Simulation of Surface Segregation in Cu-Pd-Au Alloys using Density Functional Theory, Behler-Parrinello Neural Networks, and Monte Carlo Simulations

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A R T I C L E I N F O.

Abstract

This article explores surface segregation in the multi-component Cu-Pd-Au alloy using a combined approach of Density Functional Theory (DFT), a neural network (NN)-based model, and Monte Carlo simulations. The neural model is trained on thousands of DFT calculations to accurately predict potential energies, enabling efficient simulation of surface segregation. The results show qualitative consistency with experimental data for PdAu and CuAu systems but reveal divergences for the PdCu system. The proposed approach enhances the efficiency of surface segregation simulations, aiding in the design of materials for future applications.

1 Introduction

In the industrial field, metalic alloys, especially those with multiple components, are commonly used because of their unique and adaptable properties, which can be customized for various applications like catalysis and gas separation. A key research challenge lies in optimizing the surface composition of these alloys to enhance their efficiency, stability, and selectivity. For Cu-Pd-Au ternary alloys, surface segregation—a process where the chemical composition of the surface differs from that of the bulk material—is particularly important. This phenomenon directly influences key processes like adsorption, diffusion, and desorption, which are critical for uses such as hydrogen purification. Consequently, better understanding and managing surface segregation in these alloys is essential for improving their performance in industrial applications.

2 Related work

The exploration of surface segregation in alloys has made notable progress, particularly with the advancement of computational techniques for predicting atomic arrangements and surface behavior. Boes and Kitchin (2017) employed Density Functional Theory (DFT) alongside Monte Carlo simulations to investigate segregation on AuPd(111) surfaces, underlining the necessity of combining experimental data with theoretical models for more precise outcomes. Additionally, Khorshidi and Peterson (2016) stressed the relevance of neural networks in their AMP framework, which leverages machine learning for atomistic simulations. These studies have paved the way for adopting sophisticated models to better comprehend segregation processes, especially in complex systems such as Cu-Pd-Au alloys. The incorporation of symmetry functions, neural network methodologies, and advanced data management underlines the growing reliance on computational tools in the field of surface science.

3 Issues of Surface Segregation for Cu-Pd-Au Alloys

Surface segregation in Cu-Pd-Au alloys is a complicated process, influenced by factors like temperature, Pressure and how atoms interact with each other are central to understanding materials. While experimental techniques are effective for simpler binary alloys, they often struggle to capture the complexity of ternary alloys, such as Cu-Pd-Au. This is where theoretical simulations gain importance—they allow us to predict and understand these complex surface behaviors.

The composition of the surface plays a vital role, as it directly influences hydrogen adsorption, diffusion, and the overall stability of the alloy. These characteristics are crucial for ensuring the alloy's efficiency in real-world applications.

4 Methodology

The study of surface segregation in Cu-Pd-Au alloys relies on a hybrid methodology combining Density Functional Theory (DFT) calculations and machine learning models, specifically a Neural Network ,to estimate surface energies with precision and efficiency. This theoretical approach is complemented by Monte Carlo (MC) simulations, which model atomic exchanges and surface segregation in simulated configurations that

closely resemble real-world conditions.

The objective is to overcome the limitations of classical DFT calculations, which are often too computationally expensive for large-scale simulations, by integrating a neural network model capable of estimating the potential energies of alloy configurations. The methodology is thus based on three key steps: theoretical modeling via DFT, neural network training, and the application of Monte Carlo simulations.

4.1 Density Functional Theory

Density Functional Theory (DFT) is a key tool in studying the energy and behavior of materials like Cu-Pd-Au alloys. It uses advanced mathematical models to predict how electrons interact within a material, relying on the idea that all the system's properties can be derived from the electron density rather than more complex wavefunctions.

One of the most trusted tools for these calculations is the Vienna Ab initio Simulation Package (VASP), which uses the Projector Augmented Wave (PAW) method for high accuracy. DFT calculates the total energy of a system by considering factors like the movement of electrons, their interactions, and the effects of external fields.

DFT calculations involve making crucial choices, such as selecting the right exchange-correlation functional, which determines accuracy. Common options are LDA (Local Density Approximation) for simpler systems and GGA (Generalized Gradient Approximation) for more complex ones like metals and alloys.

