DFT calculations of the high entropy alloy CoCrFeNi: elastic constants

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Abstract: This article describes the use of DFT calculations to estimate the elastic properties of CoCrFeNi, a high entropy alloy (HEA). Two different unit cells were used: one found in an online database (MaterialsProject) and one which was generated at random. After the convergence testing to optimize the calculation speed, the elastic constants were obtained by calculating the stresses that are induced when a deformation is applied. The found values were then compared to the values found in the online database.
Keywords: DFT, elastic constants, generalized Hooke's law, HEA

I. INTRODUCTION

High Entropy Alloys (HEA), materials made out of four or more metals in nearly equal amounts, might be the materials of the future as they have promising properties [1]. These materials have rather simple crystal structures allowing the materials to have a simple unit cell [2].

CoCrFeNi is a simple HEA since it has only four different elements. It is actually a medium-entropy alloy, a subset of the CrMnFeCoNi HEA [3].

The fact that these materials have such simple unit cell and that they should have promising properties is the reason that this paper handles the elastic properties of CoCrFeNi. Calculation speed for the subset is higher since it has an element less.

II. PROCEDURE

Firstly, the unit cell should be determined. Part of the research was to see whether it is possible to make a unit cell at random, that is why one self-made unit cell was used, and one that was found in the online database of MaterialsProject (MP) [4] (see Appendix C).

The first step is to determine the k-mesh and the basis sets for the wave functions and density that will be used in further calculations. This is done by convergence testing and is necessary to obtain numerically meaningful results rather than random noise and to make sure that the calculations do not take unnecessarily long. After convergence testing, the optimal structure is sought in order to have a relaxed crystal as a reference. The next step is to estimate the elastic properties using DFT. This procedure and the results are discussed below.

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A. Convergence Testing

In order to control convergence, convergence of the hydrostatic pressure of the material was used as a reference. If the hydrostatic pressure is converged, most other properties will have converged. First, the k-mesh was varied, starting from 1x1x1 going to 11x11x11 in steps of 2x2x2. It was found that 5x5x5 could be enough, but that 7x7x7 would be better. There was chosen to work with a 6x6x6 k-mesh. An example of the convergence testing can be seen in Table I. There, the convergence of the hydrostatic pressure as a function of the k-mesh was studied.

Table I: Convergence testing of k-mesh

k-mesh	Hydrostatic Pressure [kbar]	Typical Runtime [seconds]
1x1x1	-144,60	110
3x3x3	-121,45	320
5x5x5	-122,68	1080
7x7x7	-123,01	2800
9x9x9	-122,75	5400
11x11x11	-122,80	9400

Afterward, the ecutwfc and ecutrho were varied to find an optimal value. In this research, ecutwfc equal to 81 and ecutrho equal to 567 were chosen for further calculations.

Finally, the unit cell is completely relaxed, allowing the dimensions of the cell and the positions of the atoms to change. These calculations revealed that the self-made unit cell was less stable than the unit cell found in the online database (see Table II). As a result, only the unit cell from MP was used for further calculations. Table II also shows that the optimal unit cell found was not equal to the optimal unit cell according to MP. This might be because of different pseudopotentials or a different precision (MP uses a k-mesh of 72 points and a ecutrho of 520).

Table II: Energies of Formation for different Unit Cells

Unit Cell	Energy of Formation [Ry/atom]	Volume [Ang^3/atom]
self-made	-100,462	/
MP calculated	-101,215	10,6395
MP found	/	11,0485

B. Elastic Properties

The elastic properties of an elastic solid can be estimated using first principle calculations. The elastic constants are obtained by deforming the unit cell and calculating the corresponding stresses with the generalized Hooke's law (Equation 1).

$$\begin{bmatrix}\sigma_{xx}\\ \sigma_{yy}\\ \sigma_{zz}\\ \tau_{yz}\\ \tau_{xz}\\ \tau_{xy}\end{bmatrix} = \begin{bmatrix}C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16}\\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26}\\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36}\\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46}\\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56}\\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66}\end{bmatrix} \begin{bmatrix}\epsilon_{xx}\\ \epsilon_{yy}\\ \epsilon_{zz}\\ 2\epsilon_{yz}\\ 2\epsilon_{xz}\\ 2\epsilon_{xy}\end{bmatrix} \quad (1)$$

As mentioned before, first the crystal structure has to be optimized to obtain an undeformed initial unit cell. In the second step six independent deformations are applied to the relaxed unit cell. This is done by multiplying a deformation gradient with the root tensor of the initial cell (see Equation 2).

