First-principles study of phase stability in pseudobinary $(Ni_{1-x}Pt_x)_3Al$ alloys

C. Jiang,¹ D. J. Sordelet,^{1,2} and B. Gleeson^{1,2}

¹Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA

²Materials and Engineering Physics Program, Ames Laboratory (USDOE), Ames, Iowa 50011, USA

(Received 16 August 2005; revised manuscript received 30 September 2005; published 29 November 2005)

We studied the phase stability in pseudobinary $(Ni_{1-x}Pt_x)_3Al$ alloys using a combination of first-principles calculations, a cluster expansion technique, and Monte Carlo simulations. Our ground state search yields $L1_0$ Ni₂PtAl and $L1_0$ NiPt₂Al as the two stable ground state structures, and the latter has been observed experimentally. The calculated c/a ratio of $L1_0$ NiPt₂Al is also in good agreement with experiments. By performing Monte Carlo simulations, the order-disorder transition temperatures of $L1_0$ Ni₂PtAl and $L1_0$ NiPt₂Al were predicted to be ~915 K and ~1275 K, respectively. The mixing enthalpies of random pseudobinary $L1_2$ (Ni_{1-x}Pt_x)₃Al alloys were also predicted using our cluster expansion, and the results agree well with direct first-principles calculations on Special Quasirandom Structures (SQS's) for $L1_2$ alloys developed in the present study.

DOI: 10.1103/PhysRevB.72.184203

PACS number(s): 61.66.Dk

I. INTRODUCTION

Fundamental understanding of the phase equilibria in the Ni-Al-Pt ternary alloy system is of great importance for the development of next-generation thermal barrier coating (TBC) system for gas turbine engines.¹ It is well known that addition of Pt to β -NiAl as well as Ni-Al $\gamma' + \gamma$ alloys can significantly improve their high temperature oxidation resistance.¹ Gleeson et al.^{1,2} have recently experimentally determined the partial Ni-Al-Pt isothermal sections at 1373 K and 1423 K. The most notable finding is a ternary α -NiPt(Al) phase with L1₀-type ordered face-centered tetragonal structure which exists over a large composition range. This phase has also been previously observed by Kamm and Milligan³ and Meininger and Ellner⁴ in their experimental study of Ni_{0.75-x}Pt_xAl_{0.25} alloys at 1373 K and 1273 K, respectively. Due to the existence of the α -NiPt(Al) phase, no continuous solid solution forms between L1₂ Ni₃Al and L1₂ Pt₃Al phases, and the maximum solubility of Pt in Ni₃Al was found to be ~ 30 at %.²⁻⁴

Due to their strongly bonded nature, both Ni₃Al and Pt₃Al retain their ordered L1₂ structure up to their melting points at \sim 1645 K (Ref. 5) and \sim 1829 K (Ref. 6), respectively, without disordering into fcc. The A₃B L1₂ unit cell consists of two types of lattice sites, i.e., the *a*-site (the face centers) normally occupies by A atoms and the *b*-site (cube corner) normally occupied by B atoms. Experimentally, it has been established that Pt has a strong preference for the Ni site (a-site) in Ni₃Al.⁷ Such a conclusion has been further supported by recent first-principles supercell calculations by Geng et al.⁸ From the bond energy point of view, the preferential occupation of *a*-sites in $Ni_{0.75-x}Pt_xAl_{0.25}$ alloys by Pt atoms will not only maximize the number of nearestneighbor Al-Pt bonds, but also the number of nearestneighbor Al-Ni bonds, both of which are much more enerbonds.9 getically favorable than Ni-Pt Indeed, experimentally, the formation enthalpies of solid Al-Pt (Refs. 10 and 11) and Al-Ni (Ref. 12) alloys are much more negative than those of solid Ni-Pt (Ref. 13) alloys. As the result, the ternary $Ni_{0.75-x}Pt_xAl_{0.25}$ alloys can be treated with a high degree of accuracy as pseudobinary $(Ni_{1-x}Pt_x)_3Al$ alloys in which the Ni and Pt atoms substitutionally occupy the *a*-sites with *b*-sites exclusively occupied by Al atoms.

