Prediction of compositional ordering and separation in alloy nanoclusters

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Abstract

The statistical–mechanical free-energy concentration expansion method (FCEM) in conjunction with semi-empirical coordination-dependent energetic parameters was used for atomistic modeling of Ni–Cu–Al, Ni–Cu–Rh and the corresponding binary Ni–Cu, Ni–Al and Rh–Cu nanocluster systems, containing from 13 to 923 atoms with icosahedral and cuboctahedral shapes. The high efficiency of FCEM enables computations of such relatively large binary or ternary alloy clusters. Remarkable differences, governed by the opposite Ni–Cu and Ni–Al heteroatomic interactions, were noted in the surface segregated "magic-number" ordered compositional patterns of the two ternary clusters. Due to the strong Ni–Al interactions, the compositional ordering extends into the cluster core, and at elevated temperatures a sharp order–disorder transition occurs, depending on the cluster size, shape and composition. The computed site-specific atomic concentrations form the basis for evaluating pertinent thermodynamic functions. For all the alloy clusters a Schottky-type heat capacity anomaly is predicted and attributed to gradual desegregation excitation processes. In addition, inter-cluster compositional separation is computed for Rh–Cu clusters, and transition temperatures estimated from the disappearance of convexity in the free-energy vs. composition curves.
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Keywords: Equilibrium thermodynamics and statistical mechanics; Surface thermodynamics (including phase transitions); Alloys; Clusters

1. Introduction

Due to their unique properties, small particles, such as alloy nanoclusters, are attracting growing interest in recent years. In view of limitations in current experimental tools, valuable information about site-specific surface compositional structures has been obtained only by theoretical computations. When such data are obtained as function of temperature, for example, it facilitates the study of phase transitions, which raises intriguing

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questions concerning their distinctive features in *single* vs. *system* of alloy nanoclusters. As shown here, in contrast to transitions in a single small particle, which typically spread over a range of temperatures [1], alloy cluster macroscopic systems can exhibit (similarly to bulk systems) phase transition points, related to intra- or to inter-cluster compositional–structural transitions. We use the free-energy concentration expansion method (FCEM), originally derived for the theoretical prediction of surface segregation in the presence of short-range order (inter-atomic correlations) in binary alloys [2,3], and has proven to be an attractive tool for elucidating compositional structural phenomena in a system of alloy clusters capable of exchanging constituent atoms [4]. The remarkable efficiency of FCEM can yield large amounts of data concerning the roles of temperature, overall composition, size and shape in binary or ternary alloy nanoclusters, with accuracy better than the Bragg–Williams (BW) approximation. In addition, computations of related thermodynamical functions and properties, such as contributions of desegregation processes and order–disorder transitions to the cluster heat capacity, become possible. Results of such studies may have some practical implications, especially in heterogeneous catalysis and magnetic storage media.

2. Theory

FCEM applied to cuboctahedron (CO) and icosahedron (ICO) clusters consisting of atoms located at central-symmetric concentric "shells", yields all *I*-constituent *p*-shell concentrations, c_p^I. The energetic parameters entering FCEM computations comprise the nearest-neighbor (NN) interaction energy, w_{pq}^{IJ}, based [4,5] on coordination-dependent semi-empirical site energies [6], and the effective interactions, V_{pq}^{IJ}, between constituents *I* and *J* $\left(V_{pq}^{IJ} = \frac{1}{2}\left(w_{pq}^{II} + w_{pq}^{JJ} - 2w_{pq}^{IJ} \right) \right)$. Geometric input parameters include the number of atoms in each shell, N_p, and the number of NN pairs belonging to *p*- and *q*-shells, N_{pq} [4]. The FCEM correction to BW, obtained by expanding relevant thermodynamic functions in terms of

$c_p^I c_p^J$ [2,3,7,8], is reasonably accurate (and small) in cases of dilute clusters or ordered clusters with $c_p^I \approx 0$ or 1 (at some "magic-number" composition), and at relatively high temperatures, when V_{pq}^{IJ} is small compared to the thermal energy kT. It can also be derived [8] from an approximate formula for the correlation parameters $\varepsilon_{pq}^{IJ} = c_p^I c_p^J c_q^I c_q^J X_{pq}^{IJ}$, where $X_{pq}^{IJ} = 1 - \exp\left(-\frac{2V_{pq}^{IJ}}{kT} \right)$. At low temperatures X_{pq}^{IJ} approaches 1 for $V_{pq}^{IJ} > 0$, but diverges exponentially for $V_{pq}^{IJ} < 0$ (at high temperatures X_{pq}^{IJ} is an odd function of $\frac{2V_{pq}^{IJ}}{kT}$). Thus, in order to avoid the divergence problem, the free-energy formula has to be slightly modified. In accordance with the Ising model, where hyperbolic tangent appears in pair correlation functions and is used as an expansion parameter [9], X_{pq}^{IJ} is approximated here by $\tanh\left(b\frac{2V_{pq}^{IJ}}{kT} \right)$ ($b = 0.6$ is obtained by best fit of FCEM predictions to Monte Carlo simulations of (1 0 0) surface segregation in fcc solid solution [2]). The revised free-energy expression reads,

$$
F = kT \sum_p \left(N_p \sum_I c_p^I \ln c_p^I \right)
$$
$$
+ \sum_{p \leqslant q} N_{pq} \left(\frac{1}{2} \sum_I w_{pq}^{II} \left(c_p^I + c_q^I \right) \right.
$$
$$
- \sum_{\{IJ\}} \left(V_{pq}^{IJ} \left(c_p^I c_q^J + c_p^J c_q^I \right) \right.
$$
$$
\left. \left. + kT c_p^I c_q^J c_q^I c_q^J \frac{1}{b} \ln \cosh \left(b\frac{2V_{pq}^{IJ}}{kT} \right) \right) \right).
$$

Estimations of the homoatomic interactions (Table 1) are based [4,5] on coordination-dependent site energies [6,10,11], using experimental cohesion and surface tension data, and assuming uniform distribution of the site energy among its NN bonds [12–15]. Heteroatomic effective interactions were obtained from the heat of mixing [6,16] by the FCEM formula [8].

3. Compositional structural transitions

Previous FCEM computations accomplished for Ni–Cu–Pd and Ni–Cu–Rh nanocluster systems