To solve DFT problems, the Kohn-Sham equations are used. These equations describe how electrons move and interact in the material. The process involves iterative steps to adjust the electron density until the system's total energy stabilizes. This energy reveals valuable information about the material's structure, stability, and behavior.

DFT is highly efficient and balances accuracy with computational cost, making it a favorite for studying complex materials. However, its precision depends on the chosen methods and sometimes struggles with materials that have strongly correlated electrons. Even so, DFT is a powerful and essential tool for exploring material properties, predicting behavior, and designing innovative materials.

4.2 Neural Network-Based Model

The neural network model was developed to efficiently predict the potential energies of Cu-Pd-Au alloy configurations. It uses a dataset of 5278 Density Functional Theory (DFT) calculations, which include various atomic configurations and compositions of the alloy. By leveraging G2 symmetry functions, the model transforms complex atomic arrangements into numerical representations suitable for the neural network.

The neural network consists of:

- Input Layer: Represents the G2 fingerprints for each atomic configuration.
- Two Hidden Layers: Each contains ten neurons, enabling the network to learn non-linear relationships between the inputs and outputs.

- Output Layer: Predicts the potential energy of the atomic configuration.

The network's parameters, including **weights** and **biases**, are iteratively adjusted during training to minimize prediction errors.

The model was trained using the Mean Squared Error (MSE) loss function to minimize the difference between the predicted and DFT-calculated energies. The training process included generating G2 fingerprints for all configurations, splitting the dataset into training, validation, and test sets, and optimizing the model parameters using backpropagation and gradient descent. Finally, the model's performance was validated on unseen data to ensure accuracy and generalizability.

The model demonstrated high accuracy, achieving a training Mean Absolute Error (MAE) of 2.0 meV/atom, a validation MAE of 2.4 meV/atom, and a test MAE of 1.8 meV/atom. The narrow distribution of residual errors across all datasets reflects the precision and reliability of the model's predictions.
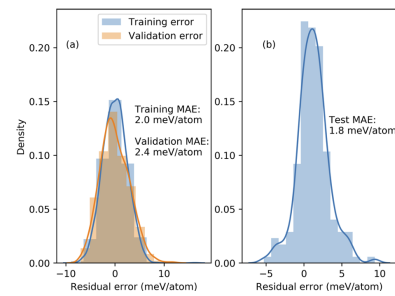

Figure 1. Residual error distributions for the training, validation, and test datasets..

The neural network model provides a computationally efficient alternative to DFT for predicting potential energies in Cu-Pd-Au alloys. Its ability to generalize to unseen configurations makes it an invaluable tool for accelerating materials simulations, such as Monte Carlo analyses.

4.2.1 Monte Carlo Simulation: Description of the MC Process for Simulating Segregation and Atomic Exchanges

Monte Carlo (MC) simulation is a probabilistic approach that enables the exploration of atomic configurations in materials like Cu-Pd-Au alloys. By iteratively swapping atoms and evaluating their configurations, this method offers insights into surface segregation phenomena under realistic thermodynamic conditions.

The MC process begins with an initial configuration, where atoms are arranged in a face-centered cubic (FCC) (111) lattice. This structure, common in dense metallic alloys, serves as the foundational framework for simulating atomic interactions. Each configuration undergoes energy evaluation, made efficient in this study through a trained neural network that replaces traditional Density Functional Theory (DFT) calculations. The energy difference (ΔE) between the current and new configurations determines their acceptance or rejection, guided by the Metropolis criterion:

$$P = \exp\left(-\frac{\Delta E}{kT}\right)$$

where k is Boltzmann's constant, and T is the temperature. If ΔE is negative, the new configuration is always accepted. Otherwise, it is accepted with a probability proportional to P. This probabilistic acceptance ensures a comprehensive exploration of the configuration space, avoiding entrapment in local minima.

For this study, simulations were conducted at 600 K, a temperature that mirrors practical conditions for catalytic and separation applications. The FCC (111) slabs, measuring $10 \times 10 \times 15$, allow detailed observation of surface, subsurface, and bulk behavior. Over 15,000 successful steps, including 6,000 for equilibration, were executed, producing reliable data on surface concentrations. The integration of Vegard's law ensured realistic lattice parameter adjustments based on alloy composition, further refining the accuracy of atomic positioning and interactions.

