First-Principles Predictions of Yet-Unobserved Ordered Structures in the Ag-Pd Phase Diagram

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The complexity of first-principles total energy calculations limits the pool of structure types considered for a ground-state search for a binary alloy system to a rather small, $O(10)$, group of "usual suspects." We conducted an unbiased search of fcc-based $Ag_{1-x}Pd_x$ structures consisting of up to many thousand atoms by using a mixed-space cluster expansion. We find an unsuspected ground state at 50%-50% composition—the $L1_1$ structure, currently known in binary metallurgy only for the $Cu_{0.5}Pt_{0.5}$ alloy system. We also provide predicted short-range-order profiles and mixing enthalpies for the high temperature, disordered alloy.

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As temperature is lowered, all equilibrium binary solids eventually either phase separate or order. Experimentally [1–4], Ag-Pd is known to form mutually miscible disordered solid solutions down to ~800 K, but no experimental studies exist at lower temperatures to reveal whether this system will phase separate or order. The distinction is important since it controls the type of short-range order *above* the transition point, e.g., whether Ag prefers to attract to it like or unlike atoms. The measured [5] and calculated [6,7] mixing enthalpy of the high temperature *random* alloy is negative, suggesting ordering tendencies. Calculations of the energy of various clusters embedded in homogeneous $Ag_{0.5}Pd_{0.5}$ alloys by Gonis *et al.* [8] suggest that clusters with all-unlike first neighbors are stabler than clusters with 50% like and 50% unlike nearest neighbors, also pointing to some ordering tendencies. Takizawa *et al.* [6] and Lu *et al.* [9] performed total energy calculations for the $L1_0$, $B2$, and $L1_1$ Ag-Pd structures, finding the latter to have the lowest negative formation enthalpy of the three candidates. However, other calculations found that ordering is unfavorable in this system. For example, Johnson [10] predicted a positive heat of solution over the full concentration regime and Takano *et al.* [11] predicted negligible short-range order in the disordered alloy. Moreover, there is a long discussion on the importance of the d bands (see, e.g., [12,13]) on the properties of Ag-Pd alloys such as resistivity and short-range order [14,15]. One can further try to guess the ordered structure using Pettifor's [16] "structure map" where each of the two elements in a binary compound is given a "coordinate value" placing it in a given structure domain of an empirical structure-sorting map. In the case of $Ag_{1-x}Pd_x$, Pettifor predicts no ordered structure for $x = 0.50$ and 0.75, but the Ag_3Pd structure was predicted in the $L1_2$ form [16]. We may also try Zunger's orbital radii method [17] which does predict ordering at $x = 0.50$ in an fcc configuration.

The problem facing both local density approximation (LDA) total-energy calculations of compounds [6,9,18,19] and diagrammatic approaches [16,17] is that the users of these methods have to be told in advance which (small) group of crystallographic configurations includes the stablest one. Since a binary $A_{1-x}B_x$ compound can appear in any of the 2^N possible crystal configurations on a lattice with N sites per cell, these approaches [6,9,16–18] opted to limit their search at the outset to only $O(10)$ possible configurations. This eliminates the possibility of a genuine surprising answer. It is, however, possible to make some progress in this direction by parametrizing the energy, $E(\sigma)$, of any of the $\sigma = 1, \ldots, 2^N$ configurations in a readily searchable way. The classic Ising representation [20], $E(\sigma) = \sum_{i,j} J_{ij}\hat{S}_i\hat{S}_j$, of the energy in terms of nearest-neighbor interactions J on a lattice whose sites i can be occupied either by an A atom (giving $\hat{S}_i = -1$) or by a B atom ($\hat{S}_i = 1$) is one such example. The ground state of such simple Hamiltonians can be readily searched over the full configurational space [21]. However, a single (or a few) arbitrarily selected "interaction parameters" J may not capture the chemical reality of bonding in actual compounds. What one needs is an electronic structure theory which independently establishes the range (first neighbors, second neighbors, ...), type (pairs, three body, four body, ...), and chemical content (charge transfer, atomic site effects, ...) of the interaction energies $\{J\}$. This is made possible by a mixed-space cluster expansion (MSCE) [22], whereby the atomically relaxed energies, $E(\sigma)$, of arbitrary lattice configurations σ are expressed as linear sums of energies characteristic of geometric figures, such as biatoms, triatoms, etc. The energies of these figures are obtained from LDA calculations of $O(15)$ compounds that do not even have to contain the low energy ground state. The simplicity and accuracy of this expansion permits an exhaustive search of the ground state [via simulated annealing Monte Carlo (MC)] of an astronomic number of candidate configurations. We predict three stable ordered structures for $Ag_{1-x}Pd_x$ that emerge at $x = 0.25$, 0.50, 0.75. No other composition gives ordered $T = 0$ structures: For $Ag_{0.25}Pd_{0.75}$ the ordered structure is $L1_2$ (Cu_3Au-type); for $Ag_{0.5}Pd_{0.5}$ it is the alternate monolayer superlattice $(Ag)_1/(Pd)_1$ along [111], i.e., the $L1_1$ structure (CuPt-type), whereas for $Ag_{0.75}Pd_{0.25}$ we have the same superlattice, but with different composition of the monolayers, i.e., $(Ag_{0.5}Pd_{0.5})_1/(Pd)_1$ along (111). This structure has no name. None of these structures were observed experimentally as yet. Remarkably, while Cu-Pt is the only known binary material so far to appear in the $L1_1$ "CuPt-type structure" (see, e.g., [23]), we now predict that its unique status is shared by another material—Ag-Pd.

