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High Entropy Alloys
An Ab Initio Study of Single Phase NbMoTaW

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B.A. Theoretical Physics

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Declaration

I have read and I understand the plagiarism provisions in the General Regulations of the University Calendar for the current year, found at: `www.tcd.ie/calendar`.

I have also completed the Online Tutorial on avoiding plagiarism 'Ready Steady Write', located at: `www.tcd-ie.libguides.com/plagiarism/ready-steady-write`.

I hereby declare that this project is entirely my own work and that it has not been submitted as an exercise for a degree at this or any other university.

Daniel Bennett	Date

Abstract

24 random configurations of single phase quaternary NbMoTaW were simulated using DFT and a number of thermodynamic and mechanical quantities were calculated. The average lattice constant was determined to be $a = 3.161$ Å with a standard deviation of 0.232 Å, which agrees with experiment. The bulk modulus was determined to be 283.268 GPa with a standard deviation of 0.983 GPa, comparing well to the bulk moduli of the individual elements. The low Gibbs free energy of formation at room temperature suggests that single phase BCC is the one that forms at equilibrium, which is indeed the case in experiment. The bonds in the different configurations were analysed. The configurations with lower energy have a higher number of bonds between different types of atoms, suggesting that mixing contributes to the stability. Finally, a discussion of the accuracy and validity of our simulation and calculations is provided.

Acknowledgements

I would like to thank my project partner, Anastasia; she is a good friend and a pleasure to work with, and our project supervisor, Stefano Sanvito, for guiding us through the project. I would like also like to thank Thomas Archer for helping me find and fix some mistakes I made.

All of the calculations in this project were performed on the Parsons high performance computing cluster hosted and managed by the Research IT unit (formerly TCHPC) in IT Services. The system is funded by research grants from Science Foundation Ireland (SFI).

All of the calculations in this project were performed using FHI-aims. FHI-aims is an accurate, all-electron, full-potential electronic structure code package for computational materials science: `aimsclub.fhi-berlin.mpg.de`.

Contents

1 Introduction and Theory

A high-entropy alloy (HEA) is a material composed of 5-13 metals in approximately equal proportions, although this is not strict definition; in some cases they can contain less than 5 constituent components. The use of conventional alloys can be traced back through history. By adding a trace amount of an additional element to a metal, its usefulness can be drastically improved. The most notable example is steel, which is formed by adding trace amounts of carbon to iron, giving it a high tensile strength and a low cost. HEAs have become popular in recent years, after a paper by Yeh was published in 2004. He coined the term “high-entropy alloy” by suggesting that the high configurational entropy leads to the stability of the solid solution phase [1]. In the last decade, research into HEAs has grown significantly.

In this project we will create a simple model of single phase NbMoTaW, which was first synthesized in 2010 [2]. We will calculate the Gibbs free energy in order to demonstrate its stability, and bulk modulus in order to demonstrate its mechanical properties. We choose NbMoTaW for a number of reasons: firstly, four elements is the ideal number for a simple model, as it allows us to use a relatively small unit cell while still having equal proportions of each element. Secondly, all of its constituent components have similar atomic radii and lattice constant, and they are all BCC phase materials. Finally, none of the elements are magnetic, so we do not have to consider effects from magnetism.

Assuming we have a mixed quaternary solution, we can generate a number of random configurations of NbMoTaW and investigate the effects of mixing on the material. One way to do this is to generate a number of random simulations of the HEA, then perform an analysis of the bonds by investigating the different bonds in each simulation.

1.1 Configurational Entropy

There are several possible contributions to the entropy of a HEA: configurational, electronic, magnetic and phonon contributions. We will focus on the configurational entropy as the electronic and phonon contributions are small corrections to the entropy, and our alloy has no magnetic elements.

The phase with the lowest Gibbs free energy of formation will be the one that forms at equilibrium[1]:

$$\Delta G = \Delta H - T\Delta S \quad , \tag{1}$$

for some constant temperature T. In our case we take $\Delta S = \Delta S_{\text{mix}}$. From this it is clear that a high configurational entropy will contribute to the stability of the HEAs. From statistical mechanics we have, for each atom,

$$T\Delta S_{\text{mix}} = -k_B T \sum_i x_i \ln(x_i) \quad , \tag{2}$$

where k_B is the Boltzmann constant, and x_i is the fraction of atoms in the alloy [3]. From (2) it is clear that the entropy is maximised if the elements occur in equal proportions. Taking $x_i = 1/4$ for each i we get

$$T\Delta S_{\text{mix}} = k_B T \ln(4) \quad , \tag{3}$$

which is approximately 35 meV at room temperature. It is clear that this contribution will increase for a HEA with a larger number of components or for one at a higher temperature.

