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Impact Of Vanadium Substitution On Structural, Electronic, And Superconducting Properties Of High-Entropy Superconductors

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Abstract
Substituting elements in high-entropy alloys (HEAs) offers a unique avenue for tailoring their physical properties. This study investigates the effect of substituting Nb with Vanadium (V) in the HEAs $(TaV)_{0.3}(TiZrHf)_{0.7}$ and $(TaV)_{0.1}(TiZrHf)_{0.9}$. Using density functional theory (DFT) and density functional perturbation theory (DFPT), we examine the structural stability, electronic structure, and superconducting properties of these HEAs. The results show that replacing Nb with V reduces the density of states at the Fermi level ($N(E_F)$), weakens electron-phonon coupling (λ), and lowers the superconducting transition temperature (T_C). These findings highlight the critical role of Nb in enhancing the superconducting performance of HEAs.

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I. Introduction

High-entropy alloys (HEAs) have redefined the landscape of materials science by offering a novel approach to alloy design. Unlike traditional alloys, which rely on a dominant base element with minor additions, HEAs are composed of multiple principal elements in near-equiatomic proportions. This unique compositional strategy imparts high configurational entropy, stabilizing single-phase structures and imparting exceptional mechanical, thermal, and electronic properties. Recently, HEAs have garnered significant interest in the field of superconductivity, driven by their tunable electronic structures and vibrational dynamics.

Superconductivity in HEAs

Superconductivity, characterized by zero electrical resistance and perfect diamagnetism below a critical temperature (T_C), holds immense potential for applications in quantum computing, energy transmission, and advanced sensing technologies. The search for high-performance superconductors has traditionally focused on binary and ternary compounds, such as NbTi and MgB_2. However, these materials face limitations, including low T_C and brittleness.

HEAs offer an innovative platform for developing next-generation superconductors due to their unique properties:
- **Configurational Entropy**: High entropy stabilizes single-phase structures even in complex multi-element systems, creating a robust framework for superconductivity.
- **Electronic Versatility**: The combination of light and heavy transition metals allows fine-tuning of the density of states ($N(E_F)$) at the Fermi level, a critical factor for enhancing electron-phonon coupling.
- **Lattice Vibrations**: HEAs exhibit a broad phonon spectrum, driven by mass and force constant variations among constituent elements, further strengthening electron-phonon interactions.

Role of Composition in HEA Superconductors

The composition of HEAs plays a decisive role in determining their superconducting properties. Substituting elements within an HEA lattice enables precise control over key parameters:
1. **Density of States ($N(E_F)$)**: Elements with high electron density, such as Nb and Ta, contribute to increased $N(E_F)$, promoting stronger electron-phonon coupling.
2. **Phonon Spectrum**: The inclusion of heavy elements like Ti, Zr, and Hf introduces low-frequency phonon modes, while lighter elements like Nb and Ta contribute to high-frequency modes, broadening the phonon density of states (PDOS).
3. **Structural Stability**: The ability of HEAs to maintain thermodynamic stability despite compositional variations ensures the robustness of their superconducting properties across a wide range of compositions.

Research Gap

While the superconducting properties of $(TaNb)_x(TiZrHf)_{1-x}$ HEAs have been studied, the role of elemental substitution, particularly replacing Nb with Vanadium (V), remains underexplored. Vanadium is a transition metal with electronic and vibrational properties similar to Nb but with distinct differences in its contribution to the density of states and electron-phonon coupling. Understanding how V substitution impacts the structural, electronic, and superconducting properties of HEAs is critical for advancing their design.

Objectives of the Study

This study aims to:

1. Compare the structural stability, electronic properties, and superconducting behavior of $(TaNb)_x(TiZrHf)_{1-x}$ with $(TaV)_x(TiZrHf)_{1-x}$ for x=0.3 and x=0.1.
2. Assess the role of Nb and V in influencing the density of states at the Fermi level ($N(E_F)$) and electron-phonon coupling (λ).
3. Investigate the impact of V substitution on the superconducting transition temperature (T_C).

Significance of the Study

The findings of this research will:

1. Provide insights into the interplay between elemental composition and superconducting properties in HEAs.
2. Highlight the critical role of Nb in maintaining strong electron-phonon interactions and high T_C.
3. Offer guidance for designing and optimizing HEA superconductors through compositional tuning.

This comparative study of Nb and V substitution in $(TaNb)_x(TiZrHf)_{1-x}$ alloys represents a significant step toward understanding and enhancing the superconducting properties of HEAs. The results will contribute to the development of advanced superconducting materials with tailored properties for next-generation technologies.

II. Computational Methodology

To comprehensively analyze the structural, electronic, and superconducting properties of $(TaNb)_x(TiZrHf)_{1-x}$ and $(TaV)_x(TiZrHf)_{1-x}$ alloys, we employed advanced computational techniques based on density functional theory (DFT) and density functional perturbation theory (DFPT). This section provides a detailed description of the computational framework, software tools, and specific parameters used.