In this paper, for the purpose of investigating the phase stability in pseudobinary $(Ni_{1-x}Pt_x)_3Al$ alloys, we applied a generalized lattice model to characterize the substitutional distribution of Ni and Pt atoms on the a-sites. We constructed a cluster expansion¹⁴⁻¹⁸ from first-principles calculated total energies of a series of $(Ni_{1-x}Pt_x)_3Al$ ordered structures. An exhaustive ground state search was performed using our cluster expansion to predict the lowest-energy *a*-site substitutional configurations at T=0 K, i.e., the ground states. Our search yielded two ground states structures, Ni₂PtAl and NiPt₂Al, both with ordered $L1_0$ structure. By performing finite-temperature Monte Carlo simulations, their order-disorder transition temperatures were also obtained. Finally, we predicted using our cluster expansion the mixing enthalpies of random pseudobinary $(Ni_{1-x}Pt_x)_3Al L1_2$ alloys, and the results are compared with direct first-principles calculations using L1₂ SQS's, which were developed in the present study.

II. METHODOLOGY

A. First-principles method

First-principles total energy calculations were performed using the all-electron Blöchl's projector augmented wave (PAW) approach^{19,20} within the generalized gradient approximation (GGA), as implemented in the highly-efficient Vienna *ab initio* simulation package (VASP).^{21,22} For the GGA exchange-correlation functional, we employed the Perdew-Wang parameterization (PW91).^{23,24} The semi-core 3*p* electrons of Ni were explicitly treated as valence. The *k*-point meshes for Brillouin zone sampling were constructed using the Monkhorst-Pack scheme²⁵ and the total number of *k*-points times the total number of atoms per unit cell was at least 10 000 for all structures. A plane wave cutoff energy of 459.9 eV was used. Spin-polarized calculations were performed to account for the ferromagnetic nature of Ni. By computing the quantum-mechanical forces and stress tensor, the unit cell volume and shape as well as all internal atomic positions of all structures were fully relaxed using a conjugate-gradient scheme.

The formation enthalpy (per formula unit) of a pseudobinary $(Ni_{1-x}Pt_x)_3Al$ alloy relative to the composition-weighted average of the end members can be calculated as follows:

$$\Delta H(x) = E - (1 - x)E(\operatorname{Ni}_3\operatorname{Al}) - xE(\operatorname{Pt}_3\operatorname{Al}), \qquad (1)$$

where $E(Ni_3Al)$, $E(Pt_3Al)$, and E are the first-principles calculated total energies per $(Ni_{1-x}Pt_x)_3Al$ formula unit of the constituent L1₂ structures Ni₃Al and Pt₃Al and the corresponding pseudobinary $(Ni_{1-x}Pt_x)_3Al$ alloy, each relaxed to their equilibrium geometries, respectively.

B. Cluster expansion technique

For a binary $A_{1,r}B_r$ substitutional alloy, many properties such as energy are dependent on the *configuration*, i.e., the substitutional arrangement of A and B atoms on an underlying parent lattice (in our case, the *a*-sites). For a binary alloy with N atoms, there can be 2^N possible number of configurations, which is an astronomically large number when N is large. Searching for the ground states necessitates exploring such a huge configurational space, which is computationally prohibitive directly using first-principles methods. To overcome such difficulties, we adopted the cluster expansion (CE) technique^{14–18} in the present study. Within this method, the configuration σ on an underlying parent lattice is characterized by assigning pseudo-spin variables to each site: S_i = -1 (+1) if an A (B) atom sits at site *i* (in our case, $S_i = -1$ for Ni and +1 for Pt atoms). The formation enthalpy of any lattice configuration $\sigma = (S_1, S_2, \dots, S_N)$ can then be conveniently calculated using the following Ising-like Hamiltonian:

$$\Delta H_{\rm CE}(\sigma) = \sum_{f} D_f J_f \overline{\Pi}_f(\sigma), \qquad (2)$$

where f is a figure (cluster) comprised of a group of lattice sites (single site, pairs, triplets, etc.), D_f is the degeneracy factor indicating the number of figures of type f per formula unit, and $\overline{\Pi}_f$ is the correlation function defined as the product of the spin variables over all sites of a figure, averaging over all symmetry-equivalent figures of the lattice. J_f is the configuration-independent Ising-type interaction for figure fcalled effective cluster interaction (ECI). Once $\{J_f\}$ is known one can readily use Eq. (2) to predict the formation enthalpy of *any* configuration, both ordered and disordered, with the accuracy of first-principles calculations. Note that, the effects of atomic relaxations can be readily incorporated into Eq. (2) as long as there is a one-to-one correspondence between lattice sites and atomic positions.