This method revealed distinct segregation tendencies: gold (Au) preferentially migrated to the surface, palladium (Pd) occupied intermediate regions, and copper (Cu) moved toward the subsurface. These trends align with experimental observations for Au, yet highlight discrepancies in Pd and Cu behaviors, which warrant further investigation.

Monte Carlo simulations, by coupling probabilistic modeling with neural network precision, offer a powerful tool for predicting atomic exchanges and surface dynamics in complex alloys. This approach bridges computational efficiency with realistic atomic modeling, enabling advancements in alloy design for industrial applications.

5 Monte Carlo Simulation Results

Monte Carlo (MC) simulations were performed using a trained neural network (NN) to analyze surface segregation in PdCuAu alloys. Simulations were conducted for 24 bulk compositions across the ternary phase diagram at a temperature of 600 K. Each simulation consisted of 15,000 successful MC steps, representing atom swaps within a $10 \times 10 \times 15$ FCC(111) slab. The last 6,000 steps were used to calculate the average surface concentration and its standard deviation.
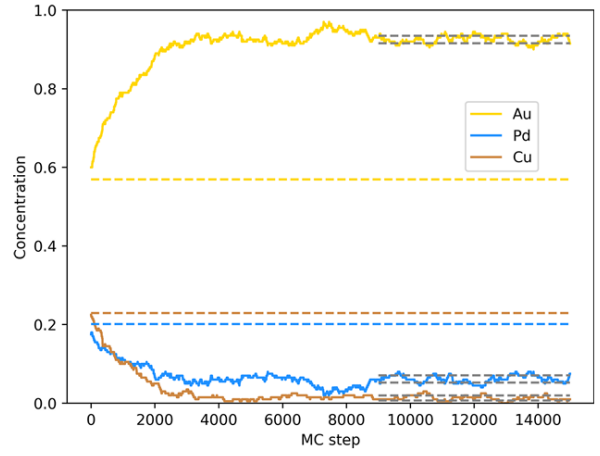

Figure 2. The MC trajectory for the top layer concentrations at a bulk composition of 20:23:47 for Pd:Cu:Au.

In the figure 2, dashed lines represent bulk concentrations, while solid lines indicate surface concentrations, with gray dashed lines showing the standard deviations. The MC simulation results, as shown in Figure 3, quantify the difference between surface and bulk concentrations for each element, represented by $\Delta C_i = C_i^{\text{surf}} - C_i^{\text{bulk}}$, where i represents Pd, Cu, or Au. Positive values ($\Delta C_i > 0$) indicate segregation to the surface (an excess compared to the bulk), while negative values ($\Delta C_i < 0$) signify depletion from the surface. The results reveal distinct segregation trends for each element.
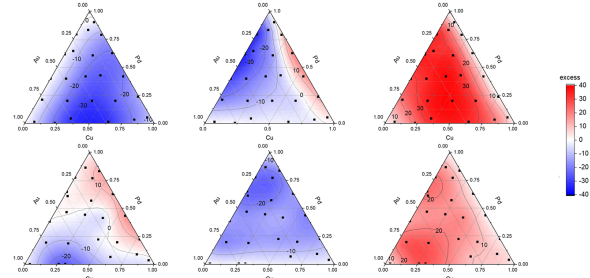

Figure 3. Surface segregation at 600 K: simulation (top) vs. experiment (bottom)

The result can be summarized in the table 1:

Element	Segregation Trend	Mathematical Representation
Pd	Segregates to surface near PdCu, depleted from surface in other regions	$\Delta C_{\text{Pd}} > 0$ (near PdCu), $\Delta C_{\text{Pd}} < 0$ (other regions)
Cu	Depleted from surface at all compositions, especially near CuAu	$\Delta C_{\text{Cu}} < 0$
Au	Segregates to surface at all compositions	$\Delta C_{\text{Au}} > 0$

Table 1. Segregation trends of Pd, Cu, and Au in PdCuAu alloys.

Interpretation: For Pd, ΔC_{Pd} is positive near the

PdCu binary region, indicating surface segregation, but is negative for most other compositions, reflecting depletion. For Cu, ΔC_{Cu} remains negative across all compositions, particularly pronounced near the CuAu region, highlighting consistent surface depletion. In contrast, Au shows $\Delta C_{Au} > 0$ for all compositions, indicating a strong tendency for surface segregation. These results provide a quantitative measure of the observed segregation behaviors, with trends aligning well with qualitative expectations for Au, but revealing discrepancies for Pd and Cu in certain binary alloy compositions.

