

Site-specific segregation and compositional ordering in Ni-based ternary alloy nanoclusters computed by the free-energy concentration expansion method

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The free-energy concentration expansion method (FCEM), originally derived for the theoretical prediction of surface segregation in the presence of interatomic correlations (short-range order) in binary alloys, is extended to multicomponent alloy nanoclusters, and is applied to unravel the compositional structure of unsupported 309 atom Ni-Cu-Pd cubo-octahedrons. It is a first attempt, to the best of our knowledge, to compute ternary alloy nanocluster site-specific compositions, which are typically inaccessible by current experimental techniques. The calculations predict surface segregation of both solutes Pd and Cu leading to separation of Ni-rich cluster core (the “finite size/matter effect”). Due to the core separation, even relatively low Ni content clusters are expected to be magnetic. The Ni enrichment and associated magnetic order can prevail up to temperatures noticeably higher than in bulk alloys of the same overall composition. Depending on temperature and overall composition, Cu and Pd form orderedlike patterns (“compositional oscillations”) or mix at the wrapping surface. As the overall Cu content in the cluster increases (on the expense of Ni), the two solutes exhibit surface multisite competition, namely, Cu displaces Pd sequentially from vertexes to edges and facets, and finally Pd desegregates from the surface sites into the core. FCEM can be conveniently applied also to calculation of “surfaces” of thermodynamic functions for all ranges of composition above the Gibbs triangle, including the currently defined “cluster mixing functions.” It is shown that sharp compositional-structural changes in Ni-Cu-Pd are reflected distinctly in the cluster mixing entropy surface, and the general shape of calculated free-energy surfaces indicates mixing properties of ternary alloy clusters that differ considerably from the corresponding bulk alloys.

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I. INTRODUCTION

Studies of site-specific compositional variations in small alloy clusters are relevant to both basic research and potential catalytic, magnetic, or other applications. For example, the high chemical reactivity and selectivity anticipated for low coordinated sites, such as vertexes and edges, should be affected by their elemental composition. In view of limitations of currently available experimental tools, theoretical modeling of clusters has gained a central position in acquiring atomic-scale compositional and structural information.

Two statistical-mechanical approaches, each with its advantages and drawbacks, were applied in calculations of site-specific compositions in binary alloy clusters (multicomponent alloy clusters have not been hitherto studied to our best knowledge). The first approach applies computer simulations,^{1–13} while innately taking into account many-particle correlations and facilitating use of rather realistic energetic models based on pair or many-body potentials, derived empirically¹⁴ or from electronic structure of alloys.^{1,2,11} However, computer simulations are time consuming and typically provide results only for quite limited sets of temperatures and compositions of alloy clusters. This may impede systematic studies of site-specific compositions in clusters and even overlook details of segregation and ordering trends. The second approach, used in a few early works,^{15,16} is based on the analytical Bragg-Williams (BW) approximation that entirely neglects interatomic correlations (short-range order).

In the present work the free-energy concentration expansion

method (FCEM) analytical approach has been chosen. Originally it was derived by us for the computation of equilibrium surface segregation in the presence of interatomic correlations in binary solid solutions,^{17–21} and was later extended to multicomponent alloy surfaces.²² This approach furnishes explicit analytical expressions for numerical minimization of the system free energy. In spite of the approximations involved and the obvious dependence on appropriate energetic parameters, FCEM is capable of conveniently shading light on temperature-dependent segregation and ordering trends in complex systems, and thus meets key requirements for handling multicomponent alloy nanoclusters: it demands much less computational effort compared to computer simulations, and can cope effectively with cluster geometries having a diversity of nonequivalent surface sites.

Before proceeding to FCEM adaptation to nanoclusters, an intriguing aspect of cluster statistical mechanics will be addressed. Since usually clusters are in contact with a substrate and/or with the parent gas, the number of constituent atoms can fluctuate. The equilibrium between clusters and the parent gas proceeds through processes of evaporation of atoms from the cluster surface and attachment of atoms to the cluster.²³ While only in macroscopic systems physical properties would not be appreciably affected by neglecting fluctuations in the overall concentrations,²⁴ hitherto almost no attention has been paid to such effects in solitary small alloy clusters. Thus, most computer simulations, using Monte Carlo *intracluster* exchanges of positions of a pair of randomly selected atoms of different type,² as well as the BW-type approach chosen,^{15,16} were applied to *single* nanoclusters with definite overall composition. Only few

works⁴⁵ employed simulation sampling in the semi-grand canonical (“transmutational”) ensemble,⁴⁶ allowing for concentration fluctuations. Recently, this approach was extended to model a bimetallic nanostructured system.⁴⁷ (For analytical approaches, the discontinuity of concentrations in single clusters encumbers the application of certain mathematical operations and formulas, e.g., differentiation of cluster free energy, Stirling’s formula etc.) In the present work, in order to circumvent these problems, a system is considered to be comprised of a large number of clusters with identical morphology, but fluctuating individual concentrations. In particular, the clusters are assumed to be able to exchange atoms directly, since the specific mechanism of exchange is irrelevant to the final equilibrium. The canonical distribution can be applied with confidence to this macroscopic system with a presumed constant overall composition, and infinitely large (in the thermodynamic limit) arrays of specific sites (e.g., the centers or vertexes of clusters), which can be characterized

by quasicontinuous concentration variables. This approach facilitates the adaptation of the analytical FCEM for studies of multicomponent alloy clusters.