In the MSCE [22], any configuration σ is defined by specifying the occupations of each of the N lattice sites by an Ag atom (spin index $\hat{S}_i = -1$) or a Pd atom ($\hat{S}_i = +1$). The formation enthalpy of any configuration σ at its atomically relaxed state is then given by

$$\Delta H_{CE}(\sigma) = \sum_{\mathbf{k}} J_{\mathrm{pair}}(\mathbf{k})|S(\mathbf{k},\sigma)|^2 + \sum_{f}^{MB} D_f J_f \bar{\Pi}_f(\sigma) + \frac{1}{4x-1} \sum_{\mathbf{k}} \Delta E_{CS}^{\mathrm{eq}}(\hat{k},x)|S(\mathbf{k},\sigma)|^2. \quad (1)$$

The first summation includes *all* pair figures corresponding to pair interactions with arbitrary separation. $J_{\mathrm{pair}}(\mathbf{k})$ is the Fourier transform of the pair interaction energies and $S(\mathbf{k},\sigma)$ the structure factor of configuration σ. The second sum includes only nonpair figures. Here J_f is the real-space effective many-body interaction of figure f, D_f stands for the number of equivalent clusters per lattice site, and $\bar{\Pi}_f(\sigma)$ are spin products. The third summation represents atomic size-mismatch effects and involves the constituent strain energy necessary to maintain coherency between bulk Ag and Pd along an interface with orientation $\hat{k}$. This term is essential for describing strained systems [22] and is included here.

We determined $\{J_{\mathrm{pair}}(\mathbf{k})\}$ and $\{J_f\}$ by fitting $\Delta H_{CE}(\sigma_{\mathrm{ord}})$ to a set of LDA calculated energies of only 15 ordered $\mathrm{Ag}_m\mathrm{Pd}_n$ compounds. The formation enthalpies, $\Delta H_{\mathrm{LDA}}(\sigma_{\mathrm{ord}})$, were calculated using the density functional theory formalism, as implemented [24] in the full potential linear augmented plane-wave method. Table I shows the input formation enthalpies, ΔH_{LDA}, and the fitted enthalpies, $\Delta H_{CE}(\sigma_{\mathrm{ord}})$, for $\mathrm{Ag}_m\mathrm{Pd}_n$. Enthalpies that have an asterisk denote structures not used in the fit. The average error for *all* 19 structures is about 2 meV/atom, and that for predicting four structures is 2.25 meV. The cluster expansion was minimized with respect to the number of used input structures; i.e., no further reduction of the number of input structures is possible without losing accuracy in the effective cluster interactions $\{J_{\mathrm{pair}}(\mathbf{k})\}$ and $\{J_f\}$.

TABLE I. Cluster expansion fit for Ag-Pd. The compounds are sorted by superlattice direction and composition; the symbols describe the name of the structures. The upper value gives the formation enthalpy from LDA calculation, the lower value the formation enthalpy from the MSCE fit. Compounds marked by an asterisk are not input structures of the cluster expansion fit, but represent predictions.