1.2 Mechanical Properties

There are many useful mechanical properties that can be measured for a solid, such as its hardness and toughness. The hardness of a material is a measure of how resistant it is to a permanent deformation when a compressive force is applied. The toughness of a material is its ability to absorb energy and deform without fracturing. While both of these are typical quantities that are measured in experiment and strong indicators of the usefulness of a material, they are very difficult to calculate theoretically. We will instead measure the bulk modulus as it can be calculated easily by applying isotropic compression and expansion.

The bulk modulus is defined as the compressibility of a material,

$$B \;=\; -V_0 \frac{\partial P}{\partial V}\bigg|_{V_0} \;=\; V_0 \frac{\partial^2 E}{\partial V^2}\bigg|_{V_0} \quad , \tag{4}$$

where V_0 is the equilibrium volume [4]. We can thus apply a small isotropic compression and expansion to our material, measure the resulting change in energy and use (4) to determine the bulk modulus. The bulk moduli of the individual elements are first calculated in order to compare to the bulk modulus of the HEA.

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[1] In this project, by ‘lower’ energy we mean ‘more negative’ energy.

2 Method

2.1 Calculations

The Density Functional Theory (DFT) package, FHI-aims, was used to simulate the materials. The type of calculation can be specified using the control file and the geometry of the materials can be manipulated using the geometry file. We first tested our methods on the individual elements of our HEA, as they require a shorter computation time. The results were useful for comparing our HEA to later, and it was the most convinient way to ensure that our method of calculation was correct.

The geometries of the four components, Niobium, Molybdenum, Tantalum and Tungsten, were obtained from [5], and geometry relaxations were performed on each to ensure that the optimal configuration for each material was obtained. In order to obtain the bulk modulus, a series of calculations was performed for each material with the unit cells stretched and compressed. Assuming that the relaxed configurations correspond to equilibrium, the unit cell was compressed and expanded by values in an interval of ±1% of the equilibrium volume. The change in energy due to compression and expansion of the unit cell can now be plotted, and fitting this data can give the bulk modulus and equilibrium lattice constant.

There are several ways to fit the data and obtain the bulk modulus and lattice constant. The simplest method is to fit the data with a polynomial; the minimum of the polynomial will give the lattice constant and (4) will give the bulk modulus. For a quadratic fit, the bulk modulus is simply determined by the quadratic coefficient. A higher order fit, such as quartic, can be used to obtain more accurate results [6].

One way to obtain even more accurate results for the bulk modulus is to fit the data to a Murnaghan equation of state (EOS):

$$E(V) = E_0 + B_0 V_0 \left[\frac{1}{B_0'(B_0'-1)} \left(\frac{V}{V_0} \right)^{1-B_0'} + \frac{1}{B_0'} \frac{V}{V_0} - \frac{1}{B_0'-1} \right] \quad , \tag{5}$$

where E_0 is the energy at equilibrium, V_0 is the equilibrium volume, B_0 is the bulk modulus, and B_0' is the pressure derivative of the bulk modulus.

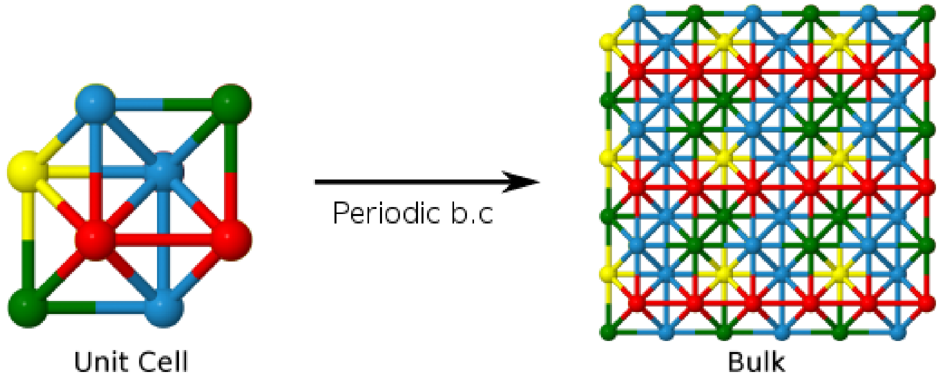
The binding energy of the HEA is required for the enthalpic contribution to (1). This is obtained by subtracting from the total DFT energy of the alloy the energies of the constituent atoms in their natural (BCC) phase. To get the binding energy per atom we divide by the number of atoms in the unit cell:

$$E_{\text{Bind}} = \frac{E_{\text{Bulk}} - \sum_i n_i \epsilon_i}{N} \quad , \tag{6}$$

where E_{bulk} is the total DFT energy of the HEA, N is the total number of atoms in the unit cell, n_i and ϵ_i are the number and energy of atoms of type i in the unit cell.

2.2 Simulating the HEAs

It has been suggested that results of a 4-component equiatomic alloy begins to converge with a cell as small as 24 atoms [7]. However, we use a 16-atom cell in the interest of shorter computation times and geometric simplicity. A 16-atom cell is easily obtained by using a $2 \times 2 \times 2$ BCC supercell, each subcell being cubic with a 2-atom basis. The size of the subcells is taken to be the average of the lattice constants of the constituent materials, but we can determine the correct lattice constant by calculating the EOS; the equilibrium lattice constant of the HEA will correspond to the minimum of this curve. For a mixed solution, the configurations of the atoms should be random, but this is difficult to achieve using DFT. The best approach is to permute the atoms randomly within the unit cell, and then the periodic boundary conditions will create a pseudo-random solution. This approach becomes more accurate as the size of the unit cell increases.



24 random configurations of NbMoTaW were generated. The methods described above were used to obtain the EOS for each of the random samples. By plotting (1) as a function of volume, all of the desired quantities were determined: Gibbs free energy of formation (at room temperature), bulk modulus, and equilibrium lattice constant.

3 Results and Analysis

The equations of state were successfully obtained for the four individual materials: Niobium, Molybdenum, Tantalum and Tungsten. A cubic lattice with a 2-atom basis was used for each as they are all BCC materials. The calculations at compressed and expanded volumes were performed using a PBE functional and an $8 \times 8 \times 8$ k-grid, and each data point took roughly 30 minutes of computation time. A Murnaghan fit was used to obtain the EOS and hence determine the bulk moduli and lattice constant of the materials. An example is shown below. Note that the energy difference is larger when the unit cell is compressed rather than when it is expanded. This isn't surprising as the bonds should break as the atomic separation increases, and the energy should diverge as it decreases; our EOS is effectively the well of an interaction potential.

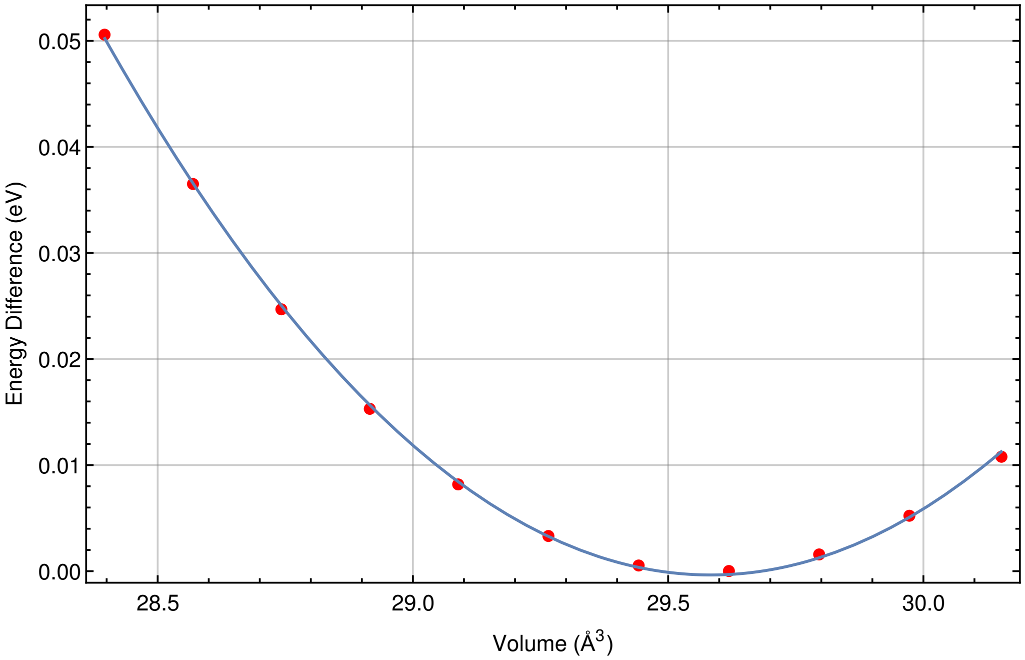


Figure 1: EOS of BCC Molybdenum. The end points on the plot correspond to a change in lattice constant of ±1%. The zero energy on this scale corresponds to the energy at the equilibrium volume.

