

Ab initio study of a CrCoFeNi high entropy alloy through density functional theory

Research project in computational materials physics, team 1

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The high entropy alloy CrCoFeNi has been studied with density functional theory. Out of two structures reported in literature, a monoclinic cell is most stable. Different properties, including elastic constants, formation energy, magnetism and the band structure, are examined.

INTRODUCTION

High entropy alloys (HEAs) are known for their high temperature properties, high ductility, creep resistance, wear resistance and excellent corrosion resistance. They show potential in a wide range of applications, for example in aerospace, in implantology, energy industry, etc. [1, 2]. HEAs are generally defined as a multi-component (typically ≥ 4) alloys with an equimolar or nearly equimolar composition. [1, 3] CrCoFeNi is an example of a quaternary high entropy alloy that has been successfully experimentally prepared.

In some literature it is stated that that CrCoFeNi crystallizes in the face centered cubic (FCC) lattice [1, 4]. However, in the Materials Project database of, the crystal is reported to have a monoclinic structure [5]. Within this study, we compare the energetics of formation of both structures and attempt to conclude which one is thermodynamically favored. Then, for the favored structure, we compute a range of properties that can be compared with pre-existing computational and experimental data.

The paper is organized as follows. In the next section, a brief description of methodology is given. Then, we describe the results of our calculations. First, we find the optimal lattice properties for FCC and monoclinic structure. Based on that, we attempt to ascertain which of the structures is favored at 0 K. Then we proceed to calculate elastic, magnetic and electronic (band structure and density of states) properties for the structure that appears to be more stable.

METHODS

Density functional theory (DFT) methods [6, 7] are used throughout our study. The PBE exchange correlation is used [8] with ultrasoft pseudopotentials [9]. Calculations are done using the plane-wave Quantum Espresso (QE) package [10].

Convergence is tested with respect to total energy of the system and hydrostatic pressure. We obtain converged results with a $5 \times 5 \times 5$ k-point grid for FCC structure, together with a E_{cutwfc} of 80 Ry and a E_{cutho} of 320 Ry. In order to correctly compare the energies for

both structures, the same settings must be used for both structures during the geometric optimization.

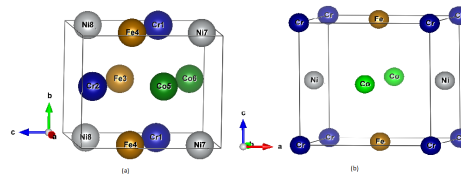


FIG. 1. (a) Monoclinic unit cell: $a=4.37046988$ Ang, $b=4.01256633$ Ang, $c=5.04023053$ Ang, $\alpha=\gamma=90$, $\beta=90.36934925$ [5]; (b) FCC unit cell: lattice parameter= 3.54 Ang [1]

RESULTS AND DISCUSSION

A. Geometric optimization and minimum energy calculations

First, a volume optimization is performed using a fit to a Birch-Murnaghan equation of state [11, 12] to determine the optimal volume. This is then used to do a full geometry optimization using the *vc-relax* calculation in QE. The final geometries are depicted in Figure 1

1. FCC structure

In Figure 2 a Birch-Murnaghan curve is fitted to total energy vs volume calculations. The optimal volume found by using this method is 42.73 Ang^3 versus the original volume of 44.57 Ang^3 . The corresponding lattice parameter for the FCC supercell corresponding to this optimal volume is: $\text{celldm}(1) = 6.6063668407 \text{ a.u}$ (or 3.495939031 Ang). Also the bulk modulus is calculated by taking the second derivative of the fit, as shown on Figure 2.

The total geometry optimization results in some small additional changes. Both the atom positions and the crystal axis change with approximately 1 to 3 %. The energy corresponding with this optimized structure is -538.62251160 Ry , which is equal to $-7940.58872072 \text{ eV}$.

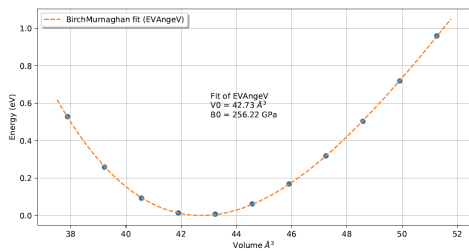


FIG. 2. BirchMurnaghan fit for the volume optimization of the FCC structure

2. Monoclinic structure

Figure 3 displays the results for the volume optimization for the monoclinic structure. The optimized volume for the monoclinic cell is 85.24 \AA^3 , whereas the original volume from the MP CIF file was 88.34 \AA^3 . Also here the bulk modulus is calculated, see Figure 3.

After full optimization, the atom positions change approximately 5 % and the crystal axes change with less than 1 %. An energy of $-1167.26793173 \text{ Ry}$ ($-15881.4891279 \text{ eV}$) is found. The monoclinic unit cell consists of 2 formula units (8 nuclei in one unit cell versus 4 nuclei for the FCC lattice), so to make a correct comparison with the energy found for the FCC structure the energy is converted to the amount of energy per formula unit, which is -7940.7445639 eV .