			Direction		
Stoich.	x_{Pd}	(100)	(110)	(111)	Others
Ag	0.0				fcc
direct:					0.0
CE:					0.0
$\mathrm{Ag_3Pd}$	0.25	$Z1$	$Y1$	$V1^*$	$L1_2$
		−21.7	−16.0	−30.1	−46.3
		−22.0	−15.9	−31.4	−46.4
$\mathrm{Ag_2Pd}$	0.333			$\alpha 1$	
				−42.9	
				−42.6	
AgPd	0.50	$L1_0$		$L1_1$	
		−29.0		−50.5	
		−28.5		−50.6	
$\mathrm{Ag_2Pd_2}$	0.50	$Z2$	$Y2$	$V2$	$SQS8a^*$
		−29.0	−20.7	−32.0	−32.6
		−28.9	−20.7	−32.4	−28.1
$\mathrm{Ag_3Pd_3}$	0.50			$V6$	
				−24.2	
				−23.9	
$\mathrm{AgPd_2}$	0.667			$\alpha 2^*$	
				−29.9	
				−27.2	
$\mathrm{AgPd_3}$	0.75	$Z3$	$Y3$	$V3*$	$L1_2$
		−5.5	−5.0	−18.4	−17.3
		−5.5	−5.1	−17.9	−17.2
Pd	1.00				fcc
					0.0
					0.0

We applied our expansion, Eq. (1), with the fitted effective cluster interactions, $\{J_{\mathrm{pair}}(\mathbf{k})\}$ and $\{J_f\}$, to an extensive $T = 0$ ground state search via MC simulated annealing method. Starting with a temperature close to the solidus line of the phase diagram, the temperature is reduced by a certain amount until the equilibrium is reached. We then construct the convex hull (E vs x) to assure us that each predicted ground state at x is stable with respect to disproportion into two structures with $x_1 \leq x \leq x_2$. The annealing process is repeated for different simulation conditions (e.g., different MC cells with up to about $30 \times 30 \times 30 = 27\,000$ sites and up to 10 000 MC steps per temperature, different initial configurations, and different temperature grids) to assure that the result is invariant. Beside the final configuration ($T \rightarrow 0$) and its formation enthalpy, the correlation functions of the final configurations were stored for identification and comparison with those of thousands of well-defined intermetallic compounds. The result of our ground state search is summarized in Fig. 1. We find that (i) the ground-state line of Ag-Pd is formed by three ground-state structures occurring at Pd concentrations $x_{\mathrm{Pd}} = 0.25, 0.50, 0.75$ [25]. (ii) For $x_{\mathrm{Pd}} = 0.25$, the $L1_2$ structure is the stablest structure, while for $x_{\mathrm{Pd}} = 0.50$, the $L1_1$ structure [$(\mathrm{Pd})_1/(\mathrm{Ag})_1$ (111) superlattice] is found to be the ground state (the two [111] planes perpendicular to the superlattice direction are marked by solid lines). The compound found for $x_{\mathrm{Pd}} = 0.75$ does not have a special name. It represents a $(\mathrm{Ag_{0.5}Pd_{0.5}})_1/(\mathrm{Pd})_1$ superlattice along [111]. The Pd and Ag atoms in the $\mathrm{Ag_{0.5}Pd_{0.5}}$ [111] layer form an in-plane $c(2 \times 2)$ superstructure. Because of the *additional* Pd atoms in the Ag(111) layers compared to $L1_1$, we may call this compound $L1_1^+$. Whereas this structure is only 3 meV below the AgPd $L1_1$ and fcc Pd tie line, its appearance as a ground state is a robust feature of our LDA and cluster-expansion fits.

