HW4 Report

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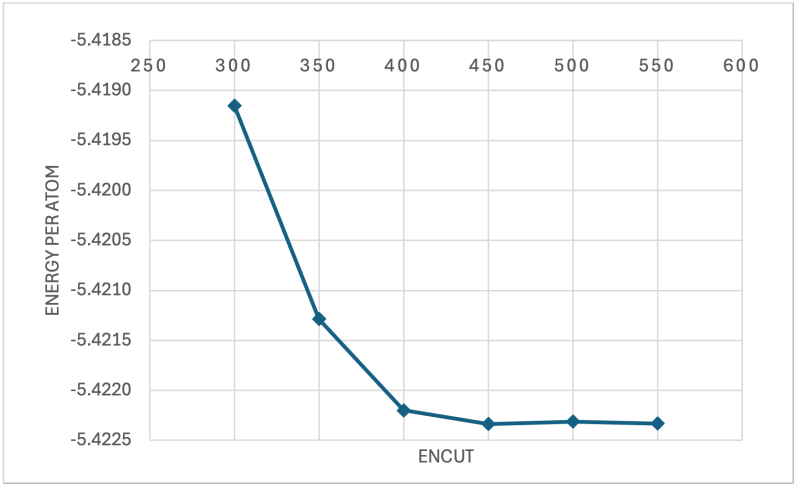
1 Static energy vs. plane-wave cutoff (Si, diamond)

The ENCUT refers to the maximum kinetic energy of the plane waves used to expand the electronic wavefunctions in the plane-wave basis set. Increasing the ENCUT number would lead to greater plane waves and higher accuracy. Thus, when the ENCUT is below 450, we do see a decrease in energy. However, when it reaches 450 or more, it is relatively stable at between -5.42231 to -5.42231.



2 Hand-building a POSCAR for Cu3Au (L12)

2.1 POSCAR file

The title line is the first line that describes the structure. The global scale is a single number that scales the lattice vectors. The lattice vectors are the simulation cell that in Cartesian coordination with three basis vector. The element line is a line that describes the number of elements and groups, and the counts are the number of atoms in each of the element groups. For the

coordinate block, we have the Direct and Cartesian as the system identifier. The Direct is the atomic positions are given in fractional coordinates relative to lattice vectors. And the Cartesian are the positions given directly in Angstroms. The Atomic coordinate block has each line giving the x, y, z position of one atom and those are the atoms are the main atoms for different crystal structures.

2.2 VASP5 POSCAR for Cu3Au

The POSCAR file for Cu3Au is listed below. I set the a value to be 3.825 for further modification. The lattice vector is set based on what I found in the Aflow website. Since there is 1 gold and 3 copper for the compound $AuCu_3$, thus that's how I determine the atom counts. Each of the atomic coordinates is based on what is listed in the problem.

```
Cu3Au L12
3.82500000
1.000000000000 0.0000000000000 0.000000000000
0.0000000000000 1.0000000000000 0.0000000000000
0.0000000000000 0.0000000000000 1.0000000000000
Au Cu
1 3
Direct
0.00000000000000 0.00000000000000 0.00000000000000 Au
0.50000000000000 0.50000000000000 0.00000000000000 Cu
0.50000000000000 0.00000000000000 0.50000000000000 Cu
0.00000000000000 0.50000000000000 0.50000000000000 Cu
```

2.3 2x1x1 structure for Cu3Au

```
Cu3Au L12
3.82500000
2.000000000000 0.0000000000000 0.000000000000
0.0000000000000 1.0000000000000 0.0000000000000
0.0000000000000 0.0000000000000 1.0000000000000
Au Cu
1 3
Direct
0.00000000000000 0.00000000000000 0.00000000000000 Au
0.50000000000000 0.50000000000000 0.00000000000000 Cu
0.50000000000000 0.00000000000000 0.50000000000000 Cu
0.00000000000000 0.50000000000000 0.50000000000000 Cu
```

case	a	perturbation	Final optimized a	Return cubic ?	Total energy per atom
unchange	3.825	N		Y	-4.3112373
plus 2%	3.9015	N	3.9015	Y	-4.4408738
Slight compression + jiggle	3.75	0.000002 0.000001 0.0003 Au 0.499995 0.5003 0.00002 Cu 0.50004 0.00003 0.5001 Cu 0.00003 0.500003 0.499996 Cu	3.75	N	-4.1567208
Light shear (2 degree)	3.825	1 0 0 0 1 0 0.0349 0 1	3.825	N	-4.3125025