Experimental data and simulation results agree qualitatively regarding the segregation of Au to the surface. However, discrepancies were observed in the binary alloy regions:

- For PdCu, simulations predict Pd segregation to the surface, while experimental data suggest depletion.
- For CuAu, simulations overestimate Au's segregation tendency and underestimate Cu's segregation.

To further analyze these discrepancies, quantitative calculations were performed for each pair of elements in equilibrium. Segregation energies were evaluated for the following reactions:

$$Au_{C,\ Bulk} + Pd_{C,\ Surface} K_{Au\text{-}Pd} Pd_{C,\ Bulk} + Au_{C,\ Surface},$$
$$\Delta G_{Au\text{-}Pd} = -RT \ln K_{Au\text{-}Pd}, \qquad (1)$$

$$Au_{C,\ Bulk} + Cu_{C,\ Surface} K_{Au\text{-}Cu} Cu_{C,\ Bulk} + Au_{C,\ Surface},$$
$$\Delta G_{Au\text{-}Cu} = -RT \ln K_{Au\text{-}Cu}, \qquad (2)$$

$$Pd_{C,\ Bulk} + Cu_{C,\ Surface} K_{Pd\text{-}Cu} Cu_{C,\ Bulk} + Pd_{C,\ Surface},$$
$$\Delta G_{Pd\text{-}Cu} = -RT \ln K_{Pd\text{-}Cu}. \qquad (3)$$

These reactions describe the segregation of one element relative to another, progressing from left to right in each equation. The equilibrium constant for each reaction, denoted as K_{A-B}, quantifies the segregation tendency.

The reaction energy (ΔG_{A-B}) quantifies the relative segregation ability of element A compared to B. A negative value of ΔG_{A-B} indicates a stronger tendency for A to segregate to the surface over B, while a positive value suggests the opposite behavior.
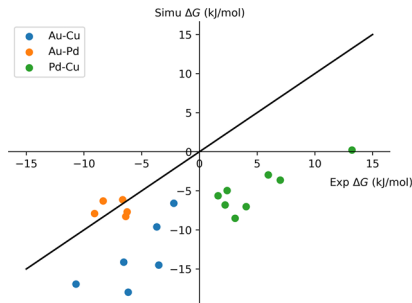

Figure 4. Segregation energies for AuCu, AuPd, and PdCu pairs derived from simulation and experimental data.

Figure 4 illustrates the segregation energies for the Au-Cu, Au-Pd, and Pd-Cu pairs, with each data point representing a specific bulk composition. Compositions with less than 20% bulk content or zero surface content for the elements were excluded from the analysis. The findings show that, for the **Au-Pd** pair, the simulated segregation energies align well with experimental results, with negative values confirming Au's strong preference to segregate to the surface over Pd. In the case of **Au-Cu**, simulations predict more negative segregation energies than experiments, suggesting an overestimation of Au's surface segregation compared to Cu. For the **Pd-Cu** pair, however, simulations and experiments show opposite trends, with notable discrepancies in the sign of the segregation energy.

These differences between simulation and experimental results highlight the need for further discussion and analysis, as detailed in subsequent sections.

6 Evaluation of Discrepancies Between Simulation and Experiment

6.1 Impact of Surface Structure

The surface structure significantly influences atomic segregation behaviors in Cu-Pd-Au alloys. Simulations reveal that crystallographic orientation and real surface features play a key role in the results.

Surface Orientation and Segregation

The fcc(111) and fcc(110) surfaces exhibit distinct segregation tendencies. The fcc(111) surface, being more stable and compact, promotes the segregation of gold (Au) to the surface while copper (Cu) migrates inward. In contrast, the fcc(110) surface, which is more open, shows greater sensitivity to relaxation, significantly altering segregation energies and, in some cases, reversing trends. Table 4 summarizes these differences, highlighting the critical impact of relaxation on fcc(110).

Surface	Segregation type	Surface relax	Segregation energy (eV)
fcc(111)	Cu in Pd	no	0.096
fcc(111)	Pd in Cu	no	-0.066
fcc(111)	Cu in Pd	yes	0.051
fcc(111)	Pd in Cu	yes	-0.122
fcc(110)	Cu in Pd	no	0.006
fcc(110)	Pd in Cu	no	-0.018
fcc(110)	Cu in Pd	yes	-0.166
fcc(110)	Pd in Cu	yes	0.007

Table 2. Segregation energy data for different surfaces and conditions.