II. FCEM ADAPTED TO MULTICOMPONENT ALLOY CLUSTERS

A system of multicomponent alloy clusters consists of distinct arrays of N_p ($p=0,1,2,\dots$) geometrically identical atomic sites (e.g., “shells” in perfect clusters, as defined in Sec. III), and is characterized by concentrations c_p^I of constituents I . The FCEM expressions were obtained using a pair-interaction model Hamiltonian and an expansion of the partition function and free energy in terms of constituent concentrations.^{17–19,22} With slight adaptation of the formalism of Ref. 22, the free energy of a multicomponent alloy cluster reads,

$$F = kT \sum_p \left(N_p \sum_I c_p^I \ln c_p^I \right) + \sum_r \sum_{p \leq q} N_{pq}^{(r)} \left\{ \frac{1}{2} \sum_I w_{pq}^{II(r)} (c_p^I + c_q^I) - \sum_{\{IJ\}} \left\{ V_{pq}^{IJ(r)} (c_p^I c_q^J + c_p^J c_q^I) + kT c_p^I c_p^J c_q^I c_q^J \left[\exp \left(-\frac{2V_{pq}^{IJ(r)}}{kT} \right) + \frac{2V_{pq}^{IJ(r)}}{kT} - 1 \right] \right\} \right\}, \quad (1)$$

where $N_{pq}^{(r)}$ are number of pairs of atoms belonging to arrays p, q and separated by a distance r ; $w_{pq}^{II(r)}$ is the homonuclear interaction energy for constituent I ; and $w_{pq}^{IJ(r)}$ and $V_{pq}^{IJ(r)}$ are, respectively, the heteronuclear interaction and effective interaction energies between constituents I and J [$V_{pq}^{IJ(r)} = \frac{1}{2}(w_{pq}^{II(r)} + w_{pq}^{JJ(r)} - 2w_{pq}^{IJ(r)})$]. In a case of nearest-neighbor (NN) interactions, superscripts denoting the distance in Eq. (1) can be omitted.

As noted above, since the system comprises a large number of clusters, fluctuations in its overall composition can be neglected and the canonical distribution applies (in contrast to a model of a single cluster with fluctuating composition that would necessitate the use of chemical potentials in the semi-grand canonical ensemble).^{45,46} Therefore, the free energy in Eq. (1) was minimized under the constraint of conservation of the overall composition of the cluster system (using the MATLAB computing environment). Thereby a set of equilibrium concentrations $\{c_p^I\}$ is obtained for given temperature and overall composition. In addition, formula (1) and the standard thermodynamic relations $E = \partial(\beta F)/\partial\beta$ with $\beta = 1/kT$ and $S = (E - F)/T$ provide expressions for the energy and entropy, in which the derived $\{c_p^I\}$ can be substituted.

While the free energy per atom in clusters should typically be higher than in the bulk material (so alloy clusters of a given size and morphology correspond to a metastable state), their stability towards separation to pure elemental ones is worth inspecting. Thus, unlike ordering, which is

confined to individual clusters, phase separation of constituents can occur either between clusters constituting the system or within individual clusters. Elemental clusters can be energetically advantageous in the case of similar homonuclear interactions and effective heteronuclear repulsion, while for considerable differences in homonuclear interaction strength, wrapping up a core by constituents with a lower “surface tension” can be energetically advantageous. (With temperature increase entropy-driven mixing between individual clusters is expected in the former case, while for the latter, intracluster mixing should occur.)

In order to explore mixing properties the approach of the present FCEM study, employing a system of clusters, facilitates the introduction of “cluster mixing thermodynamic functions,” including the mixing free energy that characterizes the tendency of constituents either to separate into pure elemental clusters or to amalgamate in alloy clusters. Thus, for a system of N -atom clusters with overall concentrations of constituents, $\{c^I\}$, a mixing function per atom, y_N^M (= free-energy, entropy, etc.), is defined by

$$y_N^M(\{c^I\}) = y_N(\{c^I\}) - \sum_I c^I y_N^I, \quad (2)$$

where $y_N(\{c^I\})$ and y_N^I are the values of the function for the alloy and for the pure I elemental clusters, respectively.

III. MODEL CLUSTERS AND INPUT PARAMETERS OF INTERACTION

fcc metal clusters tend to form cubo-octahedron (CO) or icosahedron (ICO) shapes, depending on size (e.g.,

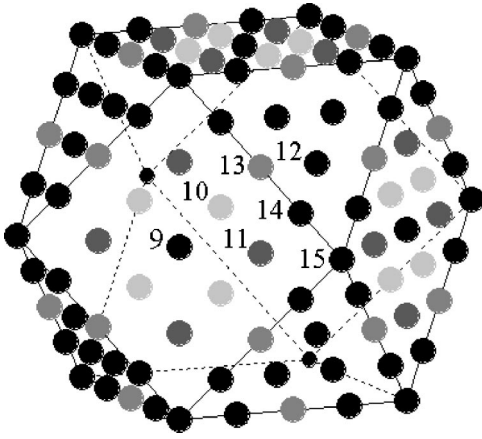


FIG. 1. Schematic cubo-octahedron with 309 atoms (cluster of the fourth order). The numbers mark sites of surface shells of the fourth crust shown in grayscale (shells 1–8 constitute the cluster core, 9,10,11—(100) facet, 12—(111) facet, 13,14—edge, 15—vertex).

Refs. 25–27). The cubo-octahedron structure can be obtained by truncating the fcc lattice. The N -atom CO cluster of ν th order can be considered as an onionlike structure with ν crusts formed by α concentric shells around a central site ($N=13,55,147,309, \dots$ and $\alpha=1,4,8,15, \dots$ for $\nu=1,2,3,4, \dots$, respectively).²⁵ The ν th crust is formed by all the surface sites of the ν th order cluster, which can belong to different shells (Fig. 1). Although in this first application of FCEM to alloy clusters, the possible distortion transforming CO to ICO is not considered, the input energetic parameters introduced below take into account experimentally based, coordination-related site energies, and therefore to some extent reflect on CO cluster relaxation.