$$\begin{bmatrix}a_{2x} & b_{2x} & c_{2x}\\ a_{2y} & b_{2y} & c_{2y}\\ a_{2z} & b_{2z} & c_{2z}\end{bmatrix} = \begin{bmatrix}F_{xx} & F_{xy} & F_{xz}\\ F_{yx} & F_{yy} & F_{yz}\\ F_{zx} & F_{zy} & F_{zz}\end{bmatrix} \begin{bmatrix}a_{1x} & b_{1x} & c_{1x}\\ a_{1y} & b_{1y} & c_{1y}\\ a_{1z} & b_{1z} & c_{1z}\end{bmatrix} \quad (2)$$

From the root tensors of the deformed unit cells the lattice parameters can be straightforwardly obtained. However the atoms in these unit cells are not yet in their optimal positions. Therefor a relax calculation for each of the deformed unit cells has to be performed. From the DFT calculation, the stresses present in the deformed unit cells are obtained. The strain tensor E corresponding to the deformation, determined by the deformation gradient F, can be calculated using Equation 3.

$$E = 1/2(F^T F - I) \quad (3)$$

The calculation of the elastic properties from the obtained stresses and applied strains is shown in Appendix A. The obtained stiffness matrix is shown below with values in GPa.

$$\begin{bmatrix}424,48 & 148,86 & 171,64 & -3,708 & -5,175 & 2,134\\ 149,15 & 482,69 & 139,40 & -8,958 & -4,091 & -13,707\\ 162,59 & 133,73 & 423,28 & -6,516 & -8,449 & -5,006\\ 0 & 0 & 0 & 108,53 & 0 & 2,2\\ -2,289 & -3,483 & 0,01 & 0,832 & 123,03 & -0,514\\ 0 & 0 & 0 & 2,6 & 0 & 100,63\end{bmatrix}$$

A first observation that can be made is that though the matrix is not exactly symmetric, the maximal deviation from symmetry is 13,7 GPa. Also a relative good agreement with the stiffness matrix given at MP, which is shown below, is obtained. The deviations can be due to different pseudopotentials used as well as a different precision. The stiffness matrix of steel is shown in Appendix B, and it can be seen that the HEA is remarkably better.

$$\begin{bmatrix}363 & 85 & 112 & 0 & 6 & 0\\ 85 & 354 & 75 & 0 & 4 & 0\\ 112 & 75 & 306 & 0 & -1 & 0\\ 0 & 0 & 0 & 92 & 0 & -1\\ 6 & 4 & -1 & 0 & 97 & 0\\ 0 & 0 & 0 & -1 & 0 & 86\end{bmatrix}$$

From the values of the elastic properties the mechanical stability of the crystal can be verified. In order to have a mechanical stable crystal following criteria must be met.

$$C_{11} > 0 \quad (4)$$

$$C_{44} > 0 \quad (5)$$

$$C_{11} - C_{12} > 0 \quad (6)$$

$$C_{11} + 2C_{12} \quad (7)$$

Implementing the values from the stiffness tensor in Equations 4 - 7 it can be concluded that the studied crystal is mechanically stable.

III. CONCLUSION

The investigation did not go smoothly. However, some interesting results were still found within the scope and duration of this investigation.

1. It is not obvious to create a unit cell at random. There are too many variables which should be taken into account. Some of them are:
   (a) size of the unit cell
   (b) number of atoms
   (c) positions of atoms
   (d) kind of atoms
2. The chosen pseudopotential and precision have a remarkable influence on the final results.
3. Even though the material had a simple structure, the calculations could take a long time. The growth of computational force will certainly be of great value for further research.
4. The HEA are indeed better than ordinary steel

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Appendix A: Calculating the elastic constants

$$\begin{bmatrix} -42,66 & -14,96 & -17,25 & -1,31 & 0,78 & 0,34 \\ -14,99 & -48,51 & -14,01 & 1,94 & 0,6 & 2,06 \\ -16,34 & -13,44 & -42,54 & 0,9 & 0,63 & 0,05 \\ 0 & 0 & 0 & -0,66 & 0 & -32,56 \\ 0,23 & 0,35 & -0,01 & 0,17 & -36,91 & -0,25 \\ 0 & 0 & 0 & -30,19 & 0 & -0,78 \end{bmatrix}$$

$$=$$

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix} * \begin{bmatrix} 0,01005 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0,01005 & 0 & 0,00045 & 0 & 0 \\ 0 & 0 & 0,01005 & 0 & 0,00045 & 0,00045 \\ 0 & 0 & 0 & 0 & 0 & 0,03 \\ 0 & 0 & 0 & 0 & 0,03 & 0 \\ 0 & 0 & 0 & 0,03 & 0 & 0 \end{bmatrix}$$