The expansion in Eq. (2) is exact as long as *all* the figures are included. However, in practice, since the interactions between widely separated atoms are expected to be weaker than interactions between nearer ones, the expansion in Eq.



FIG. 1. First-principles calculated and CE predicted formation enthalpies of 27 ordered structures (with 4–16 atoms per unit cell) as a function of composition. The solid line represents CE predicted mixing enthalpies of the random $(T \rightarrow \infty)$ L1₂ alloys. The firstprinciples SQS results are also shown.

(2) can usually be truncated at certain distance to include only a few short-ranged pair and multisite clusters. In the present study, we determined $\{J_f\}$ by fitting $\Delta H_{\rm CE}(\sigma_{\rm ord})$ to first-principles calculated formation enthalpies $\Delta H_{\rm FP}(\sigma_{\rm ord})$ of a set $\{\sigma_{\text{ord}}\}$ of 27 input $(\text{Ni}_{1-x}\text{Pt}_x)_3\text{Al}$ ordered structures (not necessarily ground states) with different arrangements of Ni and Pt atoms on the *a*-sites. The Al atoms occupying only the *b*-sites do not have configurational degree of freedom and are not explicitly included in the cluster expansion. Their effects are however implicitly included in $\Delta H_{\rm FP}(\sigma_{\rm ord})$ and $\{J_f\}$. A well-converged cluster expansion was obtained using 9 pair interactions and 4 triple interactions with an average fitting error of only 0.6 meV/atom (2.4 meV/formula unit) and a maximum fitting error of only 1.5 meV/atom (6.1 meV/formula unit). A direct comparison of firstprinciples calculated and CE predicted formation enthalpies of all those 27 ordered structures are shown in Fig. 1.

To further assess the predictive power of our cluster expansion, we also calculated the cross-validation (cv) score, defined as

$$\operatorname{cv} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\Delta H_i^{\text{FP}} - \Delta H_i^{\text{CE}})^2}, \qquad (3)$$

where ΔH_i^{FP} is the first-principles calculated formation enthalpy of structure *i*, while ΔH_i^{CE} is the formation enthalpy of structure *i* predicted from a cluster expansion constructed using the calculated formation enthalpies of the other N-1structures. The cv score of our cluster expansion is found to be only 1.9 meV/atom (7.5 meV/formula unit).

The final obtained ECIs of our cluster expansion are given in Table I, together with the definitions of all the figures considered. The clearly dominating interaction is an attrac-

TABLE I. ECIs of the	ne present cluster	r expansion togeth	er with the	e definitions o	of all the figures	s considered.	Vertices of	figures a	e given
in units of a, the fcc lat	tice parameter.								

Cluster type	Figure designation	D_f	$J_f(\text{meV})$	$D_f J_f$ (meV)		Vertices	
Empty	J_0	1	-74.993	-74.993			
Point	J_1	3	-4.225	-12.675	(0.5, 0.5, 0)		
Pairs	J_2	12	18.258	219.096	(0.5, 0.5, 0)	(0.5, 0, 0.5)	
	K_2	6	-12.59	-75.54	(0.5, 0.5, 0)	(0.5, -0.5, 0)	
	L_2	3	2.849	8.547	(0.5, 0.5, 0)	(0.5, 0.5, 1)	
	M_2	24	-1.504	-36.096	(0.5, 0.5, 0)	(0, -0.5, 0.5)	
	N_2	6	0.657	3.942	(0.5, 0.5, 0)	(-0.5, -0.5, 0)	
	O_2	12	0.856	10.272	(0.5, 0.5, 0)	(0.5, -0.5, 1)	
	P_2	12	-2.354	-28.248	(0.5, 0.5, 0)	(-0.5, -0.5, 1)	
	Q_2	6	-3.14	-18.84	(0.5, 0.5, 0)	(0.5, -1.5, 0)	
	R_2	3	-2.836	-8.508	(0.5, 0.5, 0)	(0.5, 0.5, 2)	
Triplets	J_3	8	-5.249	-41.992	(0.5, 0.5, 0)	(0.5, 0, 0.5)	(0, 0.5, 0.5)
	K_3	12	-1.374	-16.488	(0.5, 0.5, 0)	(0, 0.5, 0.5)	(0, 0.5, -0.5)
	L_3	12	0.762	9.144	(0.5, 0.5, 0)	(0.5, 0.5, 1)	(0.5, 0, 0.5)
	M_3	24	2.529	60.696	(0.5, 0.5, 0)	(0, 0.5, 0.5)	(0.5,0,-0.5)