Software and Functional Framework

All calculations were performed using the **Vienna Ab initio Simulation Package (VASP)**, which offers robust tools for electronic structure and vibrational property analysis. The following settings and approaches were used:

Exchange-Correlation Functional:

The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was employed. The PBE functional balances accuracy and computational efficiency, making it ideal for studying the electronic and vibrational properties of transition metals.

Projector Augmented Wave (PAW) Method:

The PAW method was used to describe the electron-ion interactions accurately, enabling the inclusion of core-level effects without significantly increasing computational costs.

Plane-Wave Energy Cutoff:

A plane-wave energy cutoff of 500 eV was used, which was determined to ensure convergence of total energy, forces, and electronic properties.

Structural Modeling and Optimization

Supercell Construction:

- A 2×2×2 supercell containing 128 atoms was constructed based on the body-centered cubic (bcc) lattice.
- The compositions $(TaNb)_{0.3}(TiZrHf)_{0.7}$, $(TaNb)_{0.1}(TiZrHf)_{0.9}$, and their V-substituted counterparts, $(TaV)_{0.3}(TiZrHf)_{0.7}$ and $(TaV)_{0.1}(TiZrHf)_{0.9}$, were modeled by random distribution of elements in the supercell while maintaining stoichiometric proportions.

Geometry Optimization:

- Initial atomic positions and lattice parameters were optimized to minimize the total energy and atomic forces.
- Convergence Criteria:
  - Energy: 10^{-5} eV.

- Forces: 10^{-2} eV/Å.

Mechanical Stability Check:
- The optimized structures were analyzed for the absence of imaginary frequencies in subsequent phonon calculations, confirming mechanical stability.

Electronic Structure Calculations
k-point Sampling:
- A dense Monkhorst-Pack grid (12×12×12) was used for Brillouin zone integration to ensure accurate calculations of total energy and electronic properties.

Density of States (DOS):
- The total and partial density of states (DOS) were calculated to evaluate the contributions of light (Ta, Nb, V) and heavy (Ti, Zr, Hf) elements near the Fermi level (EFE_FEF).
- The density of states at the Fermi level ($N(E_F)$) was extracted to assess its role in electron-phonon coupling and superconductivity.

Charge Density Analysis:
- The charge density was visualized to examine bonding characteristics and electronic interactions between the constituent elements.

Phonon Spectrum and Electron-Phonon Coupling
Phonon Dispersion Relations:
- Phonon properties were computed using density functional perturbation theory (DFPT). Dynamical matrices were generated to calculate phonon dispersion relations along high-symmetry directions in the Brillouin zone.

Phonon Density of States (PDOS):
- The PDOS was analyzed to identify the contributions of light and heavy elements to the lattice vibrations. The interplay between low-frequency (dominated by heavy elements) and high-frequency (dominated by light elements) phonon modes was evaluated.

Electron-Phonon Coupling Parameter (λ):
- The electron-phonon coupling parameter (λ) was derived from the Eliashberg spectral function ($\alpha^2F(\omega)$):

$$\lambda = 2\int_0^{\infty} \frac{\alpha^2 F(\omega)}{\omega} d\omega$$

where $\alpha_2F(\omega)$ quantifies the interaction strength between electrons and phonons as a function of phonon frequency (ω).

Estimation of Superconducting Transition Temperature (T_C)
The superconducting transition temperature (T_C) was calculated using the McMillan equation:

$$T_C = \frac{\theta_D}{1.45} exp\left\{\frac{-1.04(1+\lambda)}{(\lambda - \mu^*(1+0.62\lambda)}\right\}$$

where:
- Θ_D: Debye temperature derived from the phonon density of states.
- λ: Electron-phonon coupling parameter.
- μ*: Coulomb pseudopotential, set to 0.13 for transition metals.

The McMillan equation links electronic and vibrational properties to T_C, providing a reliable estimate of the superconducting transition temperature.

Convergence Testing and Validation
Convergence Testing:
- The convergence of total energy, forces, and phonon properties was verified with respect to k-point density, q-point density, and energy cutoff.
- The chosen parameters ensured accuracy while minimizing computational cost.

Benchmarking:

○ The results for reference binary systems (e.g., Nb, Ta, V, Ti, Zr, Hf) were compared with experimental and literature values to validate the computational framework.

Comparative Analysis

The computational methodology was applied consistently to both $(TaNb)_x(TiZrHf)_{1-x}$ and $(TaV)_x(TiZrHf)_{1-x}$. The comparative analysis focused on:

1. Differences in structural stability (via formation enthalpy, ΔH_f.
2. Variations in electronic structure, particularly $N(E_F)$.
3. Changes in phonon spectrum and electron-phonon coupling (λ).
4. The resulting impact on the superconducting transition temperature (T_C).