Real Surface Features

Polycrystalline surfaces, with features like steps and defects, impact segregation energies and elemental distribution, effects absent in simplified models. While fcc(111) supports uniform segregation, fcc(110) shows variability due to relaxation. These unmodeled surface features partly explain discrepancies with experiments.

6.2 Effect of Surface Relaxation on Simulation-Experiment Discrepancies

The discrepancies observed between Monte Carlo (MC) simulations and experimental results may be influenced by surface relaxation, although this study suggests its role is limited. The objective was to analyze whether accounting for surface relaxation could explain the divergences in predicted segregation trends.

A series of tests was conducted on a slab model (2×2×5) with a 1:1:1 composition (Au:Pd:Cu).
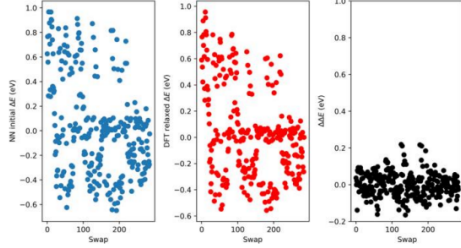

Figure 5. Energy difference before and after atomic swaps, with and without relaxation

For inter-layer swaps, the ΔE values retain the same sign between NN and DFT calculations, indicating consistent segregation trends even without relaxation. However, inconsistencies arise for very small ΔE values in intra-layer swaps, though these do not significantly affect surface concentrations. These observations show that the effect of relaxation is largely offset by error cancellation before and after atom swaps. This same trend had previously been observed for binary AuPd alloys, reinforcing the idea that surface relaxation has minimal influence in MC simulations of this type. The main conclusion is that surface relaxation is not a determining factor in simulation-experiment discrepancies. Thus, its exclusion in the MC simulations used here is justified.

6.3 Vibrational Contributions to Surface Segregation

Vibrational contributions to the Helmholtz free energy were evaluated as a potential source of discrepancies in the segregation behavior of Pd and Cu. Monte Carlo simulations assumed the Helmholtz free energy to consist only of potential energy and configurational entropy, excluding vibrational effects.

Calculations on a 1×1×7 slab at 1000 K, with full atomic relaxation and vibrational frequencies determined by finite difference, revealed minimal impact. As shown in Table 3, the vibrational contributions were too small to change the sign of segregation energies. Thus, they are unlikely to explain the discrepancies between simulations and experiments.

Segregation Type	DFT Potential Energy Change (eV)	Helmholtz Free Energy Change (eV)
Cu_3PdCu_3 to $PdCu_6$	-0.014	-0.063
Pd_3CuPd_3 to $CuPd_6$	0.146	0.168

Table 3. Potential Energy and Helmholtz Free Energy Change for Segregation of Pd in Cu and Cu in Pd.

6.4 DFT Errors in Formation Energies

DFT simulations often underestimate the interactions between copper (Cu) and gold (Au), resulting in higher calculated formation energies compared to experimental values. This limitation, attributed to exchange-correlation functionals and the modeling of electronic interactions, affects the predicted stability of Cu-Au alloys and the accuracy of their thermodynamic and mechanical properties. Consequently, DFT tends to overestimate the surface concentration of gold in segregation predictions, impacting properties such as corrosion resistance and catalytic performance. Addressing these inaccuracies through multiscale simulations or empirical corrections is essential to enhance the reliability of segregation predictions in Cu-Au systems.

6.5 Impact of Crystalline Orientation on CuPd Segregation

The segregation behavior of CuPd alloys is significantly influenced by the crystalline orientations fcc(111) and fcc(110). Variations in segregation trends are attributed to differences in atomic structure and interatomic interactions specific to these orientations.

For the $fcc(111)$ orientation, segregation of Pd to the surface is observed, with Cu diffusing into the bulk. Without considering surface relaxation, segregation energies are moderate (0.096 eV for Cu in Pd and −0.066 eV for Pd in Cu). Including surface relaxation reverses this trend, favoring Pd at the surface with a segregation energy of −0.122 eV.