Appendix B: Comparison of elastic properties of CoCrFeNi HEA and steel [5]

Stiffness matrix of steel:

$$\begin{bmatrix} 278,6538462 & 119,4230769 & 119,4230769 & 0 & 0 & 0 \\ 119,4230769 & 278,6538462 & 119,4230769 & 0 & 0 & 0 \\ 119,4230769 & 119,4230769 & 278,6538462 & 0 & 0 & 0 \\ 0 & 0 & 0 & 83 & 0 & 0 \\ 0 & 0 & 0 & 0 & 83 & 0 \\ 0 & 0 & 0 & 0 & 0 & 83 \end{bmatrix}$$

Equations of elastic moduli:

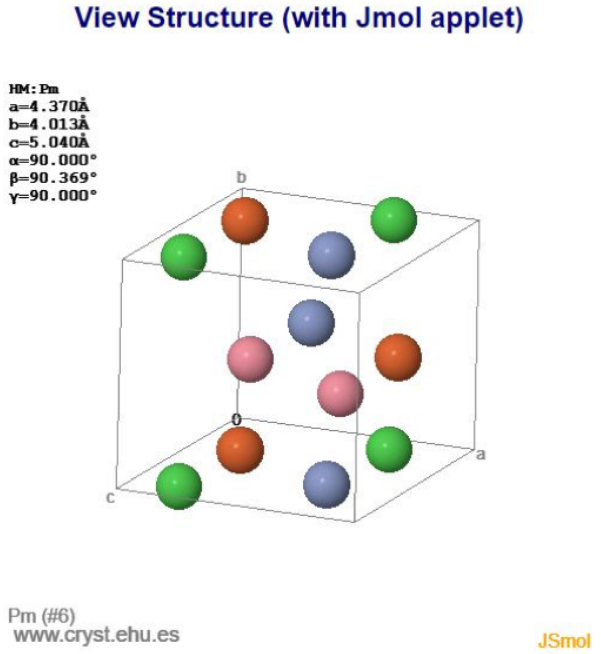
$$B = (C_{11} + 2C_{12})/3 \qquad G = (C_{11} - C_{12} + 3C_{44})/5$$

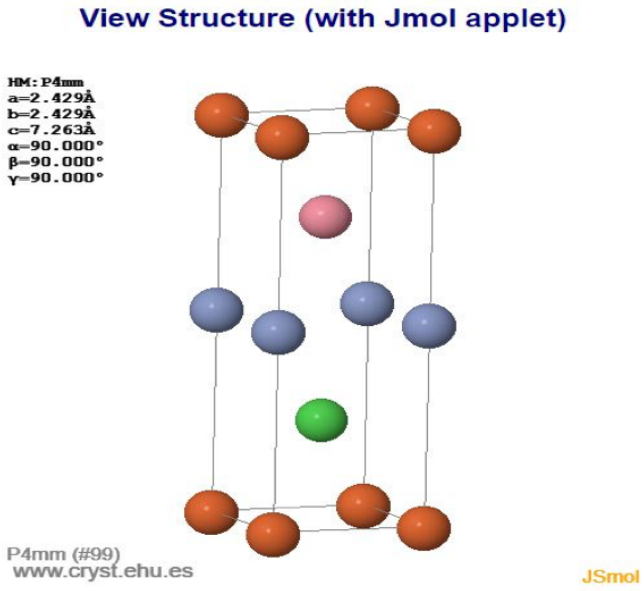
$$E = 9BG/(3B + G) \qquad \nu = (3B - 2G)/[2(3B + G)] \qquad Hv = (1 - 2\nu)E/[6(1 + \nu)]$$

Comparison between elastic constants of CpCrFeNi HEA and steel:

Elastic modulus	CoCrFeNi HEA	Steel
Bulk modulus B (GPa)	270,73	160
Shear modulus G (GPa)	120,24	83
Young's modulus E (GPa)	309,24	207
Poisson coefficient ν	0,285	0,3
Micro-hardness Hv (GPa)	17,16	10,61

Appendix C: unit cells used in this paper





Upper: unit cell from MP
Lower: self-made unit cell