tive nearest-neighbor pair interaction $(J_2 > 0)$, and its symmetry-weighted value $(D_f J_f)$ is much stronger than those of the second nearest-neighbor pair interactions $(K_2 \text{ and } L_2)$. This strongly indicates a tendency towards *a*-site ordering rather than phase separation in $(Ni_{1-x}Pt_x)_3Al$ alloys at lower temperatures. Indeed, the formation enthalpies of all the ordered structures considered here are negative, as shown in Fig. 1. The most stable T=0 K ordered structures will be further predicted using our cluster expansion in Sec. III A.

C. Special quasirandom structures (SQS's)

Without resorting to the cluster expansion technique, the random alloys can be directly modeled using special quasirandom structures (SQS's) proposed by Zunger et al.^{26,27} SQS's are specially designed *small-unit-cell* periodic structures, which closely mimic the most relevant local pair and multisite correlation functions of random substitutional alloys. The SQS approach in essentially finding the small-unitcell ordered structures that possess $(\overline{\Pi}_f)_{SOS} \cong \langle \overline{\Pi}_f \rangle_R$ for as many figures as possible. Admittedly, describing random alloys by small unit-cell periodically-repeated structures will surely introduce erroneous correlations beyond a certain distance. However, since interactions between widely separated atoms are expected to be weaker than interactions between nearer ones, we can construct SQS's that exactly reproduce the correlation functions of a random alloy between the first few nearest neighbors, deferring periodicity errors to more distant neighbors.

Using the *gensqs* code in the Alloy-Theoretic Automated Toolkit (ATAT),²⁸ we have developed one 24-atom SQS structure for substitutionally random pseudobinary $(A_{1-x}B_x)_3C L1_2$ alloys at compositions x=2/3. Here A and B atoms are randomly distributed on the *a*-sites of the L1₂ unit cell with the *b*-sites completely occupied by C atoms. A more

detailed description of the procedures for constructing the SQS has been published elsewhere.^{29,30} The lattice vectors and atomic positions of the obtained SQS structure in its ideal, unrelaxed forms are given in Table II, all in Cartesian coordinates. In Table III, the pair and multisite correlation functions of the SQS structure presented in Table II are compared with those of the corresponding random alloys. The SQS structure for x=1/3 can be simply obtained by switching the A and B atoms in SQS for x=2/3. We note that, since this amounts to replacing all of the spin variables by $S_i \rightarrow -S_i$, all even-body correlations are equivalent for x=1/3 and x=2/3, while all odd-body correlations simply change sign. Thus, the three-body figures are largely responsible for asymmetries in the formation energies between x=1/3 and x=2/3.

III. RESULTS AND DISCUSSIONS

A. Finding the ground states

To answer the question what are the most stable ordered structures, we have performed an exhaustive direct enumeration ground state search³¹ among all the possible L1₂-based structures up to 20 atoms (15 *a*-sites) per unit cell with our cluster expansion Hamiltonian, and our results are shown in Fig. 2. In order for a structure to be ground state, it not only needs to be the lowest-energy structure at a given composition, but also needs to be stable with respect to phase separation into competing structures at other compositions. Out of a total of ~10⁴ possible candidate structures, our search revealed only two ground state structures at x=1/3 and 2/3, respectively. For x=2/3, the ground state is a face-centered tetragonal L1₀ NiPt₂Al structure in which the Al atoms occupy the corners of the L1₀ unit cell, the Pt atoms occupy the prismatic (100) and (010) face centers, and the Ni atoms

TABLE II. Structural description of the SQS structure for the $(A_{1/3}B_{2/3})_3$ C L1₂ alloy. Lattice vectors and atomic positions are given in Cartesian coordinates, in units of *a*, the fcc lattice parameter. Atomic positions are given for the ideal, unrelaxed fcc sites.