The $fcc(110)$ orientation exhibits contrasting behavior. Without surface relaxation, segregation energies are close to zero, indicating weak segregation. However, when relaxation is accounted for, Cu segregation becomes highly favorable (−0.166 eV), highlighting the crucial role of surface relaxation in driving segregation trends.
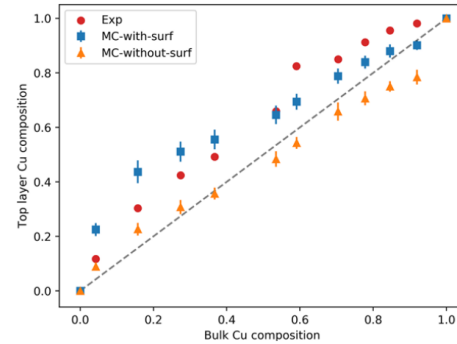

Figure 6. Profil de ségrégation de CuPd(110) à 600 K

Figure 6 illustrates the segregation profile of CuPd(110) at 600 K, comparing experimental data with Monte Carlo simulations. Simulations with surface relaxation closely match experimental results, confirming its importance for accurate predictions. Without relaxation, Cu segregation is underestimated, further emphasizing the role of surface relaxation.

Additionally, local defects such as steps and terraces, as well as the polycrystalline nature of experimental surfaces, introduce variability. These factors may

partially explain the observed discrepancies between simulations and experiments.

7 Perpectives and research Horizons

As part of our exploration into ternary alloy segregation, we came across an article [1] that examines the surface segregation behavior of Cu-Au-Pd alloys across a wide compositional range and at high temperatures. The study combines experimental techniques like Low-Energy Ion Scattering (LEIS) and Energy-Dispersive X-ray Spectroscopy (EDX) with Monte Carlo simulations to reveal key trends. It highlights Au's strong tendency to segregate to the surface, driven by its thermodynamic stability, which is supported by negative segregation energy values.
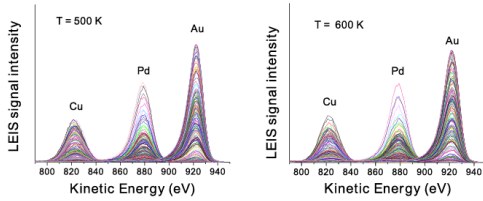

Figure 7. He$^+$ LEIS spectra for 164 bulk $C_x Au_y Pd_{1-x-y}$ alloy compositions obtained at 500 K (left) and 600 K (right).

In the Cu-Pd binary system, experiments show that Cu's segregation is suppressed within the B2 phase, while simulations tend to overestimate Pd's enrichment on the surface. In the Cu-Au system, Au's surface segregation is accurately predicted, although simulations slightly exaggerate its dominance.

At 600 K, Au's segregation becomes even more pronounced, while Pd and Cu experience further depletion due to the increased mobility of surface atoms and the removal of contaminants. Despite these findings, discrepancies between simulations and experiments—particularly in binary systems—highlight the limitations of current computational models, especially for Pd-Cu.

This study underscores the crucial interplay between thermodynamics, temperature, and crystal structure in determining surface composition.

7.1 Similar Trends Observed in Both Studies

Both articles explore surface segregation in Cu-Au-Pd ternary alloys, emphasizing the thermodynamic and compositional factors that influence segregation trends. They identify Au as the dominant surface-segregating element, consistently enriched at the surface across various compositions due to its thermodynamic preference. Both studies also observe that higher temperatures enhance Au's segregation tendency while depleting Pd and Cu from the surface.

Additionally, both studies rely on Monte Carlo (MC) simulations to model segregation, supported by experimental validation. Each highlights discrepancies between simulations and experiments, particularly for Pd and Cu, and aims to address these inconsistencies by analyzing segregation energies or exploring structural effects.

7.2 Key Distinctions Between the Two Approaches

The first article focuses primarily on binary segregation energies (ΔG_{A-B}), providing a detailed quantitative analysis of the relative segregation abilities of Au, Pd, and Cu in binary combinations. It uses a neural network-enhanced Monte Carlo (MC) simulation framework and highlights specific areas where simulations diverge from experimental data, such as underestimating Cu's segregation ability and overestimating Pd's surface enrichment in certain regions. However, it does not account for structural effects like phase ordering.
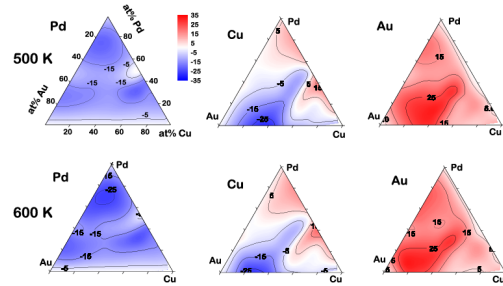

Figure 8. Ternary diagrams showing excess surface concentrations of Pd, Cu, and Au obtained at 500 K (first row) and 600 K (second row).

