective pair interactions (EPIs) $V_{ij} = \frac{1}{2}(V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB})$ from the electronic structure of the disordered alloy treated within the coherent potential approximation [CPA (Ref. 21)]. Since the EPIs are strongly damped with distance,[22] they can be limited to first neighbors, leading to a single one $V_{ij} = V$ for all first-neighbor pairs. The sign of V gives the chemical tendency of the system to order ($V > 0$) or to phase separate ($V < 0$) at low temperature (ground state). The variation of V with the average d-band filling in the alloy $N_e = cN_d^A + (1-c)N_d^B$, with N_d^a the number of d electrons in a pure a metal, has put in evidence systematic trends, among which the prediction of ordering tendency for $0.3 < N_e < 0.7$ roughly, and to phase separate otherwise, in agreement with experiment for a wide range of systems.

However, one has to keep in mind that the GPM approach has been derived by taking into account the difference in d-band positions as the only source of alloying effect. This makes it unsuited for systems presenting a weak diagonal disorder effect, for which the origin of the ordering tendency has to be found in the difference in bandwidths (off-diagonal disorder). This concerns systems of high interest, such as CoPt, NiPt, or CuAu, which are indeed exceptions to the GPM rules which predict them to phase separate, although they are archetypal systems known to form ordered phases. It is then necessary to go beyond GPM shortcomings, which can be done following two complementary directions.

The first one is to assume that the description in terms of EPIs remains valid even when not grounded, and to calculate them by *ab initio* DFT methods which obviously account for all (diagonal and off-diagonal) electronic structure effects.[6–10,23] This was indeed successful to predict, using Korringa-Kohn-Rostoker (KKR) (Ref. 7) or linear muffin-tin orbital (LMTO) (Ref. 23) calculations, the correct ordering behavior in some particular alloys (among which CuAu and CoPt). However, it does not give a general description of the ordering tendency for

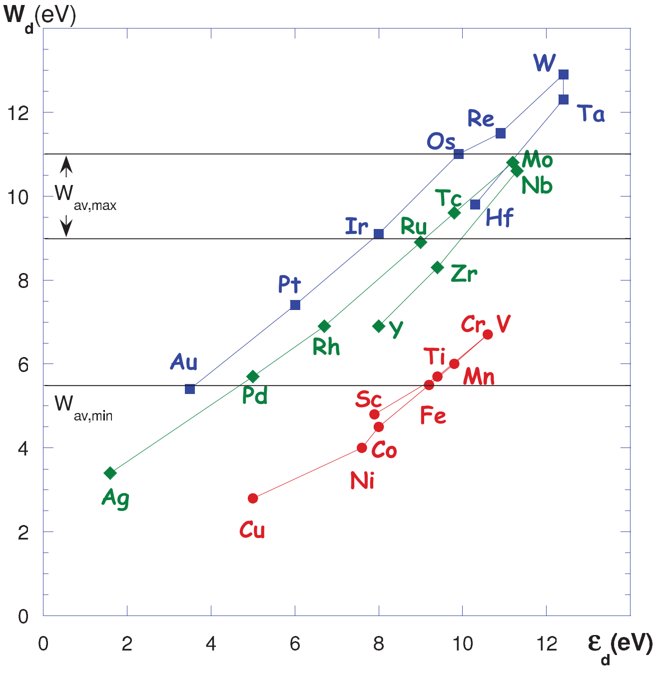

FIG. 1. (Color online) Correlated behavior of ε_d^a and W_d^a for all transition metals, compiled from Ref. 19. The lines follow the d-band filling along series.

all alloys nor an elucidation of what are its main driving forces. In addition, it can hardly (up to now) be applied in a systematic way to more complex simulations coupling atomic relaxations and chemical exchanges (e.g., semigrand canonical Monte Carlo simulations of alloy surfaces, nanoalloys, defects), even though some work has been done for limit cases (surface segregation in dilute systems[24]).