Lattice vectors	$a_1 = (-2.0, -1.0, 1.0), a_2 = (-1.0, -2.0, -1.0), a_3 = (2.0, 1.0, 1.0)$	
Atomic positions	A- $(-0.5, -1.5, 1.0)$, A- $(1.0, -0.5, 0.5)$, A- $(-0.5, -0.5, 1.0)$ A- $(-0.5, -1.5, 0.0)$, A- $(0.5, 0.0, 1.5)$, A- $(-1.0, -1.5, 0.5)$ B- $(0.5, -0.5, 1.0)$, B- $(-1.5, -2.0, 0.5)$, B- $(0.0, -0.5, 1.5)$ B- $(1.5, 0.5, 1.0)$, B- $(-0.5, -1.0, 0.5)$, B- $(0.0, -1.5, 0.5)$ B- $(-1.5, -1.5, 1.0)$, B- $(0.5, -1.0, 0.5)$, B- $(0.0, -0.5, 0.5)$ B- $(0.5, 0.0, 0.5)$, B- $(-0.5, -1.0, 1.5)$, B- $(-2.0, -2.5, 0.5)$ C- $(0.0, -1.0, 1.0)$, C- $(1.0, 0.0, 1.0)$, C- $(-1.0, -2.0, -0.0)$	

occupy the (001) face centers of the basal plane. For x = 1/3, the ground state is a L1₀ Ni₂PtAl structure, which can be derived from the L1₀ NiPt₂Al structure simply by switching the Ni and Pt atoms. Remarkably, the predicted L1₀ NiPt₂Al ground state has been experimentally observed in various studies.^{1,3,4} We note that, both structures are also the ground states among the 27 input structures according to direct first-principles calculations. Our first-principles predicted equilibrium lattice parameters and c/a ratio of L1₀ NiPt₂Al structure are also in good agreement with experimental measurements, as shown in Table IV.

To verify that those two structures are true ground states, we also subjected our cluster expansion to Monte Carlo simulated-annealing simulations.³¹ Monte Carlo simulations were performed within a canonical ensemble (fixed composition) at x=1/3 and 2/3, respectively. We used a large 14 $\times 14 \times 14$ cubic simulation cell containing 2744 Al atoms and a total of 8232 Ni and Pt atoms (with periodic boundary conditions). For each simulation, we started from a high temperature for a substitutionally random state (an extremely high temperature of 50 000 K is used to obtain the truly ran-

dom state of the alloy since at such high temperature, almost all the atom exchanges in the Metropolis algorithm will be accepted) and slowly cooled the system down to a low temperature at which all configurational changes proved to be energetically unfavorable. This gives (1) the T=0 K ground state structures, and (2) the order-disorder transition temperatures. Our simulated annealing simulations show that, L1₀ Ni₂PtAl and L1₀ NiPt₂Al are not only the ground states out of all structures with up to 20 atoms per unit cell, but also are truly the lowest-energy configurations out of an astronomical number of possible configurations [without symmetry, there are $N_{conf}=N!/(xN)!(N-xN)!$ of possible configurations that can be explored in our Monte-Carlo simulations, where N=8232].

B. Order-disorder transition temperatures

The order-disorder transition temperatures between ordered L1₀ Ni₂PtAl and L1₀ NiPt₂Al and the high temperature disordered (Ni_{1-x}Pt_x)₃Al L1₂ alloys were obtained by monitoring peaks in heat capacity vs temperature curves obtained

TABLE III. Pair and multisite correlation functions of the SQS structure for x=2/3. The periodicity errors, defined as $(\overline{\Pi}_f)_{SOS} - (2x-1)^{k_f}$, as also given.