The choice of the Ni-Cu-Pd ternary and the corresponding binary systems for model calculations was motivated by their potentially important catalytic and magnetic properties, as well as by the availability of input energetic parameters and their comparative values. The corresponding binary systems represent clusters with (i) very weak heteronuclear effective interactions (Ni-Pd), (ii) a noticeable mixing tendency (Cu-Pd), and (iii) a tendency for phase separation (Ni-Cu). Since the homonuclear Ni-Ni interactions are significantly stronger than both Pd-Pd and Cu-Cu interactions, the two solutes are expected to segregate, leaving behind a Ni-rich core that might enhance the cluster magnetic properties.

It can be noted that Cu and Ni have rather similar atomic

TABLE II. Estimation of core-core NN homonuclear interactions and heteronuclear effective interactions in units of meV.

w^{CuCu}	w^{PdPd}	w^{NiNi}	V^{NiPd}	V^{NiCu}	V^{CuPd}
–582 ^a	–648 ^a	–740 ^a	1.8 ^b	–12.5 ^c	33.3 ^b

^aBased on formula (3).

^bBased on FCEM formula of Ref. 22 with experimental heats of mixing from Refs. 4 and 39.

^cData of Ref. 40.

radii, 1.28 Å and 1.25 Å, respectively, while that of Pd, 1.37 Å, is ~ 7 –10% larger.⁴¹ Such an atomic size mismatch can, in principle, modify surface segregation in bulk alloys, as was shown for the Pt-Ni system.⁴² However, it was argued that in alloy nanoclusters a rather small effect is generally expected, except in case of much larger size mismatch (e.g., for Ni-Ag or Ni-Au).⁴ Otherwise, relaxation of the cluster structure (as compared to that of the alloy bulk) as well as finite matter effects are expected to considerably diminish size mismatch contributions to segregation.

The homonuclear interactions, w_{mn}^{II} , were estimated using site energies $e_m^I(Z_m)$ for Z_m -coordinated I -type atom ($I = \text{Ni, Cu, Pd}$) with all I -type neighbors (Table I), derived from experimental dimer bond energies, surface energies, and cohesive energies.^{2,4,5} In accordance with the approach of Refs. 3 and 28–30 uniform distribution of the site energy $e_m^I(Z_m)$ among its Z_m NN bonds is assumed. Therefore, the pairwise energy w_{mn}^{II} as a function of coordinations is given simply by

$$w_{mn}^{II}(Z_m, Z_n) = \frac{e_m^I}{Z_m} + \frac{e_n^I}{Z_n}. \quad (3)$$

In the context of Table I one can note that (i) site energies (and the corresponding homonuclear interactions) of Cu, Pd, and Ni follow an ascending order for each coordination number, except for a weak reversal of the Cu and Pd values for $Z=5$, and (ii) the site energies obey a linear dependence¹² on Z [they were used as parameters of the bond order simulator model for NiCu (Ref. 4) and PdCu (Ref. 5) clusters].

Estimations of core-core homonuclear interactions based on formula (3) and of heteronuclear effective interactions obtained from the literature or estimated by the FCEM formula²² are given in Table II. As will be shown by the detailed calculations in Sec. IV using energetic parameters

TABLE I. Site energies $e_m^I(Z_m)$ (meV) according to Refs. 2, 4, and 5. Surface energies (meV) are shown in parentheses.

Metal	Coordination number				
	12, bulk	9, (111) facet	8, (100) facet	7, edge	5, vertex ^a
Cu	–3490	–2770 (720)	–2550 (940)	–2330 (1160)	–1890 (1600)
Pd	–3890	–3000 (890)	–2690 (1200)	–2380 (1510)	–1760 (2130)
Ni	–4440	–3609 (831)	–3289 (1151)	–2970 (1470)	–2329 (2111)

^aObtained by a linear extrapolation of the data for higher coordinated sites.

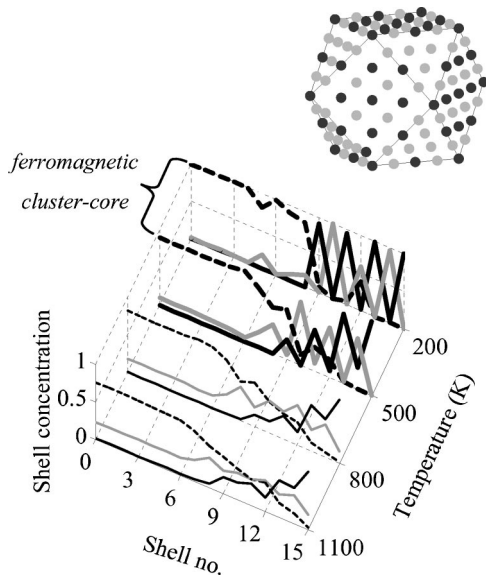


FIG. 2. The Ni (dashed line), Pd (gray line), and Cu (black line) shell concentrations vs temperature in Ni-Cu-Pd cubo-octahedral cluster with 309 atoms ($c_{\text{Ni}}=147/309$, $c_{\text{Cu}}=66/309$, and $c_{\text{Pd}}=96/309$) calculated in the FCEM approximation, using coordination dependent energetic parameters from Tables I and II. Ferromagnetic/paramagnetic clusters are indicated by thick/thin lines. Inset: the surface ordered compositional structure at 200 K with sites predominantly populated by Cu/Pd indicated by black/gray.

given in Tables I and II, the interplay of homonuclear and heteronuclear interactions having different relative strengths can give rise to segregation/separation of constituents between core and surface shells exhibiting orderlike compositional oscillations. Following Ref. 31, $\sim 50\%$ enhancement of V_{mn}^{IJ} was assumed for the cluster facets and a linear extrapolation (vs coordination) was used for a rough estimation of the enhancement for edges and vertexes.

