# First principles study of structural, electronic and charge transfer properties of high entropy alloys

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**Abstract.** High entropy alloys (HEAs) with unique structural, electronic and functional properties, have emerged as a promising class of materials for hydrogen storage. However, a fundamental understanding of the role of electronic structure and charge transfer mechanisms prior to hydrogenation is still lacking. This study employed first-principles density functional theory (DFT) to analyse the structural and electronic properties, along with the charge distribution mechanism in HEAs. Important parameters like lattice parameters, unit cell volume, formation energies, density of states, valance charge and charge transfer distribution were calculated to evaluate the performance and behaviour of these materials. The results show that $Ti_4V_3CrFe_4Al_4$ is the most thermodynamically stable. Although alloying with elements of different atomic radii improves the material's capacity to absorb hydrogen, structural integrity may be jeopardized. Nb has a strong effect on the electronic structure.

## 1 Introduction

The growing demand for developing safe and efficient energy storage technologies has driven the search for advanced materials with improved performance. Recently, High entropy alloys (HEAs), characterized by a combination of at least five or more principal elements in equal and near equal molar compositions, usually ranging between 5-35 at%, have emerged as potential energy storage materials, particularly for hydrogen storage [1]. Their outstanding mechanical and functional properties include high strength, good structural stability, and good resistance to oxidation and corrosion [2]. The unique properties of HEAs are due to slow diffusion, severe lattice distortion, high configurational entropy, and cocktail effects [3]. Their mixing entropy and the lattice distortion energy both play a significant role in the thermodynamic stability of HEAs [4]. Lattice distortion in (HEAs), resulting from differences in atomic radii of the constituent element, and is considered a key factor in promoting hydrogen absorption [4]. This effect encourages the

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formation of ordered compounds, like the Laves phase in alloys with increasing Nb content, or less compact structures, like body centered cubic structures (BCC) rather than face-centered cubic structures (FCC) [5, 6]. Sahlberg et al. [7] synthesized BCC structured TiVZrNbHf HEA and showed that atomic size difference between zirconium (Zr) and vanadium (V) in the alloy induces significant lattice distortion, expanding the volume of tetrahedral and octahedral interstitial sites and the overall unit cell volume, thus enhancing hydrogen storage capacity. Kao et al. [8] experimental study of CoFeMnTixVyZrz HEA, also demonstrated that the hydrogen storage capacity can be optimized by varying the composition of titanium (Ti), vanadium (V), and zirconium (Zr). These elements have large atomic radii that causes lattice distortion and increase the lattice parameter. Another key parameter that significantly influences the properties is the valence electron concentration (VEC). VEC strongly affects how much hydrogen a material can store with lower VEC alloys ($\leq$ 4.9) exhibiting higher hydrogen capacities, while higher VEC values reduce capacity [9].

The most studied parameters that influence the structural, electronic properties of HEAs include atomic size difference ($\delta$), electronegativity difference ($\Delta\chi$), valence electron concentration (VEC), lattice distortion, and mixing enthalpy and entropy [10]. Although numerous studies have demonstrated impact of these parameters on the properties of HEAs, the role of electronic properties and charge transfer mechanisms in HEAs remains poorly understood. Bader charge analysis and first-principles computations can be used to clarify electronic interactions [11]. First-principles methods, including density functional theory (DFT), allow for the prediction of material properties based purely on fundamental quantum mechanics, offering detailed understanding of how the atomic arrangement and electronic structure govern the overall behaviour of materials [12]. For example, the recent study on NbTiVZr HEA revealed that hydrogen atoms tend to attract electrons because they are more electronegative than the other metals in the alloy. Furthermore, changes in niobium (Nb) and vanadium (V)'s Bader charges during hydrogen absorption also suggest strong interactions between these elements and hydrogen. According to first-principles study on TiZrHfScMo by Hu et al [13], charge redistribution during hydrogen absorption influences bonding interactions, causing electron loss in Ti/Sc and gain in molybdenum (Mo). The compositional complexity of HEAs also influences these electronic interactions, as is shown in ZrTiVAlFe alloys, where iron (Fe) substitution alters phase stability and element partitioning [14].