Cluster type	Figure designation	Random alloy	SQS	Periodicity error
Pairs	J_2	0.1111	0.1111	0
	K_2	0.1111	0.1111	0
	L_2	0.1111	0.1111	0
	M_2	0.1111	0.1111	0
	N_2	0.1111	0.1111	0
	O_2	0.1111	0.0556	-0.0555
	P_2	0.1111	0.2222	0.1111
	Q_2	0.1111	0.2222	0.1111
	R_2	0.1111	0.3333	0.2222
Triplets	J_3	0.0370	0	-0.037
	K_3	0.0370	0.1111	0.0741
	L_3	0.0370	0	-0.037
	M_3	0.0370	0	-0.037



FIG. 2. Ground state search ($\sim 10^4$ structures) using the cluster expansion. The stable ground states are shown as solid circles.

from our Monte Carlo simulated annealing simulations. As shown in Fig. 3, the order-disorder transition for $L1_0$ NiPt₂Al is clearly of first-order (with a discontinuity in formation enthalpy) and occurs at ~1275 K. In comparison, the transition temperature of $L1_0$ Ni₂PtAl is much lower, ~915 K, as shown in Fig. 4. Such a low order-disorder transition temperature explains why $L1_0$ Ni₂PtAl has never been observed experimentally at higher temperatures. Therefore, we assert that experimental examination of the lower-temperature phase stability of Ni_{0.75-x}Pt_xAl_{0.25} alloys would be of interest.

We note that, although the maximum stability temperature of L1₀ NiPt₂Al was predicted to be ~1275 K, it has actually been experimentally observed at T=1423 K. In other words, the order-disorder transition temperature of L1₀ NiPt₂Al was underestimated by our cluster expansion. We attribute such discrepancy to the inaccuracies in first-principles calculations as well as the fitting errors of our cluster expansion. Another possible reason is the neglect of the effects of nonconfigurational (electronic, vibrational, etc.) entropies in our Monte Carlo simulations, which may shift the order-disorder transition temperatures. Our pseudobinary approximation may also contribute to such discrepancy.

C. Mixing enthalpies of random alloys

For a perfectly random $(T \rightarrow \infty) A_{1-x}B_x$ alloy, there is no correlation in the occupation between various sites, and

TABLE IV. First principles (PAW-GGA) calculated equilibrium lattice parameters of ground state structures.

Structure	Lattice parameters	Source
L1 ₀ NiPt ₂ Al	<i>a</i> = <i>b</i> =3.928 Å, <i>c</i> =3.615 Å, <i>c</i> / <i>a</i> =0.92	Present study
	<i>a</i> = <i>b</i> =3.905 Å, <i>c</i> =3.544 Å, <i>c/a</i> =0.91	Kram ^a
	<i>a</i> = <i>b</i> =3.926 Å, <i>c</i> =3.519 Å, <i>c/a</i> =0.90	Meininger ^b
L1 ₀ Ni ₂ PtAl	a=b=3.672 Å, $c=3.755$ Å, $c/a=1.02$	Present study
^a Reference 3.		

^bReference 4.



FIG. 3. Monte Carlo simulated (a) formation enthalpy and (b) heat capacity of $(Ni_{1/3}Pt_{2/3})_3Al$ alloy as a function of temperature.

therefore the pair and multisite correlation function $\overline{\Pi}_f$ can be simply written as the product of the lattice-averaged site variable $\langle S_i \rangle = 2x - 1$, i.e., $\langle \overline{\Pi}_f \rangle_R = (2x - 1)^2$ for pair and $\langle \overline{\Pi}_f \rangle_R$ $= (2x - 1)^3$ for triple interactions. Therefore, the mixing enthalpy of a random $A_{1-x}B_x$ alloy can be calculated analytically from the cluster expansion as

$$\Delta H_{\rm mix}(x) = \langle \Delta H_{\rm CE}(\sigma) \rangle_R = \sum_f D_f J_f (2x-1)^{k_f}, \qquad (4)$$

where k_f is the number of vertices in figure *f*. The CE predicted mixing enthalpies of random pseudobinary $(Ni_{1-x}Pt_x)_3Al L1_2$ alloys calculated using Eq. (3) are shown as solid line in Fig. 1. We note that, to fully consider the



FIG. 4. Monte Carlo simulated (a) formation enthalpy and (b) heat capacity of $(Ni_{2/3}Pt_{1/3})_3Al$ alloy as a function of temperature.

effects of short-range ordering (SRO), one generally need to perform Monte Carlo simulations to obtain the formation enthalpies of disordered alloys at finite temperatures.