In contrast, the second article integrates a broader experimental dataset, spanning 164 compositions at 500 K and 600 K, (as shown in figure 8) and maps ternary segregation trends across the full composition space. It emphasizes the structural effects of the B2 phase in Cu-Pd, showing how structural constraints suppress Cu and Pd segregation. While it lacks detailed segregation energy calculations, it provides a more comprehensive view of ternary interactions and validates trends with experimental data.

To conclude,the first article excels in its quantitative analysis of binary segregation, while the second offers a more holistic perspective on ternary systems and structural influences. Together, they complement each other by addressing both specific segregation dynamics and broader compositional trends, offering valuable insights into Cu-Au-Pd alloys.

8 Methodological Contribution: Graph Neural Networks for Alloys

Given the limitations of traditional neural networks in accurately predicting the potential energy of alloys, this research adopts a Graph Neural Network (GNN). This model, innovative in its design, is specifically developed to exploit the topological structure of atomic configurations. It incorporates the individual attributes of atoms as well as their complex interactions. This approach significantly enhances the precision in predicting the potential energy of Au-Cu-Pd ternary alloys, thus offering a modeling method more suited to the inherent complexities of material properties.

8.1 Architecture and Operation of the Graph Neural Network

This study employs a Graph Neural Network (GNN) configured with three layers of graph convolution (GCNConv) to effectively process the atomic configurations of alloys. This model inputs the spatial coordinates of atoms, utilizing this information to capture the local interactions essential to predicting the potential energy of the alloys.

8.2 Convolution Process in the GNN:

Data Input: Each atom of the alloy, identified by its X, Y, and Z coordinates, is treated as a node in the graph.

Aggregation: At each GCNConv layer, the features of the nodes are aggregated from the immediate neighbors. This aggregation is mathematically formulated as a weighted linear combination of the neighbors' features, where the weights are adjusted based on the nodes' degrees, according to the formula:

$$h_i^{(l+1)} = \text{ReLU}\left(W^{(l)} \sum_{j \in \mathcal{N}(i) \cup \{i\}} \frac{h_j^{(l)}}{\sqrt{d_i d_j}} \right)$$

where:

- $h_j^{(l)}$: The features of node j at layer l,
- d_i and d_j: The degrees of nodes i and j,
- $W^{(l)}$: The weight matrix for layer l,
- $\mathcal{N}(i)$: The set of immediate neighbors of node i,
- ReLU: The Rectified Linear Unit activation function.

Output Formation: After passing through the final GCNConv layer, the node features $h_i^{(L)}$ (where L is the last layer) are aggregated across all nodes in the graph to form a graph-level representation. This aggregation can be expressed as:

$$x = \frac{1}{N} \sum_{i=1}^{N} h_i^{(L)}$$

where:

- $h_i^{(L)}$: The features of node i after the final GCNConv layer.
- N: The total number of nodes in the graph.

This aggregated vector x, representing the entire graph, is then passed through a linear transformation, defined as:

$$\text{output} = W \cdot x + b$$

where:

- W: The weight matrix of the fully connected layer.
- b: The bias term.

This linear transformation maps the high-dimensional graph representation to a scalar value, corresponding to the predicted potential energy of the ternary alloy configuration. As the energy prediction is a continuous scalar, no additional activation function is applied at this stage, ensuring the output directly reflects the model's learned prediction.

To illustrate these concepts more clearly, Figure 9 below presents a detailed schematic of the architecture of our GNN.
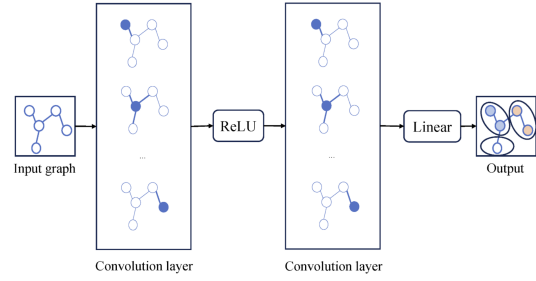

Figure 9. Schematic illustrating the GNN architecture used for predicting potential energy.