Building on this fundamental knowledge, this study investigates three carefully tailored high-entropy alloys $Ti_4V_3CrFe_4Al_4$ (HEA1), $Ti_4Nb_3V_3CrFeAl_4$ (HEA2), and $Ti_4Nb_4V_3CrFe_4$ (HEA3) with the aim of assessing how strategic compositional variation influences the structural and electronic properties of these alloys. These specific compositions were chosen due to their potential to form favourable hydrogen-storing phases such as BCC or Laves structures, and because the constituent elements are known for their affinity to hydrogen. Informed by recent density functional theory (DFT) studies [11–14], the investigation employs Bader charge analysis and electronic structure evaluation to understand the charge distribution mechanisms in these HEAs and evaluate their suitability for hydrogen storage applications.

## 2 Methodology

The study employed first-principles calculations using the Vienna Ab initio Simulation Program (VASP), a tool based on DFT and the plane-wave method [15]. The interaction between ions and electrons was modelled using the projector augmented wave (PAW) method [15], while exchange-correlation effects were treated with the Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) [16]. A

plane-wave cutoff energy of 540 eV, and a Monkhorst-Pack k-point of 8 × 8 × 8 were used to sample the Brillouin Zone [17]. The electronic self-consistent iterations were converged to a tolerance of 10^(-5) eV. Structural relaxation was performed until the forces on all ions were below 0.02 eV/Å. The Bader charge analysis code was then used to study the charge states of elements in high-entropy alloys (HEAs) [18].

DFT simulations were used to analyze the structural and electronic properties of three HEAs. The initial composition was obtained using cluster expansion, and (HEA1) was generated through a substitutional search by replacing selected chromium (Cr) atoms with iron (Fe) atoms. The other two compositions, (HEA2) and (HEA3), were obtained through random substitution to systematically explore the effects of Nb and Al. Furthermore, High Entropy Predicting Software (HEEAPS) was used to calculate the mixing entropy alloys [19].