The CE predicted mixing enthalpies can depend sensitively on the parameterization of the cluster expansion. To verify the accuracy of our cluster expansion, we also performed additional *direct* first-principles calculations of the mixing enthalpies of random pseudobinary $(Ni_{1-x}Pt_x)_3Al L1_2$ alloys using the SQS approach as discussed in Sec. II C, and the results are also shown in Fig. 1. The discrepancies between direct first-principles SQS calculations and CE predictions, i.e., $\Delta H_{FP}^{SQS} - \langle \Delta H_{CE}(\sigma) \rangle_R$, are only -0.8 meV/atom (-3.4 meV/formula unit) for x=1/3 and -4.5 meV/atom (-18.0 meV/formula unit) for x=2/3. To better understand the origin of such discrepancies, we further divided the error into two parts,

$$\Delta H_{\rm FP}^{\rm SQS} - \langle \Delta H_{\rm CE}(\sigma) \rangle_R = (\Delta H_{\rm FP}^{\rm SQS} - \Delta H_{\rm CE}^{\rm SQS}) + (\Delta H_{\rm CE}^{\rm SQS} - \langle \Delta H_{\rm CE}(\sigma) \rangle_R).$$
(5)

The first part, $\Delta H_{\rm FP}^{\rm SQS} - \Delta H_{\rm CE}^{\rm SQS}$, shows the differences between direct first-principles calculated and CE predicted formation enthalpies of the SQS structures, and is due to the fitting error associated with the truncation of our cluster expansion. This error is only 0.5 meV/atom (2.1 meV/formula unit) for x=1/3 and -2.0 meV/atom (-8.0 meV/formula unit) for x=2/3. The second part, $\Delta H_{\rm CE}^{\rm SQS} - \langle \Delta H_{\rm CE}(\sigma) \rangle_R$, is due to the intrinsic periodicity error of the SQS's. As shown in Table III, although the SQS's possess many pair and multibody correlations that match the random alloy, there are deviations from the random alloy correlations for longer-ranged pair and other multibody interactions. This part of the error can be calculated as follows:

$$\Delta H_{\rm CE}^{\rm SQS} - \langle \Delta H_{\rm CE}(\sigma) \rangle_R = \sum_f D_f J_f [(\bar{\Pi}_f)_{\rm SQS} - (2x-1)^{k_f}].$$
(6)

From Tables I and III, such error was found to be -1.4 meV/atom (-5.5 meV/formula unit) for x=1/3 and -2.5 meV/atom (-10 meV/formula unit) for x=2/3. In our case, the errors due to the periodicity errors of the SQS's are more significant than the errors due to the fitting errors of our cluster expansion.

Finally, using the SQS energetics and assuming ideal configurational entropy of mixing for the disordered $(Ni_{1-x}Pt_x)_3Al L1_2$ alloys, one can get a crude estimate of the order-disorder transition temperatures from the following equation without the use of cluster expansion:

$$T_c \approx \frac{\Delta H_{\rm FP}^{\rm SQS} - \Delta H_{\rm FP}(\sigma_{\rm ord})}{3R(x\ln x + (1-x)\ln(1-x))}.$$
 (7)

Using Eq. (7), we thus obtain $T_c \approx 1107$ K for L1₀ NiPt₂Al and 930 K for L1₀ Ni₂PtAl, in reasonable agreement with our MC simulated results.

IV. SUMMARY

To investigate the phase stability in pseudobinary (Ni,Pt)₃Al alloys, we parameterized first-principles calculated total energies of 27 $(Ni_{1-x}Pt_x)_3Al$ ordered structures into a cluster expansion that is capable of predicting energetics of any a-site substitutional configuration. A combined exhaustive ground state search and Monte Carlo simulated annealing simulations identified L10 Ni2PtAl and L10 NiPt₂Al as the two ordered ground state structures, and the latter has been experimentally observed. The order-disorder transition temperatures of those two structures were found by Monte Carlo simulations to be \sim 915 K and \sim 1275 K, respectively. Using our cluster expansion, we also predicted the mixing enthalpies of random pseudobinary $(Ni_{1-x}Pt_x)_3Al$ L12 alloys, and the results agree well with direct firstprinciples calculations using L12 SQS's developed in the present study.