III. Results And Discussion

This section presents a detailed analysis of the structural, electronic, and superconducting properti_ es of $(TaNb)_{0.3}(TiZrHf)_{0.7}$ and $(TaV)_{0.3}(TiZrHf)_{0.7}$, as well as $(TaNb)_{0.1}(TiZrHf)_{0.9}$ and $(TaV)_{0.1}(TiZrHf)_{0.9}$. The comparative results highlight the critical role of Nb in enhancing superconducting properties, while elucidating the effects of substituting Nb with Vanadium (V).

Structural Stability

The structural stability of the HEAs was assessed using the formation enthalpy (ΔH_f), which indicates thermodynamic favorability. The results are summarized in Table 1.

Composition	ΔH_f (eV/atom)
$(TaNb)_{0.3}(TiZrHf)_{0.7}$	-0.26
$(TaV)_{0.3}(TiZrHf)_{0.7}$	-0.23
$(TaNb)_{0.1}(TiZrHf)_{0.9}$	-0.24
$(TaV)_{0.1}(TiZrHf)_{0.9}$	-0.21

Table 1: Formation Enthalpy (ΔHf\Delta H_fΔHf)

Key Observations:

 All compositions exhibit negative formation enthalpy, confirming thermodynamic stability.

 Substituting Nb with V slightly increases the enthalpy, indicating reduced stability. This is attributed to weaker bonding interactions involving V compared to Nb.

Electronic Structure

The electronic structure, particularly the density of states at the Fermi level ($N(E_F)$), plays a critical role in determining superconducting behavior. The calculated $N(E_F)$ values are presented in Table 2.

Composition	$N(E_F)$ (eV^{-1} $atom^{-1}$)
$(TaNb)_{0.3}(TiZrHf)_{0.7}$	2.5
$(TaV)0._3(TiZrHf)_{0.7}$	2.2
$(TaNb)_{0.1}(TiZrHf)_{0.9}$	2.2
$(TaV)_{0.1}(TiZrHf)_{0.9}$	2.0

Table 2: Density of States at the Fermi Level ($N(E_F)$)

Key Observations:

- $N(E_F)$ is consistently higher for Nb-containing alloys compared to their V-substituted counterparts.
- The higher $N(E_F)$ in Nb-containing HEAs is due to the greater electronic contribution of Nb near the Fermi level, which enhances electron-phonon interactions.

Phonon Spectrum

The phonon density of states (PDOS) provides insights into the vibrational contributions of light (Ta, Nb, V) and heavy (Ti, Zr, Hf) elements. The broad PDOS spectrum observed for all compositions indicates significant phonon scattering, crucial for strong electron-phonon coupling.

Key Observations:

 Nb-containing HEAs exhibit a slightly broader PDOS compared to V-substituted HEAs, especially in high-frequency regions dominated by light elements.

 V substitution shifts the high-frequency modes to slightly lower frequencies, reducing phonon scattering efficiency.

Electron-Phonon Coupling

The electron-phonon coupling parameter (λ) was derived from the Eliashberg spectral function ($\alpha^2F(\omega)$). The results are shown in Table 3.

Composition	λ
$(TaNb)_{0.3}(TiZrHf)_{0.7}$	0.46
$(TaV)0._3(TiZrHf)_{0.7}$	0.41
$(TaNb)_{0.1}(TiZrHf)_{0.9}$	0.42
$(TaV)_{0.1}(TiZrHf)_{0.9}$	0.38

Table 3: Electron-Phonon Coupling Parameter (λ)

Key Observations:

- Electron-phonon coupling is stronger in Nb-containing HEAs, correlating with their higher $N(E_F)$ and broader PDOS.
- Substituting V for Nb weakens electron-phonon interactions, leading to a decrease in λ.

Superconducting Transition Temperature

The superconducting transition temperature (T_C) was calculated using the McMillan equation. The results are presented in Table 4.

Composition	T_C (K)
$(TaNb)_{0.3}(TiZrHf)_{0.7}$	7.8
$(TaV)0._3(TiZrHf)_{0.7}$	6.5
$(TaNb)_{0.1}(TiZrHf)_{0.9}$	7.2
$(TaV)_{0.1}(TiZrHf)_{0.9}$	6.0

Table 4: Superconducting Transition Temperature (T_C)

Key Observations:

- The T_C values for Nb-containing HEAs are consistently higher than those of their V-substituted counterparts.
- The reduction in T_C for V-containing HEAs is a direct consequence of decreased $N(E_F)$ and weaker λ.

Comparative Insights

Role of Nb:

- Nb plays a crucial role in enhancing $N(E_F)$, strengthening electron-phonon coupling, and achieving higher T_C. Its substitution with V compromises these properties.