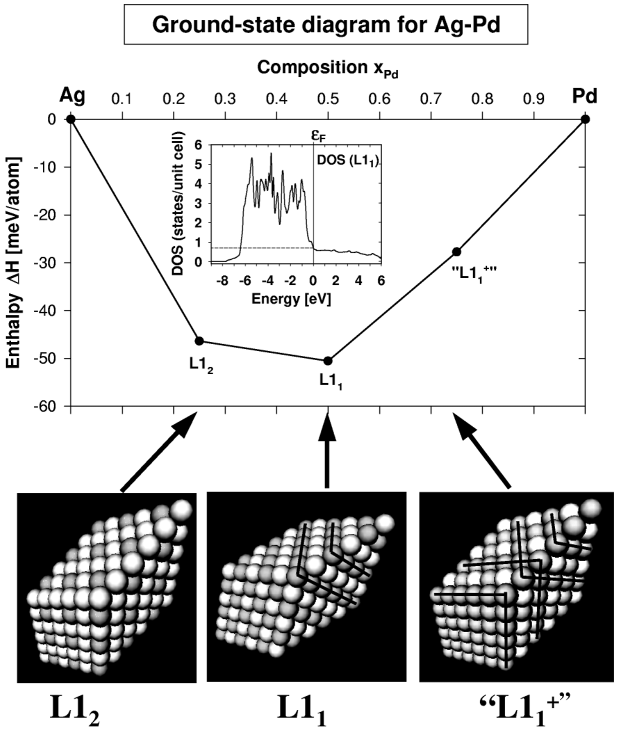

FIG. 1. Ground-state diagram for the system Ag-Pd. Three well-defined $T = 0$ structures are found for $x_{\mathrm{Pd}} = 0.25$, 0.50, 0.75. The lower part shows the crystal structures of the ground state found, and the inset shows the density of states of the geometrically fully relaxed $L1_1$ structure.

The critical temperatures corresponding to the coherent phase boundaries between disordered alloy and low-temperature ordered compound were also calculated from MC simulations to be $T_c = 340$, 320, and 270 K for $x = 0.25$, 0.50, and 0.75, respectively, and therefore, far below the solidus line ($T = 1235$ K for $x \rightarrow 0$ and $T = 1828$ K for $x \rightarrow 1$) [3]. These low transition temperatures explain why, up to now, these three structures were not observed experimentally. Unfortunately, there are also no short-range-order measurements for the random alloy at higher temperatures. As a possible motivation for future experimental studies, Fig. 2 gives our calculated short-range order (SRO) patterns at $T = 500$ K for $x = 0.25, 0.50, 075$. The SRO patterns were calculated by using the MC method for a fixed temperature and concentration. After the equilibrium is reached, the thermal averages of spin products $\langle\bar{\Pi}_{lmn}\rangle$ [see also description of Eq. (1)] for shell lmn are used to determine the SRO parameters α_{lmn} via $\alpha_{lmn}(x) = [\langle\bar{\Pi}_{lmn}\rangle - q^2]/[1 - q^2]$ with $q = 2x - 1$. The portion of diffuse scattering due to SRO is then simply proportional to the lattice Fourier transform of $\alpha_{lmn}(x)$, i.e., $\alpha(x, \mathbf{k}) = \sum_{lmn} \alpha_{lmn}(x) e^{i\cdot\mathbf{k}\cdot\mathbf{R}_{lmn}}$. For Ag_3Pd whose long-range order structure is $L1_2$, we see characteristic short-range order peaks within the (220) plane of the Brillouin zone at [100] and symmetrically equivalent positions. For AgPd ($L1_2$) and AgPd ($L1_1^+$)3 we see peaks with diffuse intensities around the L point, $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, for the corresponding disordered alloy, revealing the tendency of the solid solution to form locally the $L1_1$ structure.

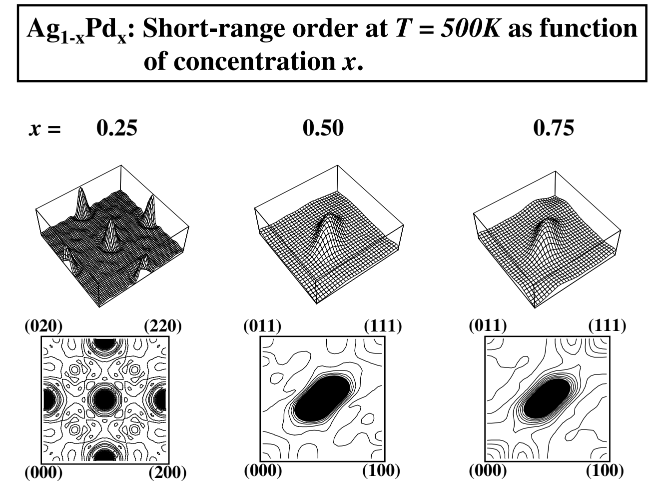

FIG. 2. SRO pattern and corresponding contour plot $T = 500$ K for Ag-Pd solid solutions with three different concentrations.