The philosophy adopted in our Rapid Communication is quite different in the sense that our goal is to identify the missing driving forces of the ordering process in order to revisit the original GPM description and to generalize its predictions. To this aim, one has to calculate the local density of states (LDOS) $n(E)$ to the required accuracy. We use a continued fraction expansion, the coefficients of which are directly related to the moments of $n(E)$ and calculated using the recursion method.[25] The simplest extension that treats on equal footing both diagonal and off-diagonal disorder effects is to use a LDOS based on a fourth moment approximation (FMA), as in the case of covalent materials.[26] This is the procedure used here with the twofold goal to revisit the GPM and to provide a well-founded basis for a generation of empirical potentials for alloys based on the FMA. We have calculated the EPIs V for $c = 0.25$, 0.5, and 0.75, from the respective values of the formation energies of the $L1_0$ ($E_{L1_0} = -4V$) and $L1_2$ ($E_{L1_2} = -3V$) ordered phases, and for both dilute limits from the solution energies ($E_{\mathrm{sol}} = -12V$). A typical LDOS and the corresponding EPIs as a function of the average d-band filling N_e are shown in Fig. 2 for $c = 0.5$ and different values of δ_d and δ_{nd}. The used average bandwidth $W_{\mathrm{avg}}[=(W_d^A + W_d^B)/2]$ falls within the extremal values $W_{\mathrm{avg,\,min}}$ and $W_{\mathrm{avg,\,max}}$ displayed in Fig. 1. The first case ($\delta_{nd} = 0$) allows to recover the results of GPM, in particular, the preference for ordered phases to appear around a half-filled d band. A comparison with the EPI calculated with a larger set of exact moments[22] shows that truncating the continued fraction expansion to the second level (fourth moment) is sufficient, which confirms the validity of the FMA. The second case ($\delta_d = 0$) shows that the influence of off-diagonal disorder alone is to favor phase separation for any d-band filling. The behavior of the EPI in these two limit cases can be easily understood from simple qualitative arguments based on the respective band edges in the ordered and phase-separated systems.[4] Finally, one sees that coupling both effects significantly modifies the previous curves by desymmetrizing the d-band filling dependence, in opposite ways depending on the sign of δ_{nd}, which displaces the range of existence of ordering phases.

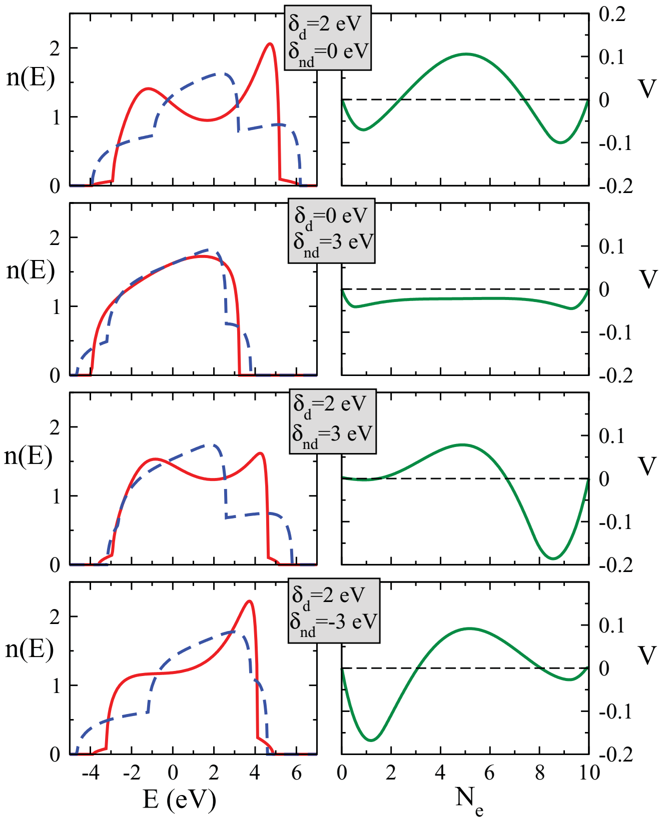

FIG. 2. (Color online) Effects of *diagonal* (δ_d) and *off-diagonal* (δ_{nd}) *disorder* on the total d-band LDOS, $n(E)$, (left-hand side) for the $L1_0$ (solid line) and demixed (dashed line) phases, and on the band-filling (N_e) dependence of the alloying effective pair interaction V (right-hand side), with $W_{\mathrm{avg}} = 8$ eV.

