

The Role of Near-Surface Bond Energetics in Shaping Nanoalloy Transformed Configurations

M. Polak,⁺ L. Rubinovich

*The Chemistry Department, Ben-Gurion University of the Negev
Beer-Sheva 8410501 ISRAEL*

In addition to the surface-layer composition, the subsurface layer in alloy nanoparticles is expected to affect their catalytic activity and selectivity. This theoretical-computational study focuses on the largely unexplored issue of nanoalloy compositional configurations arising from near-surface energetics and involved in thermally induced phase-separation transformations. Employing the statistical-mechanical Free-Energy Concentration Expansion Method (FCEM) [1] with Coordination-dependent Bond-Energy Variations (CBEV) [2] and Effective Pair Interactions (EPI) as part of the input, and the Coarse-Grained Layer Model for additional efficiency, atomic site-specific configurations were computed as a function of temperature for four heterogeneous-catalysis-related binary alloy nanoparticles having relatively small atomic-size mismatch: **Pd-Ir, Ag-Ir, Pt-Ir, and Pd-Rh**, all as 1415-atom cuboctahedrons. We predict distinct inner-core transitions between asymmetric and symmetric configurations beneath a surface-segregated monolayer (Fig. 1): Quasi-Janus (QJ) to solid-solution (SS) in Pd-Ir; QJ to asymmetric core-shell (asy-CS-a), followed by symmetric core-shell (CS-a) in Ag-Ir, and asy-CS-a transformed to CS-a in Pt-Ir and Pd-Rh. To quantify the roles of the CBEV and EPI, we introduce a straightforwardly calculated subsurface/inner-core permutation energy factor (λ) that predicts stable configurations without the need for FCEM computations (and has a clear correlation with the transformation temperature). Thus, its magnitude reflects the identity of the transformed configuration, e.g., for QJ to SS, λ is near zero. Application of the present methodology to ternary, quaternary, and quinary (high entropy) nanoalloys composed of the same elements is underway.

[1] M. Polak, L. Rubinovich, ACS Nano, 16 (12), 20186–20196 (2022).

[2] L. Rubinovich and M. Polak, Phys. Rev. B 80, 045404 (2009).

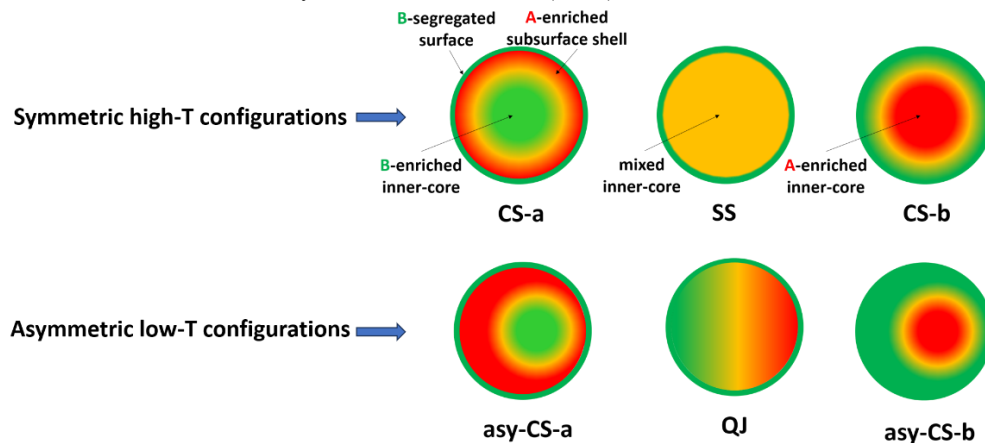
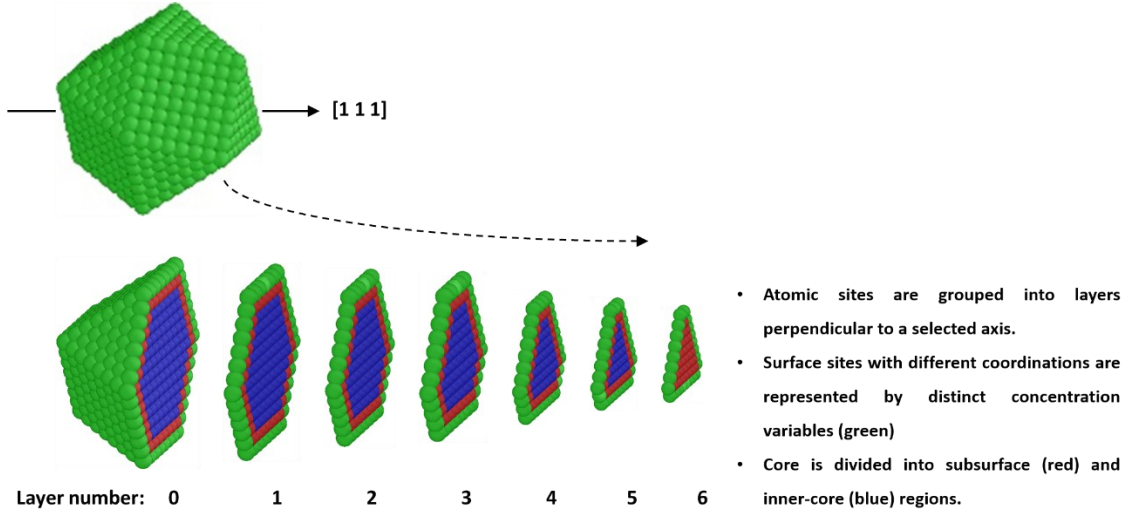


Fig. 1 Representations of several configuration candidates for the four selected A-B nanoalloy systems.