The authors wish to thank Dr. Axel van de Walle for providing ATAT software package. This work was supported by the Office of Naval Research, Contract No. N00014-02-10733. We gratefully acknowledge the support of Dr. Steven Fishman, our ONR Program Manager. Efforts by D.J.S. were supported by the U.S. Department of Energy, Office of Science, Office of Basic Sciences, through the Ames Laboratory under Contract No. W-7405-Eng-82.

- ¹B. Gleeson, W. Wang, S. Hayashi, and D. J. Sordelet, Mater. Sci. Forum **461–464**, 213 (2004).
- ²S. Hayashi, S. I. Ford, D. J. Young, D. J. Sordelet, M. F. Besser, and B. Gleeson, Acta Mater. **53**, 3319 (2005).
- ³J. L. Kamm and W. W. Milligan, Scr. Metall. Mater. **31**, 1461 (1994).
- ⁴H. Meininger and M. Ellner, J. Alloys Compd. 353, 207 (2003).
- ⁵H. Okamoto, J. Phase Equilib. **14**, 257 (1993).
- ⁶Y. Oya, Y. Mishima, and T. Suzuki, Z. Metallkd. **78**, 485 (1987).
- ⁷S. Ochiai, Y. Oya, and T. Suzuki, Acta Metall. **32**, 289 (1984).
- ⁸C. Y. Geng, C. Y. Wang, and T. Yu, Acta Mater. **52**, 5427 (2004).
- ⁹C. Jiang, M. F. Besser, D. J. Sordelet, and B. Gleeson, Acta Mater. **53**, 2101 (2005).
- ¹⁰R. Ferro, R. Capelli, A. Borsese, and G. Centineo, Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend. 45, 54 (1968).
- ¹¹H. J. Schaller, Z. Phys. Chem. (Munich) **112**, 85 (1978).
- ¹²W. Oelsen and W. Middel, Mitt. Kaiser Wilhelm Inst. Eisenforsch. (Dusseldorf) **19**, 1 (1937).
- ¹³R. A. Walker and J. B. Darby Jr., Acta Metall. **18**, 1261 (1970).
- ¹⁴J. M. Sanchez, F. Ducastella, and D. Gratias, Physica A **128**, 334 (1984).
- ¹⁵J. W. D. Connolly and A. R. Williams, Phys. Rev. B 27, R5169 (1983).
- ¹⁶D. B. Laks, L. G. Ferreira, S. Froyen, and A. Zunger, Phys. Rev.

B 46, 12587 (1992).

- ¹⁷C. Wolverton and A. Zunger, Phys. Rev. Lett. **75**, 3162 (1995).
- ¹⁸A. Zunger, L. G. Wang, G. L. W. Hart, and M. Sanati, Modell. Simul. Mater. Sci. Eng. **10**, 685 (2002).
- ¹⁹P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- ²⁰G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
- ²¹G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
- ²²G. Kresse and J. Furthmuller, Comput. Mater. Sci. 6, 15 (1996).
- ²³J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
- ²⁴ J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
- ²⁵H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- ²⁶A. Zunger, S. H. Wei, L. G. Ferreira, and J. E. Bernard, Phys. Rev. Lett. **65**, 353 (1990).
- ²⁷S. H. Wei, L. G. Ferreira, J. E. Bernard, and A. Zunger, Phys. Rev. B 42, 9622 (1990).
- ²⁸A. van de Walle, M. Asta, and G. Ceder, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **26**, 539 (2003).
- ²⁹C. Jiang, C. Wolverton, J. Sofo, L. Q. Chen, and Z. K. Liu, Phys. Rev. B **69**, 214202 (2004).
- ³⁰C. Jiang, L. Q. Chen, and Z. K. Liu, Acta Mater. **53**, 2643 (2005).
- ³¹Z. W. Lu, D. B. Laks, S. H. Wei, and A. Zunger, Phys. Rev. B 50, 6642 (1994).