The bulk moduli and lattice constants were calculated and compared to similar PBE calculations using the DFT package, GPAW: `https://wiki.fysik.dtu.dk/gpaw/setups/bulk_tests.html`. Our results do not completely agree with these calculations: the lattice constants are slightly underestimated, and the bulk moduli are about 20% too large.

Element	a (Å)	a_{GPAW} (Å)	B (GPa)	B_{GPAW} (GPa)
Nb	3.214	3.315	230.1	178.8
Mo	3.093	3.168	321.9	269.4
Ta	3.244	3.333	228.40	200.0
W	3.132	3.203	343.7	303.4

Table 1: Results for the bulk moduli of the individual materials compared to the values calculated using a PBE functional in GPAW

This is either due to a difference in calculation method and settings, or differences between the two different DFT packages. In any case, the calculation method and settings are consistent for both the bulk and HEA calculations, meaning comparisons between the results will still be valid.

The equations of state were then successfully obtained for 24 random configurations of NbMoTaW. The same settings were used as before but a $4 \times 4 \times 4$ k-grid was used since there are 16 atoms in the unit cell. The binding energy was obtained using (6), and then 35 meV was subtracted from each curve to obtain the Gibbs free energy. Each data point took roughly 10 hours of computation time. The low values of ΔG illustrates the stability of the HEA, suggesting that single phase BCC is the equilibrium phase of the material.

The average lattice constant of the HEA was determined to be $a = 3.161$ Å with a standard deviation of 0.232 Å, which agrees with experiment [2]. The average bulk modulus was determined to be $B = 283.268$ GPa, which compares well with the bulk moduli of the constituent materials. The standard deviation is 0.983 GPa, indicating that the configuration of the HEA does not significantly affect the bulk modulus.

Although the bulk modulus is unaffected, there is a difference of about 30 meV in the binding energy from the lowest to the highest configurations, indicating that the binding energy of the HEA depends strongly on the configuration of the atoms. To investigate this further, an analysis of the bonds in the different random configurations was performed.