We also calculated the mixing enthalpy of the disordered alloy as a function of the Pd concentration for $T = 1200$ K, where experimental data exist and therefore, a quantitative comparison between experiment and on quantum-mechanic based prediction becomes possible. The resulting curves are given in Fig. 3 showing that experimental and theoretical data agree very well. If SRO is neglected, we find that the mixing enthalpy is about 0.5–1 kJ/mole higher in energy, so that the agreement between experiment and theory becomes worse.

The most surprising result of our ground state search is the prediction of the $L1_1$ structure for low temperatures, since up to now the only binary metal alloy system known possessing $L1_1$ as ground state is the Cu-Pt alloy system

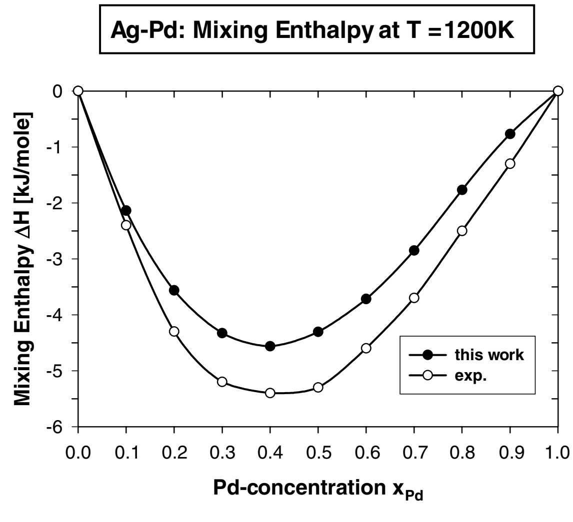

FIG. 3. Experimentally determined [2] and calculated mixing enthalpy ΔH of $Ag_{1-x}Pd_x$ at $T = 1200$ K as a function of composition.

(see, e.g., [23]). The question arises, how can this unsuspected result be explained *ex-post-facto*. Clark *et al.* [26] described the existence of the $L1_1$ structure in Cu-Pt by a coupling between electronic states at L and X Van Hove singularities at the Fermi level, ϵ_F. Furthermore, they suggest that $L1_1$ is stabilized over $L1_0$ by the fact that at the Fermi level the d-electron density of states (DOS) is lower for the $L1_1$ than for the $L1_0$ structure. Indeed, we find that the DOS of $L1_1$ AgPd at ϵ_F (0.7 states/unit cell; see inset of Fig. 1) is lower than that of the $L1_0$ structure (0.9 states/unit cell), in accord with the lower formation enthalpy of $L1_1$ over $L1_0$ (22 meV/atom, see Table I). However, these results hold only for the atomically relaxed structures. For atomically unrelaxed structures, the formation enthalpy of $L1_1$ is still lower than that of $L1_0$ (by 15 meV/atom), but the DOS at ϵ_F are practically equal. So, in the case of Ag-Pd, for unrelaxed systems the DOS argument is not indicative of the stability of $L1_1$. Analyzing the individual energy parts of the quantum-mechanic Hamiltonian leads to the result that the stabilization of $L1_1$ is due to the Ewald energy being about 400 meV/atom lower for $L1_1$ than for $L1_0$. Although all remaining energy parts (e.g., the Hartree term) show higher energies for $L1_1$ than for $L1_0$, they cannot compensate this large Ewald energy of $L1_0$. Interestingly, the inset of Fig. 1 also shows that the d band is pushed below the Fermi level. Indeed, we found the same behavior for the $L1_1^+$ ($x_{\mathrm{Pd}} = 0.75$) ground-state structure, different from, e.g., the $L1_2$ ($\mathrm{AgPd_3}$) structure, where the opposite is true. This probably stabilizes $L1_1^+$ over $L1_2$ for $x_{\mathrm{Pd}} = 0.75$.

The three predicted well-ordered Ag-Pd structures represent not only an important addition to the phase diagram of the system, but could also significantly influence mechanical and electronic properties in the low-temperature regime. However, an experimental proof of the existence of these compounds is still lacking, probably due to the low transition temperatures between low-temperature compound and disordered alloy. The found compounds lead to characteristic SRO patterns above the transition point. We therefore hope that our predicted SRO maps for $T = 500$ K may act as fingerprints for future experimental studies.

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