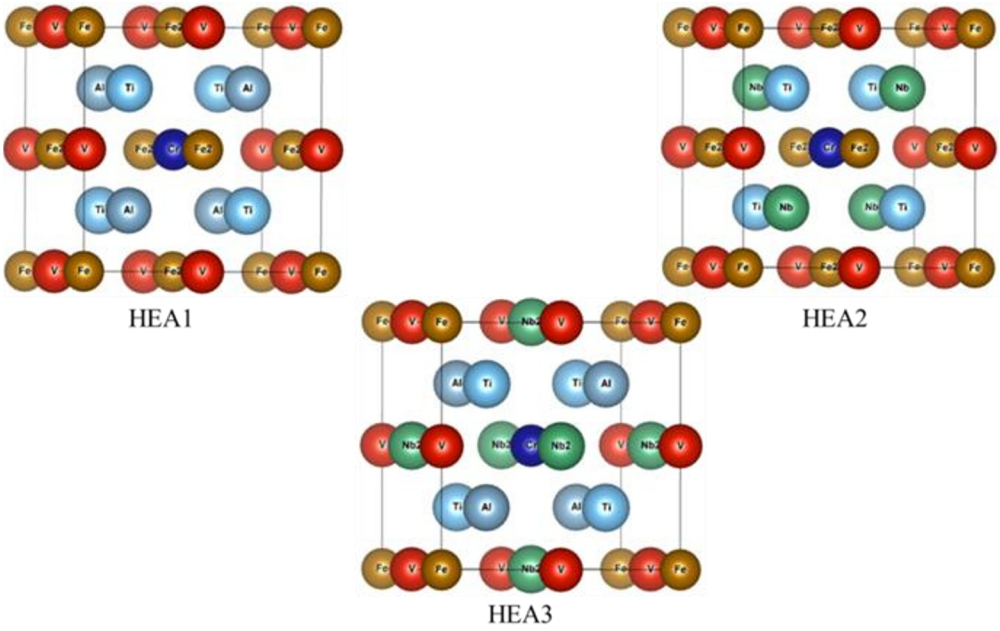


**Fig. 1.** Schematic diagram of geometrically optimized crystal structures of the three HEAs, each with 16 atoms.

## 3 Results and discussion

### 3.1 Structural parameters

Configurational entropy, also referred to as mixing entropy ($\Delta S_{mix}$) plays a fundamental role in the thermodynamic stabilization of high-entropy alloys (HEAs). Prior to investigating their structural or functional properties, it is essential to evaluate the entropy of mixing to verify whether the alloys meet the established thermodynamic criteria for HEA classification. A $\Delta S_{mix}$ value exceeding 1.5 J/mol·K is widely recognized as the threshold for identifying high-entropy systems [20]. As shown in Table 1, the calculated configurational entropy values for the three investigated alloys surpass this benchmark, confirming their classification within the high-entropy regime. To further assess their potential for hydrogen storage applications, key structural parameters were investigated.

Fig. 1 displays their optimized crystal structures, while Table 1 summarizes key calculated parameters, including lattice parameters, unit cell volumes, average bond distances and formation energies.

Previous studies have shown that alloying with elements possessing large atomic radii such as V (1.34 Å), Ti (1.47 Å), and Nb (1.46 Å) leads to increased lattice distortion and larger lattice constants [5, 6]. A similar trend is observed in the results presented in Table 1 across the three studied alloys, with lattice parameters increasing from 5.977 Å in HEA1 to 6.257 Å in HEA2. This expansion is attributed to the addition of elements with relatively large atomic radii, such as niobium (1.46 Å) and aluminium (1.43 Å). The observed increase in lattice parameter leads to longer average bond distances and larger unit cell volumes, particularly in HEA2. Volume expansion, as reflected by the larger unit cell volumes in Table 1, is very key characteristic for hydrogen storage application. It indicates that larger atoms, such as niobium (Nb) push neighbouring atoms and induce lattice distortions within the structure These distortions create additional interstitial spaces, which can facilitate greater hydrogen accommodation and improve storage capacity [7]. HEA1 shows the greatest thermodynamic stability among the three compositions, as evidenced by its lowest formation energy of −218.68 kJ/mol. The stability trend follows the order of HEA1>HEA3>HEA2. The addition of Nb in HEA2 and HEA3 leads to higher (less negative) formation energies, indicating the impact of Nb which results in increased lattice distortion and chemical inhomogeneity, due to its relatively large atomic radius (1.46 Å). The results agree with high-throughput computational approaches commonly used in HEA design, which emphasize the role of atomic size, formation energy, and phase stability in screening alloy candidates for functional applications such as hydrogen storage [21, 22].

**Table 1.** Lattice parameters, unit cell volumes, formation energies and mixing entropy alloys required to form the three HEA alloys.

| Structure | Lattice parameters (Å) | Volume (Å) | Average bond distance (Å) | Formation energy (kJ/mol) | $\Delta S_{mix}$ (J/mol.K) |
|---|---|---|---|---|---|
| $Ti_4V_3CrFe_4Al_4$ (HEA1) | a = 5.98 | 213.54 | 1.17 | -218.68 | 12.70 |
| $Ti_4Nb_3V_3CrFeAl_4$ (HEA2) | a = 6.26 | 244.99 | 1.20 | -25.51 | 13.86 |
| $Ti_4Nb_4V_3CrFe_4$ (HEA3) | a = 6.11 | 227.65 | 1.20 | -127.78 | 12.70 |

## 3.2 Electronic properties

Bader charge analysis was used to evaluate the contribution of the constituent elements in the electronic properties of high entropy alloy materials [11].

### *3.2.1 Valence charge analysis*

High-entropy alloys (HEAs) are composed of multiple principal elements with varying atomic sizes and valence electron concentrations. These variations give rise to complex electronic behaviour, which is crucial to understand especially for hydrogen storage. Valence charge distribution offers insight into how electrons are shared or localized among the constituent elements. Since hydrogen absorption involves electron exchange with the host lattice, analyzing valence electron distribution helps reveal the nature of bonding interactions within these alloys [11]. The valence charge distribution for each element in the three high-entropy alloys is presented in Fig. 2. The results reveal noticeable variations in how each element contributes to the overall charge distribution, reflecting their distinct