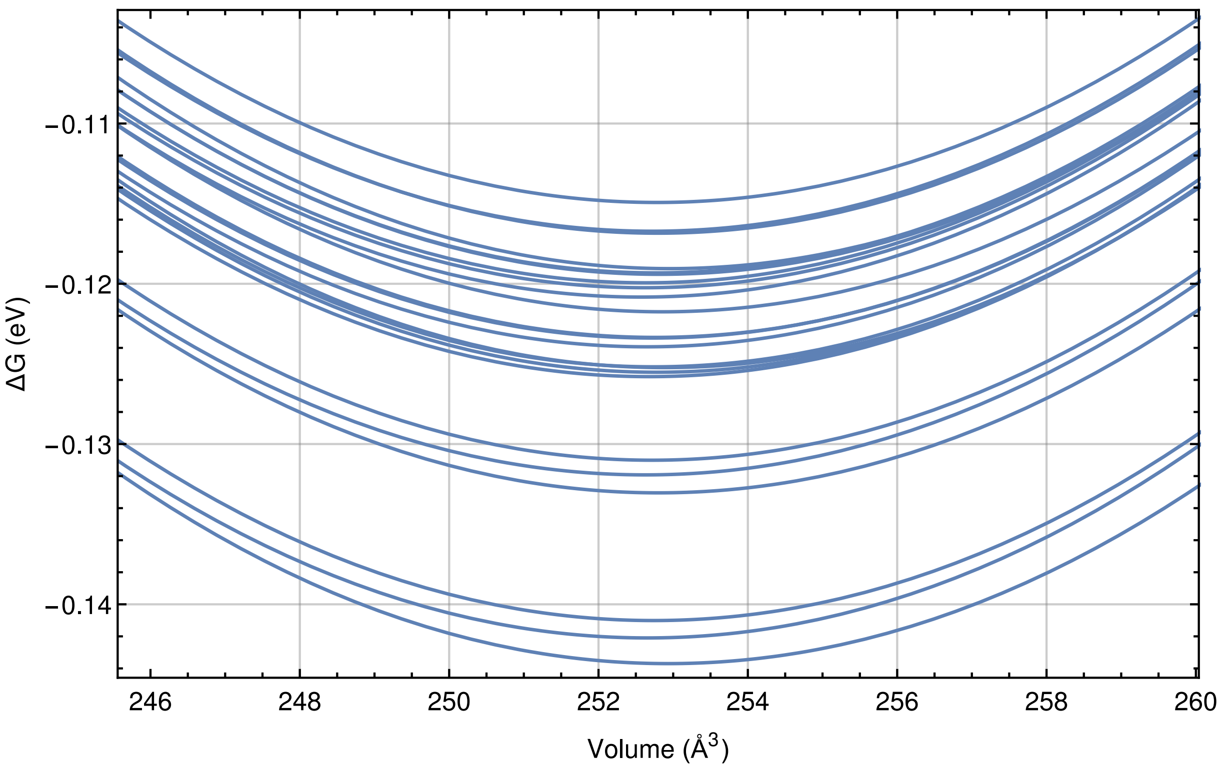


Figure 2: Dependence of Gibbs free energy on unit cell volume for the 24 configurations of NbMoTaW.

The bonds were analysed from the geometries of the 24 alloys. This was done by calculating the bond matrix for each configuration: taking only nearest neighbour interactions into account, each possible type of bond is represented by a matrix element, where each row and column represents a different element. A bond between two nearest neighbours contributes 1 to that matrix element, but we only contribute one half for each bond to avoid double counting. A bond between an atom in the unit cell and a periodic image of an atom in the unit cell contributes only $\frac{1}{2}$, as it contributes evenly to both unit cells. The nearest neighbour bonds of each atom in the unit cell were identified, and the bond matrix was then constructed. As an example, the bond matrices of the configurations with the lowest and highest binding energies, respectively are:

$$M_2 = \begin{bmatrix} 0 & 8 & 2 & 6 \\ 8 & 0 & 6 & 2 \\ 2 & 6 & 3 & 5 \\ 6 & 2 & 5 & 3 \end{bmatrix}, \quad M_7 = \begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 5 & 4 & 3 \end{bmatrix} \tag{7}$$

For every bond matrix, the entries of every row and column adds up to 16, and the sum of all entries is 64 in each case, as expected.

One observation is that the configurations with lower energy have a larger number of bonds between atoms of different type whereas the ones with higher energy have a more evenly spread bond matrix, which is shown from the plot below of the trace of the bond matrices in order of binding energy from lowest to highest. This suggests that the more mixed the solution is, the more stable it becomes. This would agree with the conclusions from experiment, where the exceptional microhardness of NbMoTaW is attributed to a solid-solution-like strengthening mechanism [2].