Calculation of constituent atom distributions can provide some information concerning cluster magnetic properties. The corresponding Curie temperature θ as a function of overall composition can differ considerably from bulk alloy values, because of specific compositional structure of the clusters, such as Ni-rich core separation in Ni-Cu or Ni-Pd. Since the NN atomic coordination in the cluster core and in the bulk alloys are similar, a simple estimation of the cluster (cl) Curie temperature can be based on bulk data³² for a solid solution (ss) with a composition equal to the calculated average core composition (shell-specific concentration variations in the core are neglected), e.g., $\theta^{\text{NiCu,cl}}(c_{\text{Cu}}) \approx \theta^{\text{NiCu,ss}}(c_{\text{Cu}}^{\text{core}})$. Curie temperatures of the Ni-based ternary clusters were roughly estimated assuming additive effects of the two constituents.

IV. RESULTS AND DISCUSSION

A. Site-specific competitive segregation

The calculations confirm quantitatively the anticipated general tendency of Ni-rich core formation due to Cu and Pd segregation, and reveal ordering (or mixing) features at the

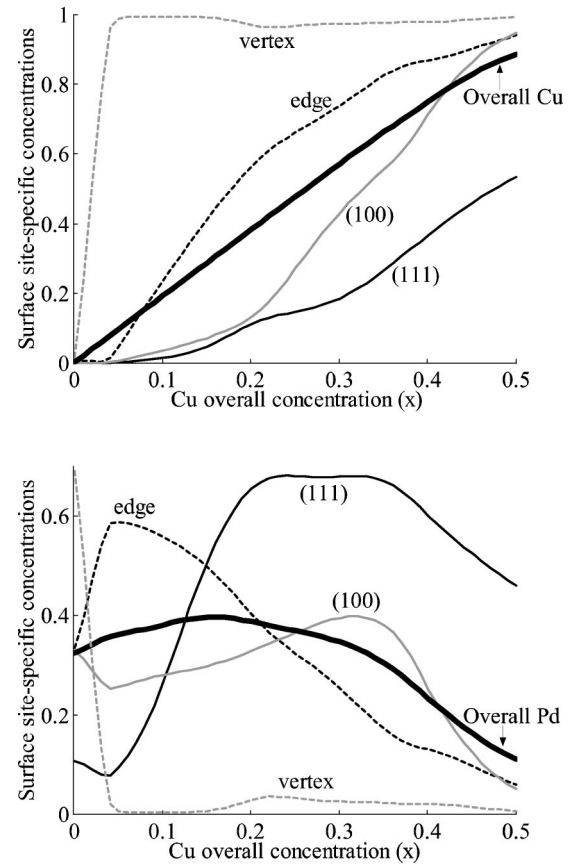


FIG. 3. Sequential multisite segregation of copper (top) and palladium (bottom) computed by FCEM for $\text{Ni}_{1-x-0.25}\text{Cu}_{0.25}\text{Pd}_{0.25}$ 309-atom alloy clusters (500 K, energetic parameters from Tables I and II).

309 atom Ni-Cu-Pd cluster surface sites. These tendencies become most prominent in the first example chosen (Fig. 2). In particular, an overall Ni concentration $c_{\text{Ni}}=147/309$ corresponds to complete Ni population of core sites (shells 0–8). Since vertexes (shell 15) are expected to be occupied by the most surface active constituent, the Cu concentration was chosen to equal the total concentration of sites belonging to odd surface shells (9,11,13,15), $c_{\text{Cu}}=66/309$. Hence, $c_{\text{Pd}}=96/309$ corresponds to the total concentration of sites belonging to the remaining (even) surface shells (10, 12, and 14). Indeed, the calculations show such compositional structure (at 200 K) with almost perfect Ni-core separation and Cu-Pd surface concentration oscillations (the nearly ordered surface compositional pattern is schematically depicted in the inset of Fig. 2). Few Ni atoms displaced from the core to the surface share with Pd the most closed (111) facets (12th shell). At higher temperatures, Cu remains exclusively at the surface, whereas Pd, having intermediate homonuclear interactions, gradually mixes in the core concurrently with damping of the surface oscillations. At the same time, Ni atoms appear at (100) facets (9,10,11 shells) and eventually at edges (shells 13 and 14). As illustrated in Fig. 2 and discussed below, the cluster compositional structure is expected to affect magnetic properties.

While this example represents a rather particular case of cluster compositional structure, additional calculations for