3 Do relaxations find the same final structure?

4 Prototype identification and decoration

4.1 Generate L12 automatically

By comparing the POSCAR of AuCu3 (the L12 prototype) generate by aflow and the POSCAR written by me. I found that while the general lattice vector, atomic counts, and atomic coordination remain the same, the a value is so much larger.

```
   -54.238100
  1.00000000000000   0.00000000000000   0.00000000000000
  0.00000000000000   1.00000000000000   0.00000000000000
  0.00000000000000   0.00000000000000   1.00000000000000
1 3
Direct(4) [A1B3]
  0.00000000000000   0.00000000000000   0.00000000000000  Au
  0.00000000000000   0.50000000000000   0.50000000000000  Cu_pv
  0.50000000000000   0.00000000000000   0.50000000000000  Cu_pv
  0.50000000000000   0.50000000000000   0.00000000000000  Cu_pv
```

4.2 Identify a prototype from a CIF.

To generate a POSCAR from a CIF file. We would first use the command below to find AFLOW label, params, and params values.

```
cat MgSiO3.cif | aflow --prototype
```

Then, to get the POSCAR, we would use the AFLOW label and parameter values as below:

```
aflow --proto=AB3C_oC20_63_a_cf_c.ABC:Mg:O:Si \>
--params=3.1003,3.27443,2.48086,0.077,0.747,0.631,0.936
```

From there, we are able to print out the POSCAR file:

```
 MgOSi/AB3C_oC20_63_a_cf_c.ABC
 params=3.1003,3.27443,2.48086,0.077,0.747,0.631,0.936 SG=63
 [ANRL doi: 10.1016/j.commatsci.2017.01.017 (part 1),
 doi: 10.1016/j.commatsci.2018.10.043 (part 2)]
1.000000
   1.55015000000000  -5.07585766450000   0.00000000000000
   1.55015000000000   5.07585766450000   0.00000000000000
   0.00000000000000   0.00000000000000   7.69141025800000
2 6 2
Direct(10) [A2B6C2]
   0.00000000000000   0.00000000000000   0.00000000000000  Mg
   0.00000000000000   0.00000000000000   0.50000000000000  Mg
   0.92300000000000   0.07700000000000   0.25000000000000  O
   0.07700000000000   0.92300000000000   0.75000000000000  O
   0.36900000000000   0.63100000000000   0.93600000000000  O
   0.63100000000000   0.36900000000000   0.43600000000000  O
   0.36900000000000   0.63100000000000   0.56400000000000  O
   0.63100000000000   0.36900000000000   0.06400000000000  O
   0.25300000000000   0.74700000000000   0.25000000000000  Si
   0.74700000000000   0.25300000000000   0.75000000000000  Si
```

4.3 Decorate a related hypothetical compound.

By changing the elements listed in the command, we are able to get the POSCAR file for $CaGeO_3$ with the prototype as the $MgSiO_3$.

```
 1.000000
   1.55015000000000  -5.07585766450000   0.00000000000000
   1.55015000000000   5.07585766450000   0.00000000000000
   0.00000000000000   0.00000000000000   7.69141025800000
2 2 6
Direct(10) [A2B2C6]
   0.00000000000000   0.00000000000000   0.00000000000000  Ca
   0.00000000000000   0.00000000000000   0.50000000000000  Ca
   0.25300000000000   0.74700000000000   0.25000000000000  Ge
   0.74700000000000   0.25300000000000   0.75000000000000  Ge
   0.92300000000000   0.07700000000000   0.25000000000000  O
   0.07700000000000   0.92300000000000   0.75000000000000  O
   0.36900000000000   0.63100000000000   0.93600000000000  O
   0.63100000000000   0.36900000000000   0.43600000000000  O
   0.36900000000000   0.63100000000000   0.56400000000000  O
   0.63100000000000   0.36900000000000   0.06400000000000  O
```

We might not be able to use other cations that are out of the same group to decorate the prototype, since the ratio has to be fixed with the prototype but

other cations with different charges might change the ratio and thus change the prototype.

5 Constructing a Convex Hull

5.1 a. sample Ca-Pt

The structure chosen is a binary system, Ca-Pt. The compositions lie on the hull (thermodynamically stable) are Ca_3Pt, Ca_2Pt, Ca_5Pt_3, CaPt, $CaPt_2$, $CaPt_5$, Ca, and Pt. The rest prototypes are above the hull (metastable) including all the prototypes in Ca_8Pt, Ca_7Pt, Ca_5Pt, Ca_4Pt, Ca_7Pt_3, Ca_3Pt_2, Ca_7Pt_5, Ca_4Pt_3, Ca_5Pt_4, Ca_6Pt_7, Ca_4Pt_5, Ca_3Pt_4, Ca_5Pt_7, $Ca_{12}Pt_{17}$, Ca_2Pt_3, Ca_3Pt_5, $CaPt_3$, Ca_2Pt_7, $CaPt_4$, $CaPt_7$, and $CaPt_8$ as well as some of the prototypes in that is higher than the hull even they have the similar composition as those in the thermodynamically stable.