influences within the metallic bonding environment. In HEA1 and HEA2, elements such as vanadium (V) and chromium (Cr) exhibit high valence charges, indicating strong metallic bonding. These elements are characterized by moderate atomic radii and relatively low electronegativity, tend to donate electrons to the surrounding lattice, which enhances bonding strength within the alloy. On the other hand, aluminium (Al) exhibits significantly lower valence charge values, indicating a relatively weak involvement in metallic bonding within the alloy. A similar behaviour has been observed in previous studies where Al exhibits a passive electronic role in HEAs, particularly in systems where it is alloyed with more electronegative transition metals like Cr and Fe [23]. The addition of niobium (Nb) in HEA2 and HEA3 leads to a noticeable shift in how valence charge is distributed across the alloy. Due to its relatively large atomic radius and strong tendency to retain electrons, Nb consistently shows higher valence charge compared to the other elements [24]. Interestingly, as the Nb content increases, changes in the valence charge of titanium (Ti) also emerge, indicating a compositional dependence in charge redistribution. This phenomenon is also demonstrated in recent study by Meng et al [25] that analyses the charge-transfer effect in multi-principal element alloys and is driven by differences in atomic size and electronegativity.

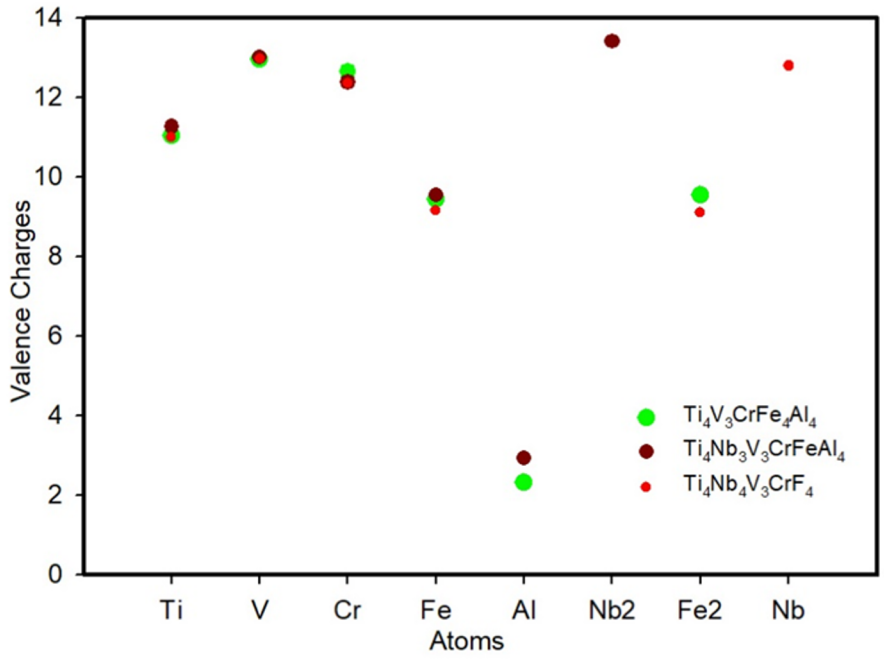


**Fig. 2.** Distribution of valence electron per atom for the three investigated high entropy alloys (HEAs)

### *3.2.2 Density of state analysis*

To determine the contribution of each element to the electronic structure of the high-entropy alloys, the total density of states (DOS) for the three alloys was calculated, as shown in Fig. 3. These provide valuable understanding into their electronic structures, which are critical for evaluating their atomic bonding behaviour and thermodynamic stability. All three alloys exhibit a finite DOS at the Fermi level (EF = 0 eV), demonstrating a metallic behaviour and the presence of delocalized électrons. This property is particularly beneficial for hydrogen storage applications, as it enhances charge mobility and facilitates

