Density functional theory study of the mechanical properties of CoCrFeNi

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Abstract

This paper investigates two main mechanical properties (bulk modulus and Poisson's ration) of the high entropy alloy CoCrFeNi, as well as convergence testing based on density functional theory (DFT) calculations.

1 Introduction

High entropy alloys (HEA) made their appearance in the last decade [1], which are alloys characterised by being made out of at least 4 chemical elements. Since then they have attracted a lot attention since they show a variety of novel physical properties such as excellent specific strength, high mechanical performance and superconductivity [1, 2] to name only a few. Recently the equiatomic CoCrFeNi HEA has been synthetized [3, 4, 5] and widely used as base alloy to construct may other HEAs [6]. The CoCrFeNi based alloys show great properties holding significant promise for industrial application. Considering the potential application, exploring the physical properties of CoCrFeNi is of great importance for both technological and fundamental aspect. In this paper, the bulk modulus and Poisson's ratio of the CoCrFeNi HEA are calculated by the use of density functional theory (DFT).

2 Computational details

The DFT calculations are performed using the plane wave formalism as implemented in the Quantum Espresso (QE) simulation package. All calculations are performed using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional and using the high performing computer (HPC) of the Flemish Supercomputer Centre (VSC). Firstly, convergence tests are executed for the k-mesh and energy cut-offs to assure precise results for a calculation time that was as small as possible. Based on those results, it was decided to work with a 7x7x7 k-mesh and energy cut-offs of 104 and 1270.

k-mesh	3x3x3	5x5x5	7x7x7	9x9x9	11x11x11
Energy (Ry)	-1526.906	-1526.906	-1526.907	-1526.906	-1526.906
Hydrostatic pressure (kbar)	-89,26	-91,66	-91,16	-91,96	-92,23

Table 1: Convergence testing for the k-mesh size. Performed using an energy cut-off of 64 Ry for the wavefunction and 782 Ry for the charge density.

Energy cut-offs	54 - 660	64 - 782	74 - 904	84 - 1026	94 - 1148	104 - 1270	114 - 1392
Energy (Ry)	-1526.899	-1526.907	-1526.917	-1526.924	-1526.925	-1526.926	-1526.926
Hydrostatic pressure (kbar)	-96,01	-91,16	-97,02	-89,77	-84,15	-85.30	-86.65

Table 2: Convergence testing for the energy cut-offs (wavefunction - charge density). Performed using a k-mesh of 7x7x7.

3 Results and discussions

3.1 Geometry optimization

In order to determine the bulk modulus as well as the Poisson's ratio of the HEA, the optimized volume was calculated using DFT. The full optimization was done using a 'vc-relax calculation' in QE. The first Brillouin zone was sampled by a (7x7x7) k-mesh. An energy cut-off of 104 Ry has been used for the planes waves and 1270 Ry for the electrons density. The found optimized volume is 82.598 å^3 with a minimal energy of -1526.9296 Ry.

3.2 Bulk Modulus

The bulk modulus of the optimized crystal structure of the CoCrFeNi HEA has been computed through the volume dependent energy curve. Slightly higher and lower value of the optimal volume were taken at constant b/a, c/a ratio and angles between lattice vectors followed by a 'relax calculation'. The energy for each of these volumes was determined. As can be seen on the graph,