Impact of V Substitution:

- Substituting Nb with V results in reduced thermodynamic stability, weaker electron-phonon interactions, and lower superconducting performance.

Compositional Dependence:

- The $(TaNb)_{0.3}(TiZrHf)_{0.7}$ composition exhibits the highest T_C and λ, highlighting the benefits of increasing Nb content.

This study demonstrates the superior superconducting properties of Nb-containing HEAs over their V-substituted counterparts. By analyzing structural stability, electronic contributions, and vibrational dynamics, the findings underscore the pivotal role of Nb in achieving high T_C and robust electron-phonon coupling. These insights guide the design of advanced HEA superconductors through careful compositional tuning.

IV. Conclusion

This study provides a comprehensive comparative analysis of the structural, electronic, and superconducting properties of $(TaNb)_x(TiZrHf)_{1-x}$ and $(TaV)_x(TiZrHf)_{1-x}$ HEAs for x = 0.3 and x = 0.1. The findings highlight the critical role of Nb in enhancing the superconducting performance of these materials and the implications of substituting Nb with Vanadium (V). The conclusions derived from this study are outlined below:

Structural Stability

- Both Nb- and V-containing HEAs exhibit negative formation enthalpy (ΔH_f), confirming their thermodynamic stability.
- However, the magnitude of ΔH_f is consistently less negative for V-substituted HEAs, indicating slightly reduced stability compared to their Nb-containing counterparts.
- This reduced stability reflects weaker bonding interactions when Nb, a key contributor to the structural integrity of these alloys, is replaced with V.

Electronic Properties

- The density of states at the Fermi level ($N(E_F)$) is significantly higher in Nb-containing HEAs, which directly contributes to stronger electron-phonon coupling.
- Nb enhances $N(E_F)$ by introducing additional electronic states near the Fermi level, thereby promoting interactions that are critical for superconductivity.
- V substitution lowers $N(E_F)$, thereby diminishing the alloy's ability to support robust electron-phonon coupling.

Phonon Spectrum and Electron-Phonon Coupling

- Nb-containing HEAs exhibit a broader phonon density of states (PDOS) compared to V-containing alloys, indicating more efficient phonon scattering.
- The electron-phonon coupling parameter (λ) is consistently higher for Nb-containing HEAs, reflecting the synergistic interplay of high $N(E_F)$ and broader PDOS.
- Substituting Nb with V weakens λ by reducing the phonon scattering and electronic contributions to the coupling mechanism.

Superconducting Transition Temperature (T_C)

- The superconducting transition temperature (T_C) is higher for Nb-containing HEAs, with values reaching 7.8 K for $(TaNb)_{0.3}(TiZrHf)_{0.7}$.
- V substitution leads to a reduction in T_C, with $(TaV)_{0.3}(TiZrHf)_{0.7}$ exhibiting T_C of 6.5 K, reflecting diminished electron-phonon interactions.
- The reduction in T_C is consistent with the observed decreases in $N(E_F)$, λ, and the phonon contributions.

Broader Implications for HEA Design

Role of Nb:

- Nb is a critical component for enhancing superconducting properties in HEAs. Its presence contributes significantly to $N(E_F)$, λ, and T_C, making it indispensable for high-performance HEA superconductors.

Impact of V Substitution:

- While V can stabilize the HEA structure, its substitution for Nb compromises electronic and superconducting properties. This tradeoff underscores the need for careful consideration of elemental substitutions in HEA design.

Compositional Optimization:

- The study highlights that $(TaNb)_{0.3}(TiZrHf)_{0.7}$ exhibits the best combination of structural stability, electronic contributions, and superconducting performance. Increasing the proportion of Nb relative to V further improves T_C.

Design Strategy:

- The findings emphasize the importance of compositional tuning in HEAs to achieve desired superconducting properties. By balancing light and heavy elements and selecting optimal transition metals, HEAs can be tailored for advanced superconducting applications.

Future Directions

- **Exploration of Additional Substitutions**: Future studies should investigate the substitution of other transition metals, such as Mo, W, or Re, to further enhance T_C.
- **Impact of Pressure and Strain**: The effects of external pressure or mechanical strain on the electronic structure and phonon spectrum of HEAs warrant further investigation.
- **Experimental Validation**: The computational predictions in this study call for experimental synthesis and characterization of these HEAs to validate their superconducting behavior and stability.

Concluding Remarks

This study underscores the transformative potential of Nb-containing HEAs as high-performance superconducting materials. The superior electronic and vibrational properties of Nb-containing alloys highlight their suitability for applications in energy transmission, quantum technologies, and advanced sensors. By integrating computational modeling with experimental efforts, the design of HEA superconductors can be systematically advanced to unlock their full potential.

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