hydrogen diffusion, consistent with valence charge distribution analyses in Fig. 2 Among the three compositions, HEA1 displays the lowest DOS at the Fermi level, indicating a more electronically stable configuration. This result aligns with the formation energy values inTable 1, where HEA1 exhibits the most negative formation energy, indicating its superior thermodynamic stability. The stability of HEA1 demonstrates that this material is capable of withstanding repeated hydrogenation cycles without significant structural degradation. Niobium (Nb) is widely recognized for its ability to modify bonding interactions and the electronic density of states in complex alloys [26]. As shown in Fig. 3, HEA2 and HEA3 containing higher amounts of Nb exhibit an increased density of states (DOS) at the Fermi level, indicating a higher number of available electronic states for conduction While this enhances the metallic character of the alloys, it may also introduce local electronic instabilities, contributing to the less negative formation energies observed in these compositions. These findings highlight the dual role of Nb in enhancing electronic conductivity while potentially compromising thermodynamic stability, and this is in good agreemenet with the formation energy trends in Table 1.

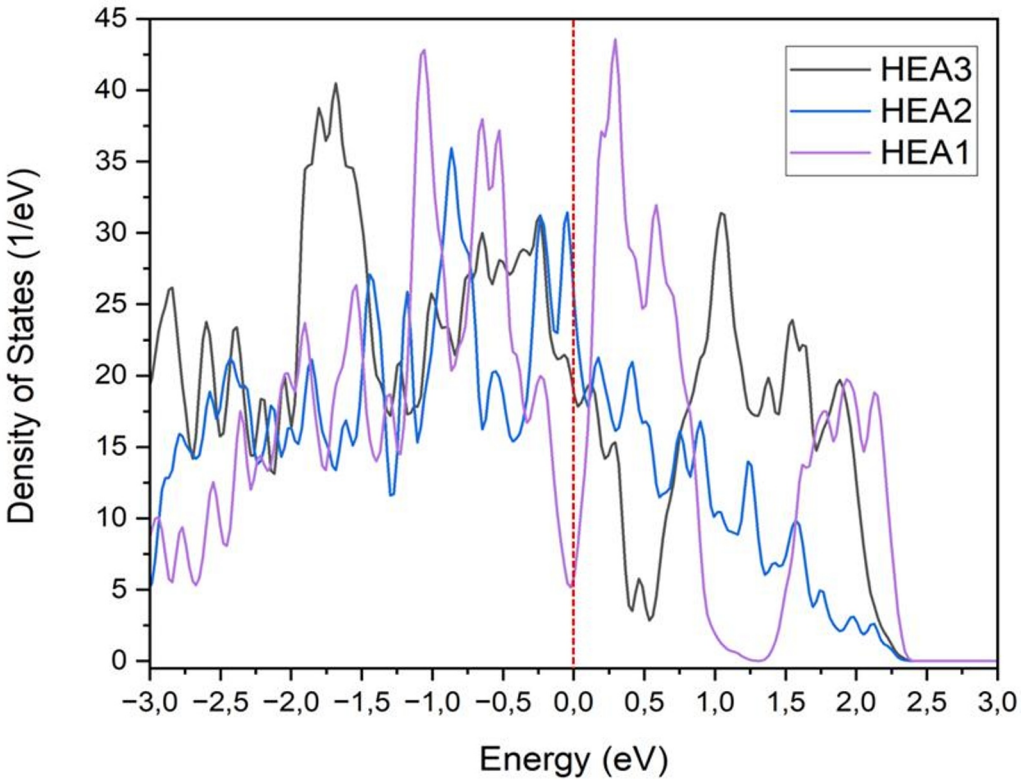


**Fig. 3.** Comparison of density of states (DOS) for the three HEAs. Fermi level is located at 0 eV and marked with red broken vertical line.

### 3.3 Charge transfer properties

Charge transfer analysis in high-entropy alloys (HEAs) is very crucial for understanding how electrons are redistributed among constituent elements with different electronegativities. This property is important for hydrogen storage applications, as determines how hydrogen interacts with the alloy. Elements that donate electrons tend to form stronger bonds with hydrogen atoms, while electron-accepting elements can influence

hydrogen adsorption and energetics [11, 27]. It has been reported a positive Bader charge indicates electron loss, whereas a negative value indicates electron gain and an element's capacity to gain or lose electrons increases with the size of its charge, whether it be positive or negative [27]. The charge transfer distribution in the three high entropy alloys (HEAs) under investigation in Fig. 4 shows that iron (Fe) and chromium (Cr) atoms consistently exhibit negative charge transfer, indicating their ability to gain electrons. On the other hand, titanium (Ti) Titanium (Ti) is the most charged element in all compositions, which indicate electron loss. When Nb is added to the system, as in HEA2 and HEA3, the charge transfer behaviour changes noticeably, especially for Bader charge of Fe, which exhibit more negative values than other elements. Bader charge of Al atoms maintains a relatively high positive charge transfer, especially in the HEA1 composition. The charge transfer distribution found in this investigation, highlight the crucial role that compositional tuning plays in determining the electronic structure and functional properties of HEAs.