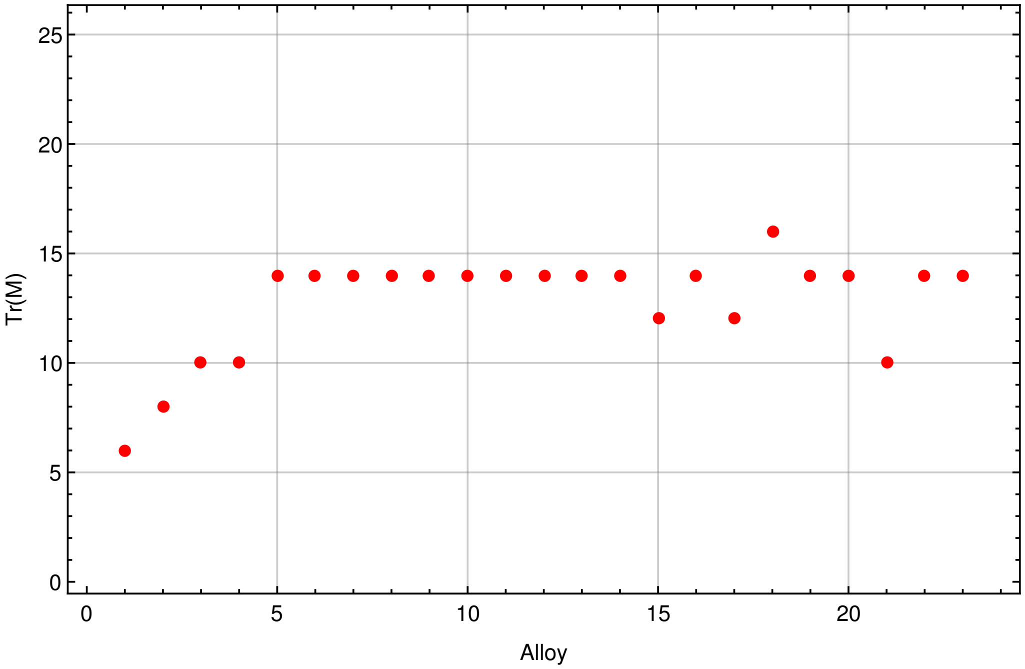


Figure 3: The trace of the bond matrices for the random configurations of the HEA in order of lowest binding energy to highest. The first point corresponds to the alloy with lowest energy (alloy 2) whereas the last point corresponds to the alloy with highest energy (alloy 7).

A full table of results for all of the alloys including the lattice constants, bulk moduli, bond matrices and their traces is given in Appendix A.

4 Discussion and Conclusions

A brief summary of the DFT settings used in the project is provided below:

- **DFT Functional**: The PBE functional, developed by Perdew, Burke and Ernzerhof [8], belongs to the class of generalised gradient approximation (GGA) functionals for exchange-correlation energy. It is a parameter free functional and is known for its applicability and accuracy for a wide range of systems. The PBE functional was used for all of the calculations in this project.

- **k-grid size**: DFT calculations are performed on a numerical grid in k-space, called the k-grid, and a finer grid can lead to more accuracte calculations at the cost of a longer computation times. An analysis of the convergence of binding energy and bulk modulus of Molybdenum with grid size was performed to determine a suitable grid size and is included in Appendix B. The binding energy converges to 0 from $k = 8$, making it a suitable grid size to use for the 2-atom cell calculations. We then use $k = 4$ for the HEA calculations for consistency, since the number of atoms times the number of k-points is the same in each case.

- **Basis Set**: We used the ‘tight’ basis set provided by FHI-aims. There is a ‘really-tight’ basis set but it results in a much longer computation time and is only suggested for tests of convergence.

There are many sources of inconsistency in DFT calculations and so it is important to be consistent with the settings of the calculation when comparing simulations of materials. Since most of our energies are above 10^6 eV, it is very difficult to be accurate even to order 1 eV. However since we are interested in energy differences, we rely on cancellation of errors to get reasonable binding energies of the order 100 meV.

The lattice constants of the bulk materials were slightly smaller than those obtained in the similar PBE calculations. The bulk moduli have errors of around 20%, which could have resulted from the smaller lattice constants obtained in our case. After checking our method of calculation, we are condfident that it agrees with the methods used in the relevant literature [6]. Thus, the error can either be attributed to differences between the aims DFT package and the the GPAW package, or an unseen error in calculation. One possible way to reduce the error would be to use a smaller isotropic compression and expansion; while 1% seems small, it is actually a considerable amount to isotropically compress or expand the unit cell by. In any case, the bulk modulus calculation is consistent for the bulk materials and the HEA.

The lattice constant of NbMoTaW was determined to be $a = 3.161$ Å with a standard deviation of 0.232 Å. The lattice constant determined from experiment is $a = 3.213$ Å, so our result agrees with this to within 2%.

The low ΔG for our model of NbMoTaW indicates that single phase BCC is the equilibrium phase for the quaternary alloy, which is the phase observed when it was constructed experimentally [2]. The bulk modulus was determined to be 283.268 GPa with a standard deviation of 0.983 GPa. There have been no such calculations in the literature to compare to, but this compares well to the bulk moduli of the individual materials; it is sligthly higher than those of the individual materials, but not much higher, which is reasonable.

An analysis of the bonds in the random configurations showed that the binding energy is lower in the configurations with more bonds between different types of atoms. One explanation is that the HEA is more stable in a more mixed solution phase, which agrees with experiment. The results of the bond analysis could be improved upon by taking the second nearest neighbour interactions into account, since in the BCC case, the distance from an atom to its second nearest neighbours is only slightly larger than the distance to its first nearest neighbours.

A 16 atom unit cell may be too small to approximate random configurations of a HEA, which is evident from the similarity of the bond matrices. The larger the unit cell, the larger the number of possible configurations there are, which would result in more mixed solutions. This comes at the cost of a much longer computation time. A 64 atom BCC $4 \times 4 \times 4$ supercell would be the next possible for NbMoTaW, although the computation time that would be required is not feasable.