The total energy of the monoclinic crystal is approximately 0.16 eV per formula unit lower than for the FCC crystal. Consequently, the HEA CrCoFeNi will more likely be found in the monoclinic structure.

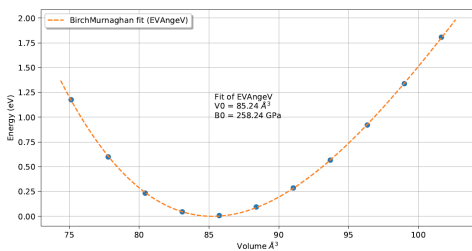


FIG. 3. Birch Murnaghan fit for the volume optimization of the monoclinic structure

B. Formation Energy

The formation energy is calculated by comparing the total energy of free atoms and the total energy of the monoclinic unit cell. The sum of all the individual total free energies is $-7911.56812653 \text{ eV}$, while the total energy of the monoclinic structure is equal to -7940.7475206 eV . Subtracting these two, yields a formation energy of -29.179394029 eV .

C. Elasticity

The elasticity is an important engineering property since it defines how a material will respond to an applied stress [13]. The important information for the elasticity is collected in the stiffness tensor. The elastic constants that form this tensor can be calculated using DFT.

This is calculated by varying the strain (ϵ) in all the different directions with 0.01 . The following strains are adapted: ϵ_{xx} , ϵ_{xy} , ϵ_{yy} , ϵ_{zz} , ϵ_{xz} and ϵ_{yz} . The stress tensor is then calculated through DFT and with those calculations, the stiffness tensor can be calculated.

$$C[\text{GPa}] = \begin{bmatrix} 405.1 & 147.3 & 159.7 & 0 & 2.05 & 0 \\ 144.8 & 470.7 & 133.7 & 0 & -3.45 & 0 \\ 161 & 136.3 & 416.9 & 0 & 1.45 & 0 \\ -4.8 & -8 & -7.9 & 109.7 & 1.3 & 1.2 \\ -0.5 & -16.3 & -5.5 & 0 & 126.75 & 0 \\ -0.7 & -18.1 & -6.8 & 0.55 & 0.5 & 98.55 \end{bmatrix}$$

In principle, the stress tensor should be symmetric. That is not the case here. We attribute this effect to the convergence threshold for our calculations, set to 10^{-6} . This could cause a small error for our optimal geometry and stress calculations and therefore errors of approximately 10 GPa are possible.

The values of particular matrix elements determine the stability of the crystal, according to the Born criteria [13]. All of these criteria are fulfilled by the above stiffness tensor. We can therefore see that, in addition to being energetically stable as shown in a previous section, the crystal is also mechanically stable.

D. Electronic structure

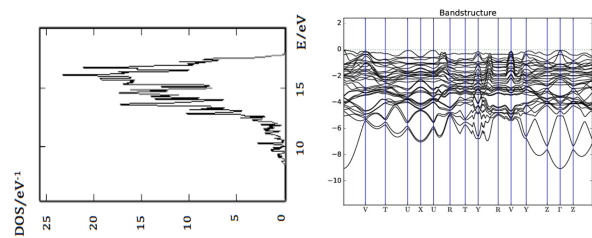


FIG. 4. The density of states (left) and the band structure calculation (right)

Figure 4 shows the density of states and band structure calculations. From the band structure we can see clearly that CrCoFeNi is metallic. The Fermi energy is probably not correctly plotted by VNL due to communication confusion between QE and VNL. The Fermi energy calculated by a scf-calculation is 17.7642 eV . If this value is plotted on the density of states figure, then this Fermi energy is located at a energy with a high density of states. Based on this, a magnetic calculation can be useful. [13]

E. Magnetism

The magnetic properties of a material can be crucial for certain applications. In the MP database we can see that the magnetic ordering for the HEA CrCoFeNi is ferrimagnetic. Spin down has been used for Cr and spin up for the other three elements. Inspiration to use this was retrieved from Niu et al. [14]

The total energy after applying magnetism is -15881.996781576 eV, this is indeed lower than the -15881.4891279 eV calculated by the geometry optimization calculation without magnetism. The total magnetization is equal to $2.13 \mu_B$ per cell, while the absolute magnetization equals $10.14 \mu_B$ per cell.

No geometry optimization has been done on this, but the values in the stress tensor are very low, therefore we would not expect significant change compared to the

optimized structure.

CONCLUSIONS

The HEA CrCoFeNi will more likely be found in the monoclinic structure than the FCC structure since the energy of the monoclinic structure is lower and so, this structure will be more stable. Several properties of the monoclinic CrCoFeNi are calculated using DFT. Further, the stiffness tensor is calculated to represent the elastic properties. Additionally the band structure and density of states are obtained, as well as the magnetic properties.

Our results are in reasonable, albeit not very good agreement with the MP database. The optimized cell volume is slightly lower and the crystal is stiffer. This can be attributed either to the choice of pseudopotentials, the size of the basis set or convergence criteria.

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