The ΔH for CaPt from 123 prototype to the hull point is 32 meV/atom, it is a small but positive $Delta$H which indicates mild instability. The ΔH for CaPt from 405 prototype to the hull point is 227 meV/atom, it is a positive $Delta$H and the value is greater than the first case, which indicates are larger instability (potentially leads to decomposition) compared to the 123 prototype.

5.2 The composition of AuCu3

From the information in part 1, we are able to know that the the L12 strucutre of the AuCu3 generated by POSCAR is $AB3\_cP4\_221\_a\_c$ with the space group of $Pm3m\#221$. Thus, to match the corresponding prototype in the hull, we find two prototypes that matche it, they are 25 and the slightly different result from the ICSD database, $ICSD\#40351.AB$. The formation energy are -40 meV/atom and -37 meV/atom, which are both close to the hull (-40 meV/atom). ΔH_{hull} is 1 for prototype 25 and 4 for prototype $ICSD\#40351.AB$. Thus, it mostly lies on the hull or slightly above the hull; the structure is relatively stable. As the polymorphs of AuCu3, the structure with the prototype at the hull point is slightly tilted, with the unequal lattice vector comparing to the $AB3\_cP4\_221\_a\_c$. Those two phases are probably have nearly degenerate energies.

6 Modeling Disorder with POCC

6.1 50/50 on one sublattice.

I have constructed a 50/50 mix alloy of NaCl with the pure Br.

```
aflow --proto=AB_cF8_225_a_b:Na:Cl:Br --pocc_params=S0-1xA_S1-0.5xB-0.5xC
```

The maps placeholders in order is: A → Na, B →Cl, C → Br. In this case, Cl and Br are in the same site family and they have the 50/50 ratio.

The output is as below:

```
 NaClBr/AB_cF8_225_a_b.AB:POCC_P0-1xA_P1-0.5xB-0.5xC params=-1 SG=225
 [ANRL doi: 10.1016/j.commatsci.2017.01.017 (part 1),
 doi: 10.1016/j.commatsci.2018.10.043 (part 2)]
-60.725450 0.001 0.001
   0.00000000000000   0.50000000000000   0.50000000000000
   0.50000000000000   0.00000000000000   0.50000000000000
   0.50000000000000   0.50000000000000   0.00000000000000
1*1 1*0.5 1*0.5
Direct(3) Partial [A1B0.5C0.5]
   0.50000000000000   0.50000000000000   0.50000000000000  Na    pocc=1
   0.00000000000000   0.00000000000000   0.00000000000000  Cl    pocc=0.5
   0.00000000000000   0.00000000000000   0.00000000000000  Br    pocc=0.5
```

6.2 Build, run, and inspect.

The structure I am using is PdS with the prototype of $AB\_tP16\_84\_cej\_k-001.\{AB\}$. I use Pd as the site family, so that i have 0.25 of Pd and 0.75 of Pt from the same site family of Pd, while the S is keep ordered. The command is listed as below:

```
aflow --aflow_proto=AB3_cP4_221_a_c:Pd:Pt:S --pocc_params=S0-0.25xA-0.75xB_S1-1xC
```

And I then run the calculation with aflow via the command:

```
aflow --run
```

The PARTCAR file I got with the header is as listed:

```
 Pd_pvPtS/AB3_cP4_221_a_c.AB:POCC_P0-0.25xA-0.75xB_S1-1xC params=-1 SG=221
 [ANRL doi: 10.1016/j.commatsci.2017.01.017 (part 1),
 doi: 10.1016/j.commatsci.2018.10.043 (part 2)]
1.000000 0.001 0.001
   3.97595048668009   0.00000000000000   0.00000000000000
   0.00000000000000   3.97595048668009   0.00000000000000
   0.00000000000000   0.00000000000000   3.97595048668009
1*0.25 1*0.75 3*1
Direct(5) Partial [A0.25B0.75C3]
   0.00000000000000   0.00000000000000   0.00000000000000  Pd_pv pocc=0.25
   0.00000000000000   0.00000000000000   0.00000000000000  Pt    pocc=0.75
   0.00000000000000   0.50000000000000   0.50000000000000  S     pocc=1
   0.50000000000000   0.00000000000000   0.50000000000000  S     pocc=1
   0.50000000000000   0.50000000000000   0.00000000000000  S     pocc=1
```

From the aflow.pocc.structures_unique.out file, I am able to know that there are total of 9 unique structures. And throughout the 9 structures, the energy is in the range between 51.037768558049002 to 51.037783103689002.

7 Contribution

Our group contributes equally. People discuss the confusion, and everyone is engaging in helping each other.