From these EPIs one can derive three-dimensional (3D) maps which, for a given concentration c, show the tendency of a system to order or phase separate as a function of δ_d, δ_{nd} (within the physical ranges in Fig. 1) and N_e. Sections of these 3D maps for different concentrations and selected values of δ_d are displayed in Fig. 3. Each section shows the respective domains for the existence of ordered and separated phases as a function of N_e (x axis) and δ_{nd} (y axis). The tendency to either order or phase separate is maximal in the middle of a domain (roughly), and vanishes toward the domain boundaries. As can be seen, off-diagonal disorder strongly changes the overall trends derived from calculations taking into account diagonal disorder only ($\delta_{nd} = 0$ in the maps), which were up to now

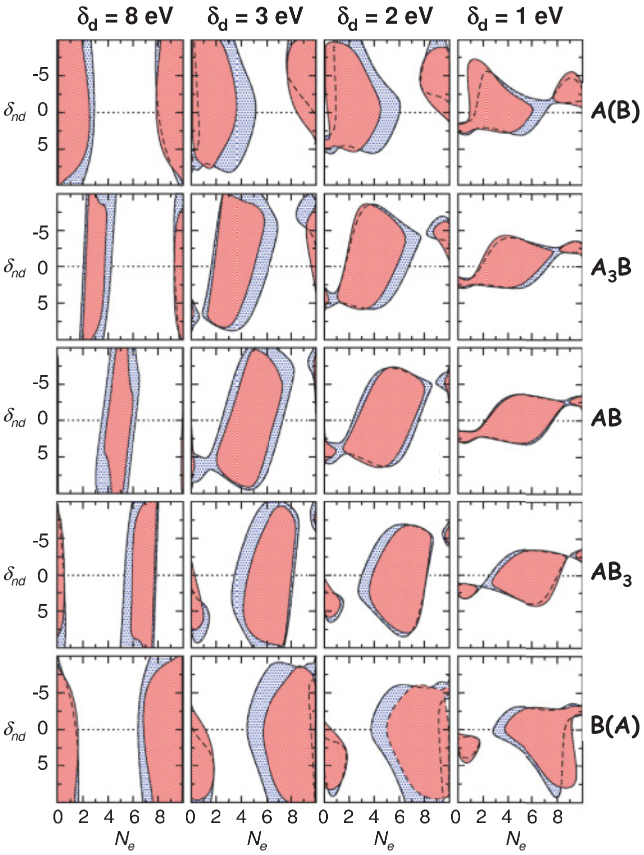

FIG. 3. (Color online) Ordering (shaded area) and demixing (white areas) domains in the parameter space spanned by δ_{nd} and N_e for different values of δ_d. The five rows correspond to the five compositions detailed in the text. The dark (red on line) and light (blue on line) shaded areas represent the results for extremal values of W_{av} derived from Fig. 1: $W_{\mathrm{avg,\,min}} = 5.5$ eV and $W_{\mathrm{avg,\,max}} = 11.0$ eV (except for $\delta_d = 8$ eV for which $W_{\mathrm{avg,\,max}} = 9.0$ eV).

and to the best of our knowledge, the only commonly admitted trends. The most interesting effect in this sense is probably the opening of ordering tendency domains, for reasonable values of the off-diagonal parameter, in the limits of small or large d-band fillings for which only phase separation was predicted before. The overall effect of concentration is to shift the ordering domains from larger to lower d-band filling from one dilute limit to the other. As a consequence, a given system can reverse its ordering tendency as a function of concentration, in particular, for the largest values of δ_d. However, let us keep in mind that the solution energy is very sensitive to atomic relaxations around the impurity which could change the map in the dilute case in presence of strong size mismatch (e.g., in the CuAg case[27]).

Locating a given system in the appropriate map of Fig. 3 requires the corresponding value of δ_d, δ_{nd}, and N_e. Note, however, that the actual value of δ_d should be the one determined after a self-consistent treatment of charge transfer induced by alloying. This is performed by self-consistent TB calculations based on the local charge neutrality rule *per site, orbital* and *chemical species*, recently derived from DFT calculations.[28] Results are given in Table I for systems involving one element of the first transition series and one element of the second or third one. For two noble metals the non-self-consistent values were maintained as they already yield self-consistency approximately. Note that, for the sake of generality, magnetism was not included in our calculations. However, our maps can still be used for a magnetic system by inserting an appropriate d-band filling being two times that of the minority band, which actually drives the cohesion in this case.