different compositions demonstrate mainly Cu-Pd sequential multisite competition. Figure 3 shows prominent variations in surface site-specific compositions with increase in the overall Cu content of $\text{Ni}_{1-x-0.25}\text{Cu}_x\text{Pd}_{0.25}$ clusters. Already at low Cu contents it occupies vertexes, predominantly filled by Pd in the binary Ni-Pd clusters. Displaced Pd moves to edges, while larger Cu contents displace Pd from the edges to facets, and eventually from facets to the cluster core. The vertexes-edges-facets(-core) sequence of Cu/Pd multisite competition is consistent with the known, energetically advantageous, preferential segregation to lattice sites with lower coordination (e.g., Refs. 2 and 13). Homonuclear interactions entering formula (1) range from core-core interactions equal to the cohesive energy per atom (e_{12}^I , Table I) divided by 6 to surface-core and surface-surface interactions involving “surface energies” of the pure constituents ($e_2^I - e_{12}^I$). According to commonly used qualitative considerations, the latter control, among other factors, solute segregation in clusters:⁴ the surface energies are smallest for Cu and the difference between the Ni or Pd and the Cu values follows a descending order vertexes-edges-(100)-(111). Moreover, the Ni-Cu effective repulsion (Table II) tends to decrease the number of Cu bonds with the Ni core, thereby strengthening Cu affinity to low coordinated sites. The constituent cohesive energy itself also plays a role in surface segregation. Since in the simple bond-breaking model both cohesive energy and surface energy of a pure constituent are proportional to the constant bond energy, the segregation driving force (neglecting mixing and size-mismatch contributions) can be expressed in terms of either of them. However, in case of the more realistic energetics (Table I), this proportionality is violated, and hence contributions of cohesive and surface energies should be considered independently. In Ni-Pd, unlike the case of Ni-Cu, they can even induce opposite segregation trends. In particular, the predicted Pd segregation in Ni (in spite of the slightly higher Pd surface energy) can be comprehended by its lower cohesion energy.

It should be noted that up to $c_{\text{Cu}} \sim 0.2$ (Ni-based clusters) the overall Pd surface concentration slightly increases with Cu. This apparent “cosegregation” is associated with a synergetic effect of Cu-Pd attraction, Cu-Ni repulsion, and their assumed surface enhancement. Calculations for uniform (core vs. surface) effective interactions show nearly constant overall Pd surface concentration up to $c_{\text{Cu}} \sim 0.2$, corresponding to nearly complete population of all cluster surface sites by the two solutes. Hence, in both cases (uniform and enhanced Cu-Pd surface attractive interactions) comprehensive site competition starts after almost full coverage is attained with Pd desegregating into the core.

Monte Carlo computer simulations, applied so far to binary alloy systems only, predicted for Ni-Cu truncated cubo-octahedron clusters^{4,8,9} the occupation of core sites by Ni, in qualitative agreement with trends calculated here. Similarly, preferential vertex-edge segregation of Pd followed by facet segregation was computed for Ni-Pd clusters.^{2,5,6} On the other hand, unlike the quite strong copper segregation predicted for Cu-Pd in the present study, Monte Carlo

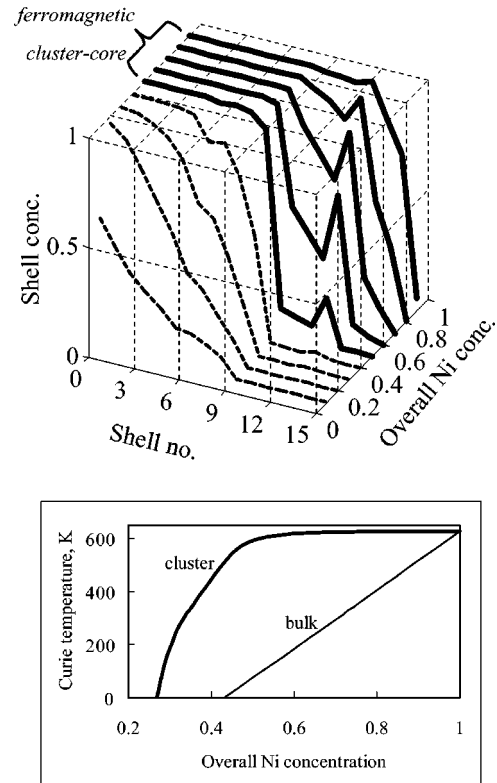


FIG. 4. Ni shell compositions and the corresponding magnetic order in Ni-Cu 309-atom cubo-octahedral clusters. Top: Segregation induced separation of Ni-rich cores as a function of overall Ni concentration at $T=500$ K (ferromagnetic clusters are indicated by solid lines). Due to the Ni core enrichment, the cluster remains magnetized at considerably lower overall concentration ($c_{\text{Ni}} \approx 0.43$) compared to the bulk alloy ($c_{\text{Ni}} \approx 0.88$) at this temperature. Bottom: Comparison between Curie temperatures of the Ni-Cu clusters and bulk alloys of the same overall compositions. The curve for the cluster was obtained by finding the critical Ni overall concentration needed for the onset of core ferromagnetism at each temperature.

simulations¹ indicated only weak segregation of Cu in cubo-octahedra and a reversal to Pd segregation for the Pd-rich clusters.

B. Cluster magnetism

The separation/enrichment of the core by Ni is expected to induce cluster magnetic order that is preserved at higher temperatures or at lower overall concentrations of the magnetic constituent, as compared to the corresponding bulk solid solutions. Estimations of compositional structure effects on magnetic order in the ternary clusters given in Fig. 2 were extended in more detail for the binary Ni-Pd and Ni-Cu clusters. Thus, for a 309-atom Ni-Pd cluster with $c_{\text{Ni}} = 0.48$ the calculated Curie temperature is 521 K, exceeding the bulk value of 459 K.³² Moreover, at 500 K the overall cluster concentration of Ni when the core becomes magnetic (~ 0.43) is lower than the corresponding bulk concentration (~ 0.55). The compositional effects are even more pronounced in Ni-Cu clusters, as a result of stronger surface

segregation of Cu and resultant core enrichment by Ni. Thus, as shown in Fig. 4, the Curie temperature vs overall cluster concentration is significantly enhanced as compared to the bulk values.³² For example, for $c_{\text{Ni}} \sim 0.43$ that nearly equals the critical concentration for the onset of ferromagnetism in the alloy bulk at 0 K, magnetic order in the clusters is preserved up to 500 K (at this temperature the bulk magnetizes at a much higher concentration, $c_{\text{Ni}} \sim 0.88$). The Curie temperature enhancement is maximal near $c_{\text{Ni}} \sim 0.48$, when the number of Ni atoms fits the number of core sites (147, a sort of “magic” number, similar to the example in Fig. 2), corresponding to nearly perfect surface-core separation (see Fig. 4, top). As expected, below this Ni overall concentration, the cluster Curie temperatures start to decrease.