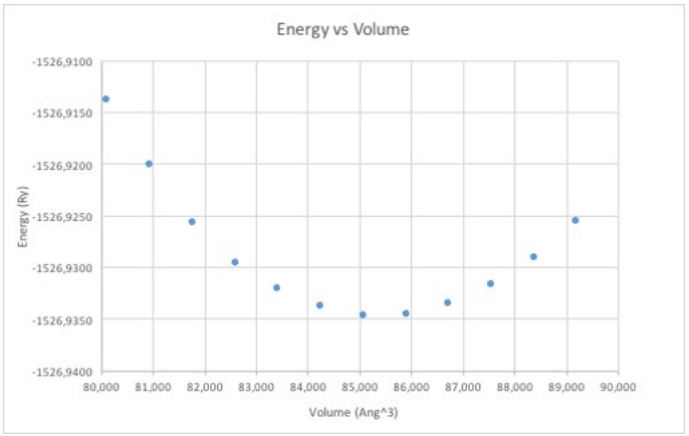

Figure 1: Energy vs volume curve

the actual optimal energy should be around 85.5å^3. Since the optimized volume differs quite a lot from the initial volume an additional calculation was executed, which resulted in an optimal volume of 85.248 å^3. The curve has been fitted with the Murnaghan equation of state using the fitting tool in QE. From the fitting a bulk modulus of 248.7 GPa was found with an optimal volume of 85.34 å^3. This number is rather high, indicating that this HEA is in fact a strong material.

3.3 Poisson's ratio

The idea to calculate Poisson's ratio was to increase one parameter by a certain constant, as if a certain strain was imposed in that direction, and then increase or decrease the other two parameters by a certain (equal) constant across the range of possibilities, based on the restrictions for Poisson's ratio. This was meant to model the induced strain in the transverse direction. By taking several values across that range, it was intended to minimize the energy and thus extrapolate Poisson's ratio. First, it was attempted to increase one parameter by one percent (imposed relative axial strain). This yielded some strange results: instead of the expected parabola-like graph, a straight line going down was obtained. The energy decreased when increasing the induced transverse strain, even when going further than the theoretical limit caused by the limitations of Poisson's ratio (bigger than -1). It was thought that the imposed strain might be too large, so it was decided to try again for a relative strain of 0,1‰, which resulted in the exact same linear graph. It was concluded that either something went wrong with the DFT calculations, or that the material is not capable of handling such strains. The latter meaning the alloy breaks before reaching the imposed strains.

Relative transverse strain	-1‰	-0,5‰	0‰	0,5‰	1,5‰	2,5‰
Energy (Ry)	-972,649	-972,750	-972,848	-972,942	-973,122	-973,290

Table 3: Energy for various values of induced transverse strain when imposing a relative axial strain of 1‰.

Relative transverse strain	-0,5‰	0‰	0,5‰	1‰
Energy (Ry)	-972,605	-972,594	-972,584	-972,574

Table 4: Energy for various values of induced transverse strain when imposing a relative axial strain of 0.1‰

References

[1] J.-W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, C.-H. Tsau, and S.-Y. Chang, "Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes," *Advanced Engineering Materials*, vol. 6, no. 5, pp. 299–303, 2004.

[2] Y. Ye, Q. Wang, J. Lu, C. Liu, and Y. Yang, "High-entropy alloy: challenges and prospects," *Materials Today*, vol. 19, no. 6, pp. 349–362, 2016.

[3] Z. Wu, H. Bei, F. Otto, G. M. Pharr, and E. P. George, "Recovery, recrystallization, grain growth and phase stability of a family of fcc-structured multi-component equiatomic solid solution alloys," *Intermetallics*, vol. 46, pp. 131–140, 2014.

[4] F. He, Z. Wang, Q. Wu, J. Li, J. Wang, and C. Liu, "Phase separation of metastable cocrfeni high entropy alloy at intermediate temperatures," *Scripta Materialia*, vol. 126, pp. 15–19, 2017.

[5] Y.-J. Hsu, W.-C. Chiang, and J.-K. Wu, "Corrosion behavior of feconicrcu x high-entropy alloys in 3.5% sodium chloride solution," *Materials Chemistry and Physics*, vol. 92, no. 1, pp. 112–117, 2005.

[6] K. M. Youssef, A. J. Zaddach, C. Niu, D. L. Irving, and C. C. Koch, "A novel low-density, high-hardness, high-entropy alloy with close-packed single-phase nanocrystalline structures," *Materials Research Letters*, vol. 3, no. 2, pp. 95–99, 2015.