We have seen that NbMoTaW forms in a single phase BCC solution, successfully calculated the lattice constant using DFT, and demonstrated that the mechanical properties compare well to those of the individual components. We are satisfied with the results obtained in the project, but conclude that a much more detailed and sophisticated investigation into HEAs is required to obtain more accurate results.

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Appendix A: Table of Results

Alloy	a (Å)	B (GPa)	ΔG (meV)	**Bond Matrix**	**Tr(M)**
2	3.16206	284.598	-143.7	$\begin{bmatrix} 0 & 8 & 2 & 6 \\ 8 & 0 & 6 & 2 \\ 2 & 6 & 3 & 5 \\ 6 & 2 & 5 & 3 \end{bmatrix}$	6
10	3.16091	284.736	-142.1	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 0 & 8 & 4 \\ 4 & 8 & 0 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	8
11	3.16125	283.627	-141.0	$\begin{bmatrix} 3 & 6 & 3 & 4 \\ 6 & 0 & 6 & 4 \\ 3 & 6 & 3 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	10
4	3.16152	282.702	-133.0	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 6 & 3 \\ 4 & 6 & 0 & 6 \\ 4 & 3 & 6 & 3 \end{bmatrix}$	10
12	3.16080	283.244	-131.9	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 5 & 4 \\ 4 & 5 & 3 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	14
13	3.16116	285.031	-131.0	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 5 & 4 \\ 4 & 5 & 3 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	14
21	3.16101	284.27	-125.8	$\begin{bmatrix} 3 & 5 & 4 & 4 \\ 5 & 3 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	14

Alloy	$\boldsymbol{a}$ **(**$\boldsymbol{\mathring{A}}$**)**	$\boldsymbol{B}$ **(GPa)**	$\boldsymbol{\Delta G}$ **(meV)**	**Bond Matrix**	**Tr(**$\boldsymbol{M}$**)**
24	3.16143	283.878	-125.5	$\begin{bmatrix} 3 & 4 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 5 & 4 & 4 & 3 \end{bmatrix}$	14
19	3.16185	283.555	-125.2	$\begin{bmatrix} 3 & 4 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 5 & 4 & 4 & 3 \end{bmatrix}$	14
17	3.16126	283.907	-125.1	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 5 & 4 & 3 \end{bmatrix}$	14
15	3.16088	282.501	-123.9	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 3 & 5 \\ 4 & 4 & 5 & 3 \end{bmatrix}$	14
18	3.16117	281.710	-123.4	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 5 & 4 \\ 4 & 5 & 3 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	14
1	3.16134	282.332	-123.3	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 5 & 4 \\ 4 & 5 & 3 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	14
14	3.16176	282.577	-121.7	$\begin{bmatrix} 3 & 4 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 5 & 4 & 4 & 3 \end{bmatrix}$	14
3	3.16055	282.871	-120.8	$\begin{bmatrix} 3 & 3 & 5 & 5 \\ 3 & 3 & 5 & 5 \\ 5 & 5 & 3 & 3 \\ 5 & 5 & 3 & 3 \end{bmatrix}$	12

Alloy	$\boldsymbol{a}$ **($\boldsymbol{\mathring{A}}$)**	$\boldsymbol{B}$ **(GPa)**	$\boldsymbol{\Delta G}$ **(meV)**	**Bond Matrix**	**Tr($\boldsymbol{M}$)**
6	3.16075	282.845	-120.2	$\begin{bmatrix} 3 & 5 & 4 & 4 \\ 5 & 3 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	14
22	3.16082	282.845	-119.9	$\begin{bmatrix} 3 & 5 & 5 & 3 \\ 5 & 3 & 3 & 5 \\ 5 & 3 & 3 & 5 \\ 3 & 5 & 5 & 3 \end{bmatrix}$	12
9	3.16156	283.552	-119.4	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \end{bmatrix}$	16
8	3.16138	284545	-119.3	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 5 & 4 & 3 \end{bmatrix}$	14
20	3.16217	282.774	-119.1	$\begin{bmatrix} 3 & 4 & 3 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 5 & 4 & 4 & 3 \end{bmatrix}$	14
23	3.16147	283.654	-116.8	$\begin{bmatrix} 0 & 4 & 6 & 6 \\ 4 & 4 & 4 & 4 \\ 6 & 4 & 3 & 3 \\ 6 & 4 & 3 & 3 \end{bmatrix}$	10
16	3.16118	281.414	-116.7	$\begin{bmatrix} 3 & 4 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 4 & 4 & 4 \\ 5 & 4 & 4 & 3 \end{bmatrix}$	14
7	3.16144	282.098	-114.9	$\begin{bmatrix} 4 & 4 & 4 & 4 \\ 4 & 3 & 4 & 5 \\ 4 & 4 & 4 & 4 \\ 4 & 5 & 4 & 3 \end{bmatrix}$	14