C. Mixing properties

Cluster mixing properties can be characterized by the corresponding thermodynamic functions introduced in Sec. II. FCEM computation is capable of covering a large number of alloy compositions in the Gibbs triangle, yielding complete surfaces of the thermodynamic functions.

For the Ni-Cu-Pd ternary system the mixing free energy turns out to be always negative, and its surface is uniformly concave (Fig. 5, top) revealing an amalgamation tendency of the constituents in this system of clusters. Thus, no separation to Ni rich and Cu rich individual clusters is predicted. This finding exemplifies the possibility, discussed in Sec. II, of considerable difference between mixing properties of the system of Ni-Cu-Pd ternary clusters and the corresponding bulk alloys (having among others, a Ni-Cu phase separation tendency).

Ordering or segregation/separation related variations in cluster compositional structures can be instructively presented by cluster mixing entropy surfaces. As can be seen from the three-dimensional (3D) plot (Fig. 5, bottom), in the Pd-dilute region the intracluster separation to Ni-rich core and Cu-rich surface reduces the mixing entropy down to a pronounced minimum corresponding to the maximal Cu/Ni surface segregation/core separation mentioned above. In case of pure binary Ni-Cu clusters further calculations predict gradual weakening of the minimum in the mixing entropy curve with temperature, but it still persists even above 1000 K, which is significantly higher than the temperature range of bulk separation (< 627 K) (Fig. 6, top). Thus, the FCEM calculations seem to indicate that due to geometrical “finite-size” effects (in a combination with energetics) intracluster segregation/separation features can prevail at temperatures considerably higher than temperatures of phase separation in the corresponding bulk systems, in agreement with conclusions based on BW-type calculations.¹⁶

In the Ni-dilute region, the apparent entropy minimum in Fig. 5, bottom, corresponds to a sharp increase in even/odd shell Pd-Cu compositional oscillations at $c_{\text{Pd}} \approx 0.75$. These oscillations resemble the ordered bulk $L1_2$ structure having the corresponding stoichiometric composition (recently, magic concentration numbers corresponding to filling of sublattices in ordered clusters were mentioned by Mottet *et al.*¹).

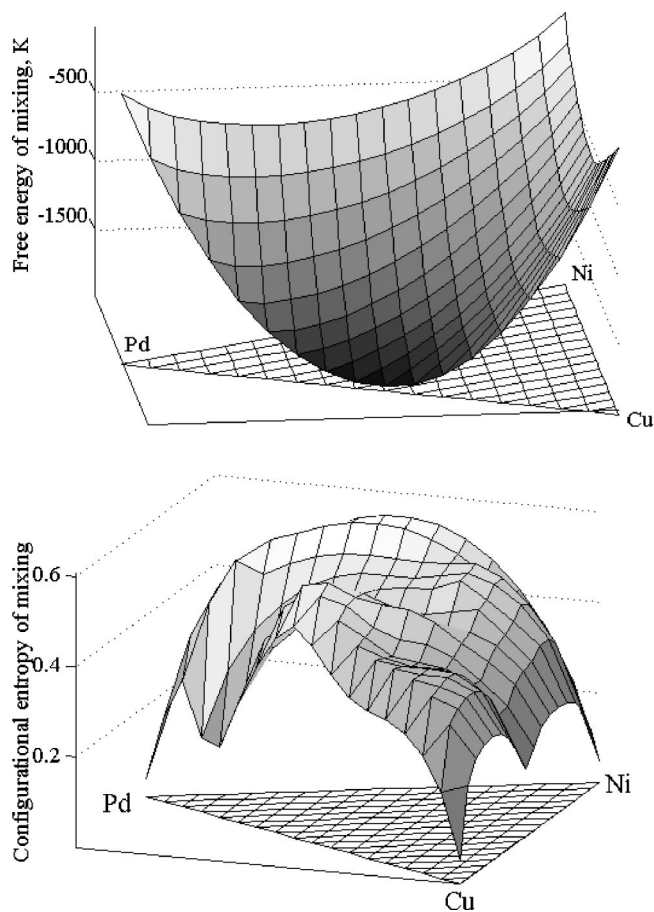


FIG. 5. 3D plots (over the Gibbs triangle) of mixing functions per atom in Ni-Cu-Pd 309-atom clusters calculated in the FCEM approximation (500 K). Top: The mixing free energy. The minimum at $c_{\text{Ni}} = 0$, $c_{\text{Cu}} \approx 0.53$, $c_{\text{Pd}} \approx 0.47$, corresponding to maximal stability relative to separation to pure elemental clusters, is associated with the Cu-Pd mixing tendency. Bottom: The mixing entropy. The intermediate minima along the Cu-Ni and Cu-Pd lines reflect intra-cluster separation and ordering, respectively.

In calculations made for pure binary Pd-Cu clusters the minimum in the mixing entropy curve disappears and the oscillations become weaker quite abruptly at a “disordering” temperature of ~ 695 K (Fig. 6, bottom), but some intracluster order persists at higher temperatures. Yet, the “disordering” temperature is lower than that of the binary bulk alloy, in general agreement with the known depression of phase transition temperatures in small particles associated with the reduced coordination.^{33–38} While some composition-dependent differences in ordering patterns are possible between the differently coordinated cluster core and surface atoms, typically a common order-disorder transition temperature is expected, due to the cluster finite size.⁴³ Indeed, the calculations consistently indicate the same transition temperature for core and surface sites, reflecting rather strong coupling (in bulk alloys, on the other hand, the surface can have a different critical temperature⁴⁴). Comparative calculations we made within the less accurate BW approximation that neglects correlations predict stronger compositional oscillations, which prevail even above the disordering temperature of the bulk alloy.