There remains to check to what extent the mixing behavior of systems such as CoPt, NiPt, or CuAu which could not be explained by considering only diagonal disorder fall to their place in the new domains. Using values of Table I, one sees that it is indeed the case for both CoPt and NiPt, respectively, which now fall into ordering regions of Fig. 3 as they should. The present maps also allow us to find the right places for alloys made of two noble metals, which slipped through the previous description. In particular, they reveal opposite behaviors depending on whether the noble metal of the first transition series Cu is alloyed with that of either the second (Ag) or third (Au) series. Indeed, the off-diagonal parameter increases from the former to the latter, which makes the system evolve from the phase separation domain (favored for the almost filled d band at $\delta_{nd} = 0$) for CuAg to the ordering one opened by the off-diagonal disorder effect for CuAu, in perfect agreement with experiment.

Once elucidated, the fundamental question of the tendency of an alloy to order or not, a subsidiary question would be (in the former case) that of the nature of the ordered phase, which requires calculating EPIs beyond first neighbors to discriminate between competing structures. This has already been done by *ab initio* methods for a few cases[8,10] and more generally by TB-GPM, only taking into account the diagonal disorder effect.[3,22] Establishing such maps is not the purpose of the present Rapid Communication, but they can be determined using the same methodology as for first-neighbor EPIs, taking into account both diagonal and off-diagonal disorder.

In summary, we have presented an accurate way to describe and predict the main thermodynamic characteristic of alloys, namely, their mixing behavior, from the single knowledge of the electronic structure of their pure constituents, using the fourth moment approximation (FMA) within a TB approach. This allowed us to classify the transition element compounds as a function of their d-band filling and the difference between not only the d levels of the components but also their d bandwidths from generalized (δ_d,δ_{nd},N_e) structural maps. Such a methodology is both complementary to existing *ab initio* calculations and necessary since it allows to identify the main electronic structure driving forces for ordering and to set the general framework in which all systems can be classified. In this framework, the present maps can also be used to predict the ordering behavior of more complex systems, through the evolution of these driving forces. Thus, the influence of dimensionality could be accounted for through the effect of bond breaking on both the d-bandwidth and d-level displacements,[29] in order to determine how the ordering behavior of an alloy evolve at the surface or in a cluster. Ordering trends in nanoalloys could then be estimated from our maps by just shifting accordingly the corresponding (δ_d,δ_{nd}) points.

TABLE I. Self-consistent values of δ_d (eV) at equiconcentration for alloys involving one element of the first transition series and one element of the second or third one. According to our notation, $\delta_d = \varepsilon_d^A - \varepsilon_d^B$ and $\delta_{nd} = W_A - W_B$. Here $\delta_{d,0}$ is the non-self-consistent value derived from Fig. 1.

A	Co	Ni	Pd	Co	Ni	Cu	Co	Ni	Pt	Co	Ni	Cu
B	Pd	Pd	Cu	Ag	Ag	Ag	Pt	Pt	Cu	Au	Au	Au
N_e	8.5	9.0	9.4	8.95	9.45	9.85	8.35	8.85	9.25	8.85	9.35	9.75
$\delta_{d,0}$	3.2	2.6	~0.0	6.6	6.0	3.4	2.2	1.5	1.0	4.7	4.1	1.6
δ_{nd}	−1.2	−1.7	−2.9	1.1	0.6	−0.6	−2.9	−3.4	4.6	−0.9	−1.4	−2.6
δ_d	1.0	0.4	2.7	5.3	4.4	–	1.0	0.2	3.5	3.3	2.5	–

Finally, the present approach provides the minimal level of accuracy or sophistication required in alloy modeling to capture the essential physics, or equivalently the essential ingredients which have to be included in a simplified method to make it reliable. Thus dealing with alloy problems requires to treat on equal footing both diagonal and off-diagonal effects. This implies to go beyond second moment approximation (SMA), which can be done within FMA by adding a repulsive term to the band term treated here. Indeed, FMA is computationally not much slower than the SMA models but much faster than DFT and standard TB methods, since it yields a computation time scaling linearly with the systems size. Our maps then provide a well-founded basis for future extensive use of such interatomic FMA potentials in problems coupling atomic displacements and chemical rearrangements in complex alloys (nanoalloys, for instance).

This work was founded by the French National Agency ANR through SimNanA Project No. ANR-08-NANO-003. We thank all the partners of this consortium for enlightening discussions.

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