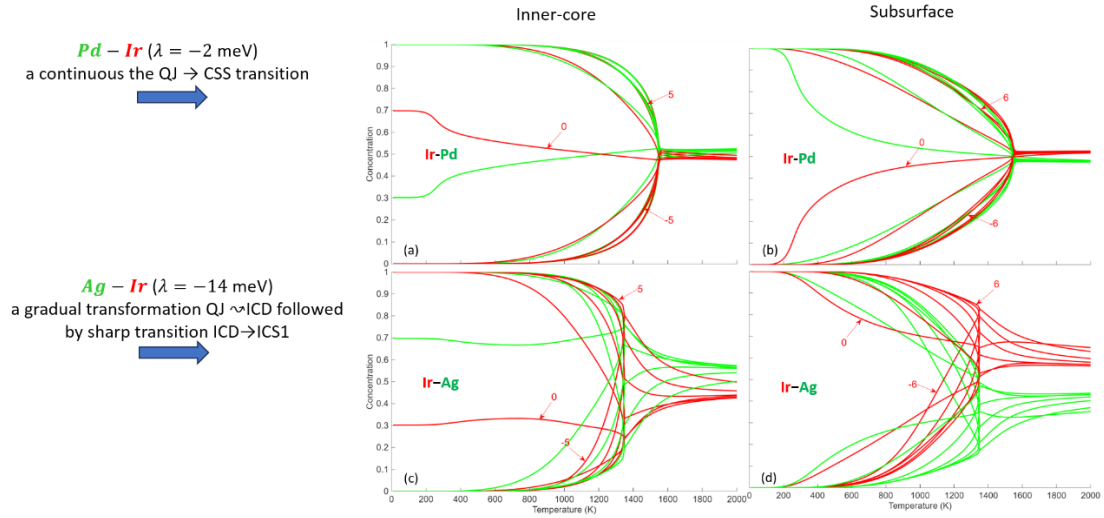
⁺ Author for correspondence: mpolak@bgu.ac.il

Supplementary information:

Site grouping for extra efficiency: Coarse-grained layer model (CGLM) of $O_h(1415)$



Temperature-dependent layer concentrations in $O_h(1415)$ (equiatomic core for pure B surface)



Mini text abstract:

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Subsurface composition can strongly influence the catalytic activity and selectivity of alloy nanoparticles, yet the role of near-surface energetics in determining their inner-core chemical order remains insufficiently understood. This theoretical-computational study examines thermally induced transformations in 1415-atom cuboctahedral Pd-Ir, Ag-Ir, Pt-Ir, and Pd-Rh nanoparticles with small atomic-size mismatch and strong intrinsic surface segregation. Temperature-dependent, atomic-site-specific concentration profiles are calculated using the statistical-mechanical Free-Energy Concentration Expansion Method (FCEM) [1], incorporating Coordination-dependent Bond-Energy Variations (CBEV) [2] and effective pair interactions, together with a coarse-grained layer model for improved computational efficiency.

The calculations reveal distinct transformations beneath a surface-segregated monolayer. Pd-Ir undergoes a continuous transition from a low-temperature quasi-Janus configuration to a nearly random core solid solution. Ag-Ir transforms gradually from quasi-Janus to an asymmetric core-shell arrangement, followed by a sharp transition to a symmetric core-shell configuration. Related asymmetric-to-symmetric core-shell transformations are predicted for Pt-Ir and Pd-Rh. These contrasting pathways demonstrate that the subsurface is a key region controlling the organization and thermal evolution of the nanoparticle core, rather than merely an extension of the segregated surface.

To rationalize this behavior, we introduce a subsurface/inner-core permutation-energy parameter, λ . It captures the competition between the global phase-separation tendency, governed by effective pair interactions, and the local preference of elements for subsurface sites, governed by coordination-dependent bond strengthening. The sign and magnitude of λ identify the preferred transformed configuration and correlate with the transformation temperature. In particular, λ near zero favors a solid solution core, whereas finite positive or negative values favor core-shell-type structures with element-specific subsurface enrichment. The λ criterion can thus predict stable symmetric configurations without full free-energy calculations and provides a transparent framework for interpreting and potentially controlling chemical-order transformations in catalytically relevant nanoalloys. Application to multicomponent, including high-entropy, nanoalloys is underway.

[1] M. Polak, L. Rubinovich, ACS Nano, 16 (12), 20186–20196 (2022).

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