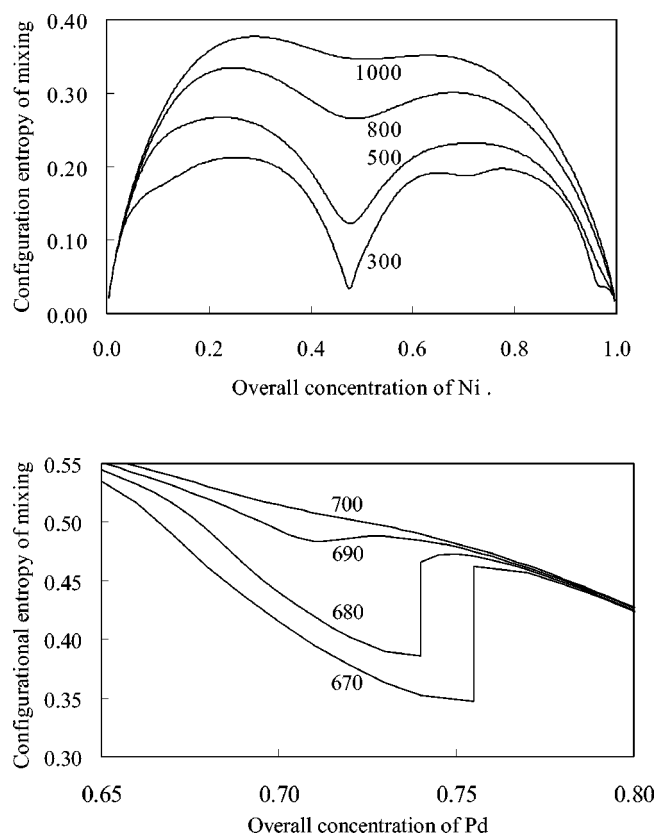


FIG. 6. Mixing entropy per atom in binary alloy 309-atom clusters as a function of temperature (K). Top: Ni-Cu. Bottom: Pd-Cu.

V. CONCLUSIONS

This paper presents results of our first attempt to compute site-specific cluster equilibrium compositions by means of the adapted FCEM, which facilitates studies of multicomponent alloys. To our best knowledge this is the first computational study of ternary alloy nanoclusters. By taking into account interatomic correlations FCEM is more accurate than the Bragg-Williams approximation, and is much less time consuming compared to computer simulations. Thus, FCEM can be used for systematic studies of complex cluster compositional structures as a function of temperature and overall concentration. In addition, covering a large number of com-

positions in the Gibbs triangle, this work introduced calculated surfaces of “cluster thermodynamic mixing functions.” The mixing free energy characterizes the tendency of constituents to separate into pure elemental clusters or to be alloyed in the clusters, whereas the intracluster mixing entropy reflects compositional order variations.

Instructive conclusions concerning concrete Ni-Cu-Pd clusters were derived from detailed site-specific compositions and integrative mixing function calculations. The cluster compositional structure consists of Ni-rich core and segregated Cu and Pd exhibiting concentration oscillations at the surface. Sequential multisite competition of Cu and Pd with increase in Cu content is predicted, by which Cu displaces Pd atoms gradually from vertexes, edges, facets, and finally into the core. Some insight into the predicted trends was achieved by inspecting the site-specific coordination dependent energetic parameters used as input for the FCEM calculations. In spite of weakening of order with temperature, accompanied by possible compositional-disordering transitions, a certain, finite size/matter related, order/separation can prevail in clusters up to temperatures significantly higher than temperatures of compositional transitions in the bulk alloys. Likewise, the increased Ni concentration in the core enhances cluster magnetic order and the Curie temperatures vs overall composition. It should be noted also that mixing properties of the alloy nanoclusters differ considerably from the corresponding bulk alloys, e.g., in spite of the Ni-Cu effective repulsion, the calculated cluster free-energy surface is concave, so no separation to Ni rich and Cu rich individual clusters is predicted.

The methodology introduced here together with computation results is just the first part of a comprehensive plan to elucidate atomic-scale compositional/structural characteristics of multicomponent alloy nanoclusters via model computations. Preliminary FCEM results for Ni-Cu-Al nanoclusters reveal significant differences with respect to Ni-Cu-Pd, such as strong intracore Ni-Al concentration oscillations. Additional aspects to be explored include the role of cluster-support interactions, effects of the cluster size and shape (e.g., concrete calculations for icosahedron clusters), and, eventually, the prediction of modified segregation/ordering patterns induced by cluster site selective interactions with catalysis-related chemisorbed molecules, such as oxygen and carbon monoxide.

¹C. Mottet, G. Treglia, and B. Legrand, Phys. Rev. B **66**, 045413 (2002).

²L. Yang, T.J. Raeker, and A.E. DePristo, Surf. Sci. **290**, 195 (1993).

³J.K. Strohl and T.S. King, J. Catal. **116**, 540 (1989).

⁴L. Zhu and Andrew E. DePristo, J. Catal. **167**, 400 (1997).

⁵L. Zhu, K.S. Liang, B. Zhang, J.S. Bradley, and Andrew E. DePristo, J. Catal. **167**, 412 (1997).

⁶L. Zhu and A.E. DePristo, J. Chem. Phys. **102**, 5342 (1995).

⁷Badal C. Khanra and M. Menon, Physica B **270**, 307 (1999).