8.3 Application of the Model and Performance Evaluation

Following the examination of the internal workings of the Graph Neural Network, the model was applied to a database of 10,081 atomic configurations to assess its ability to predict the potential energy of alloys. The data were meticulously divided into separate sets for training, validation, and testing.

A total of 70% of the data, approximately 7,057 configurations, was allocated for training the model. This substantial allocation facilitates a thorough exploration of atomic characteristics and interactions, crucial for effective parameter learning. The remaining 30% were evenly distributed between validation and testing, allocating about 1,512 configurations for each phase. This segmentation ensures a rigorous evaluation of the model's ability to generalize and adapt to new data, a crucial element for validating the integrity and accuracy of the predictions.

The validation phase plays a vital role in adjusting hyperparameters and ensuring the model's generalization beyond the training data, thereby preventing overfitting. The test set, subsequently used, allows for an independent evaluation of the model's performance via the mean absolute error (MAE). This metric, chosen for its accuracy in quantifying the discrepancy between predictions and actual values, provides a reliable measure of the model's precision.

The results obtained during the training and validation phases are presented below, illustrating the evolution of the mean absolute errors (MAE) over the 100 epochs.
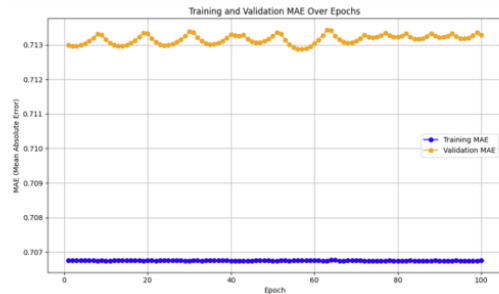

Figure 10. Training and Validation MAE Over Epochs

8.4 Discussion of Results

The data reveal remarkable stability in the training MAE, which remains around 0.707 meV/atom. This consistency suggests that the model has effectively learned the relevant characteristics without falling into the trap of overfitting. Meanwhile, the validation MAE fluctuates slightly around 0.713 meV/atom, indicating that the model generalizes well to new data, a critical quality for practical applications in alloy analysis.

The performance of the GNN model demonstrates a significant advancement over traditional neural network approaches, where a MAE of 2.4 meV/atom had been observed. This substantial improvement in prediction accuracy is not only an indicator of the robustness and generalization capability of the GNN model but also highlights its superiority in terms of reliability for practical applications.

The significant reduction in the mean absolute error (MAE) observed with the GNN model makes it particularly suitable for Monte Carlo simulations, where the accuracy of input values is crucial. A reduced MAE in initial predictions directly contributes to decreasing uncertainties in these simulations, thereby enhancing the quality and reliability of performance evaluations for the studied ternary alloy Au-Cu-Pd.

9 Conclusion

In this study, we investigated surface segregation in ternary Cu-Pd-Au alloys through an innovative approach that combines Density Functional Theory (DFT), Neural Networks (NN), and Monte Carlo (MC) simulations. Notably, our contribution is distinguished by the integration of Graph Neural Networks (GNN), which played a pivotal role in modeling complex atomic interactions with higher precision.

To begin with, DFT was employed to generate training data, while the GNNs leveraged the topological structure of atomic configurations to predict potential energies efficiently. This integration significantly enhanced the computational efficiency, allowing large-scale MC simulations with near-DFT accuracy. As a result, we were able to simulate surface segregation trends effectively.

Our findings reveal distinct segregation behaviors: gold (Au) strongly migrates to the surface, copper (Cu) tends to move toward the bulk, and palladium (Pd) exhibits intermediate behavior, which varies depending on the local atomic environment. Nevertheless, despite qualitative agreement with experimental data, some discrepancies were observed, particularly in the PdCu system. These differences highlight the need to address simplifications in the models, such as the lack of explicit polycrystalline surface representation and surface relaxation effects.

In conclusion, this work demonstrates the potential of GNNs in advancing material science by enabling precise and efficient simulations. Moving forward, it would be beneficial to incorporate additional complexities, such as vibrational contributions and more realistic surface environments, to refine predictions further and broaden the range of industrial applications.

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