Appendix B: Analysis of k-grid Size

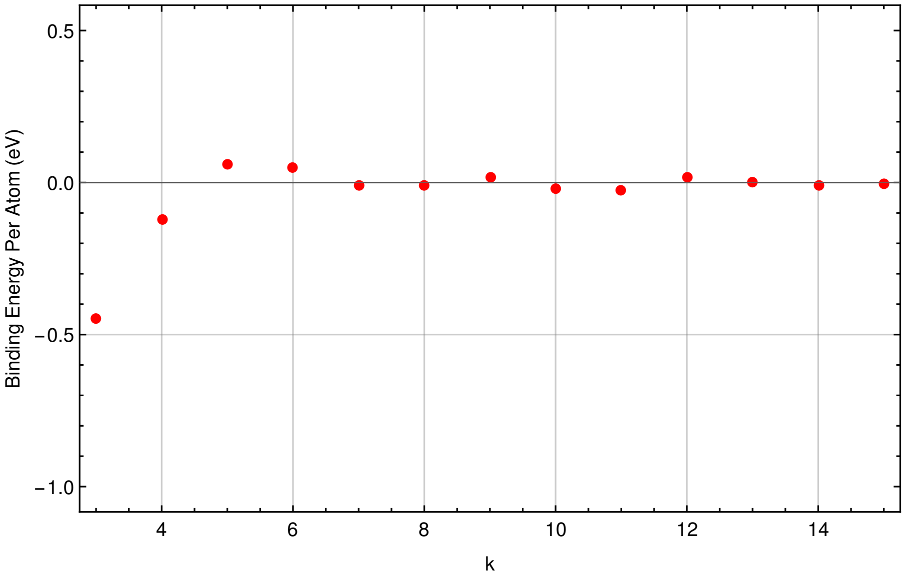

Figure 4: Measure of binding energy of bulk BCC Molybdenum as a function of k-grid size. The binding energy roughly converges at $k = 8$.

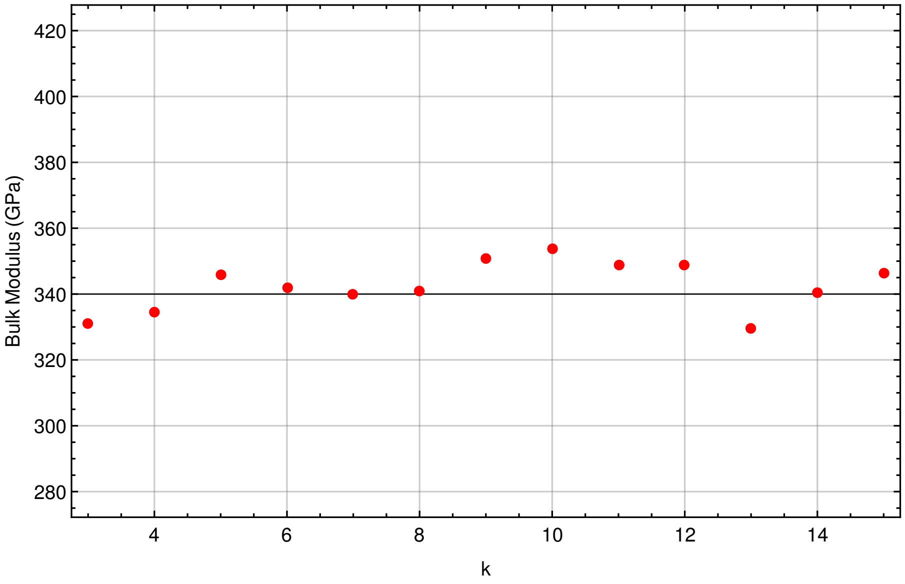

Figure 5: Measure of modulus of bulk BCC Molybdenum as a function of k-grid size. The bulk modulus fluctuates about $B = 340$ GPa, but doesn't appear to converge.