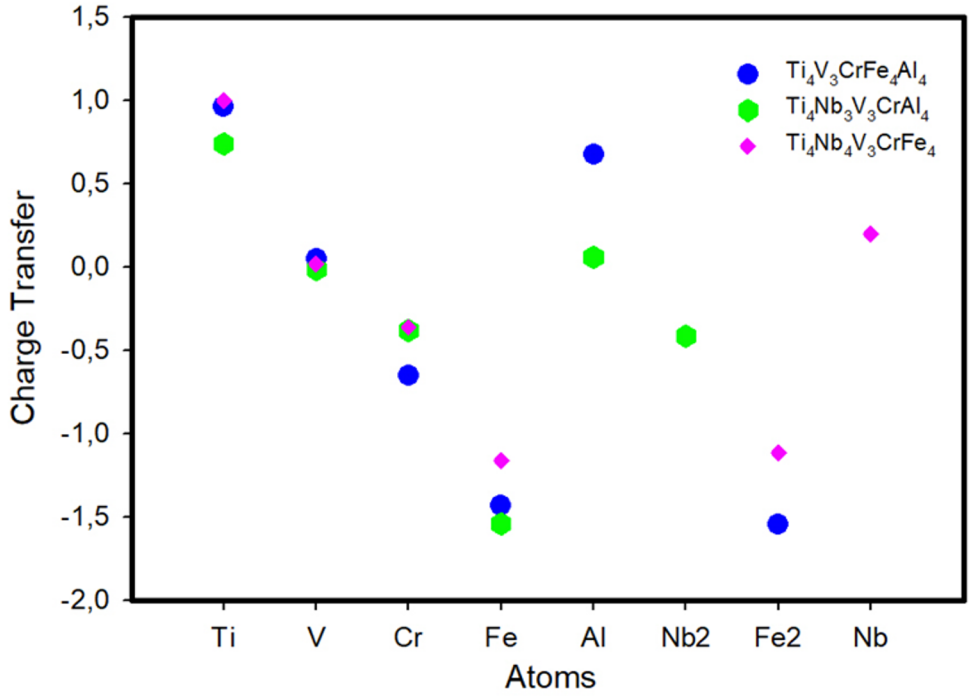


**Fig. 4.** Distribution of charge transfer per atom for the three investigated high entropy alloys (HEAs)

## 4 Conclusion

Density functional theory (DFT) simulations were successfully employed to investigate the structural, electronic and charge transfer properties of high entropy alloys, namely $Ti_4V_3CrFe_4Al_4$ (HEA1), $Ti_4Nb_3V_3CrFeAl_4$ (HEA2), and $Ti_4Nb_4V_3CrFe_4$ (HEA3), with an emphasis on their potential for hydrogen storage applications. Among the studied HEAs, HEA1 exhibits strong structural stability with formation energy of −218.68 kJ/mol, indicating that it is more thermodynamically stable compared to both HEA2 and HEA3. The findings demonstrated that alloying with elements such as Nb and Al causes lattice distortion which result in more interstitial sites that are favourable for hydrogen absorption while also having a significant impact on bond distances, lattice expansion, and charge transfer behaviour. However, as evidenced by the higher formation energy of Nb-rich

compositions (HEA2 and HEA3), this structural expansion can also compromise thermodynamic stability. The elemental composition and charge distribution were clearly related, according to electronic structure analysis, especially when it came to Nb's function in changing the density of states and valence charge. These results highlight importance of compositional tuning in optimizing the structural stability and functional performance of HEAs for hydrogen storage.

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