⁸Daniela S. Mainardi and Perla B. Balbuena, Int. J. Quantum Chem. **85**, 580 (2001).

⁹Daniela S. Mainardi and Perla B. Balbuena, Langmuir **17**, 2047 (2001).

¹⁰L. Yang and A.E. DePristo, J. Catal. **148**, 575 (1994).

¹¹M.J. Lopez, P.A. Marcos, and J.A. Alonso, J. Chem. Phys. **104**, 1056 (1995).

¹²L. Yang and A.E. DePristo, J. Catal. **149**, 223 (1994).

¹³S. Helfensteyn and C. Creemers, Surf. Sci. **507/510**, 783 (2002).

¹⁴S. Darby, T.V. Mortimer-Jones, R.L. Johnston, and C. Roberts, J. Chem. Phys. **116**, 1536 (2002).

¹⁵J.M. Montejano-Carrizales and J.L. Moran-Lopez, Surf. Sci. **239**, 169 (1990).

- ¹⁶J.M. Montejano-Carrizales and J.L. Moran-Lopez, *Surf. Sci.* **239**, 178 (1990).
- ¹⁷M. Polak, J. Deng, and L. Rubinovich, *Phys. Rev. Lett.* **78**, 1058 (1997).
- ¹⁸M. Polak and L. Rubinovich, *Surf. Sci. Rep.* **38**, 127 (2000).
- ¹⁹J.M. Roussel, A. Saul, L. Rubinovich, and M. Polak, *J. Phys.: Condens. Matter* **11**, 9901 (1999).
- ²⁰M. Polak and L. Rubinovich, in *Alloy Surface Segregation and Ordering Phenomena: Recent Progress*, edited by D.P. Woodruff, *Surface Alloys and Alloy Surfaces*, The Chemical Physics of Solid Surfaces Vol. 10 (Elsevier Science, Amsterdam, 2002).
- ²¹M. Polak, C.S. Fadley, and L. Rubinovich, *Phys. Rev. B* **65**, 205404 (2002).
- ²²L. Rubinovich and M. Polak, *Surf. Sci.* **513/1**, 119 (2002).
- ²³B. M. Smirnov, *Clusters and Small Particles: in Gases and Plasmas* (Springer-Verlag, New York, 2000).
- ²⁴F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).
- ²⁵J.M. Montejano-Carrizales, F. Aguilera-Granja, and J.L. Moran-Lopez, *Nanostruct. Mater.* **8**, 269 (1997).
- ²⁶F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, and C. Motet, *J. Chem. Phys.* **116**, 3856 (2002).
- ²⁷D. Reinhard, B.D. Hall, P. Berthoud, S. Valkealahti, and R. Monot, *Phys. Rev. Lett.* **79**, 1459 (1997).
- ²⁸R.L. Schwoebel, *J. Appl. Phys.* **38**, 3154 (1967).
- ²⁹R.G. Donnelly and T.S. King, *Surf. Sci.* **74**, 89 (1978).
- ³⁰T.S. King and R.G. Donnelly, *Surf. Sci.* **141**, 417 (1984).
- ³¹G. Treglia, B. Legrand, and F. Ducastelle, *Europhys. Lett.* **7**, 575 (1988).
- ³²*Numerical Data and Functional Relationships in Science and Technology*, edited by J.J.M. Franse and R. Gersdorf, Landolt-Boernstein, New Series, Group III, Vol. 19, pt. a (Springer-Verlag, Berlin, 1986), p. 622; G. Zibold, *ibid.*, Group III, Vol. 19, pt. b (1987), p. 54.
- ³³M. Takagi, *J. Phys. Soc. Jpn.* **9**, 359 (1951).
- ³⁴J.R. Sambles, *Proc. R. Soc. London, Ser. A* **324**, 339 (1971).
- ³⁵G.L. Allen, R.A. Bayles, W.W. Gile, and W.A. Jesser, *Thin Solid Films* **144**, 297 (1986).
- ³⁶T. Castro, R. Reifengerger, E. Choi, and R.P. Andres, *Phys. Rev. B* **42**, 8548 (1990).
- ³⁷H. Yasuda and H. Mori, *Z. Phys. D: At., Mol. Clusters* **37**, 181 (1996).
- ³⁸H. Yasuda and H. Mori, *J. Cryst. Growth* **237/239**, 234 (2002).
- ³⁹O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry* (Pergamon, Oxford, 1979).
- ⁴⁰G. Treglia, B. Legrand, and P. Maugain, *Surf. Sci.* **225**, 319 (1990).
- ⁴¹C.J. Smithells, *Metals Reference Book*, 3rd edition (Butterworths, London, 1962).
- ⁴²B. Legrand, G. Treglia, and F. Ducastelle, *Phys. Rev. B* **41**, 4422 (1990).
- ⁴³E.M. Sosa-Hernandez, F. Aguilera-Granja, and J.L. Moran-Lopez, *Phys. Rev. B* **52**, 5392 (1995).
- ⁴⁴K. Binder, in *Phase Transitions at Surfaces*, edited by D.G. Pettifor, *Cohesion and Structure of Surfaces*, Vol. 4 (Elsevier, Amsterdam, 1995).
- ⁴⁵E.E. Zhurkin and M. Hou, *J. Phys.: Condens. Matter* **12**, 6735 (2000).
- ⁴⁶S.M. Foiles, *Phys. Rev. B* **32**, 7685 (1985).
- ⁴⁷M. Hou, S. Khyarlamov, and E.E. Zhurkin, *Phys. Rev. B* **66**, 195408 (2003); P. Moskovkin and M. Hou, *Eur. Phys. J. D* **27**, 7685 (1985).