NANO 266 - Lab 3

Zhi Deng
PID:A53058446

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Q1

First of all, perform the k-point convergence test on both bcc and hcp Fe with convergence criteria set to 1 meV/atom.

- For bcc Fe, set the lattice parameter $a = 5.42$ a.u. Use a $k \times k \times k$ k-point grid, where k increases from 8 to 20 with increment 1.
- For hcp Fe, set the lattice parameters $a = 4.8$ a.u. and $c/a = 1.73$. Use a $k_1 \times k_1 \times k_3$ k-point grid, where k_1 increases from 8 to 20 with increment 1, k_3 is automatically determined by k_1 and c/a. For more details on k_3, please see the following program and table.

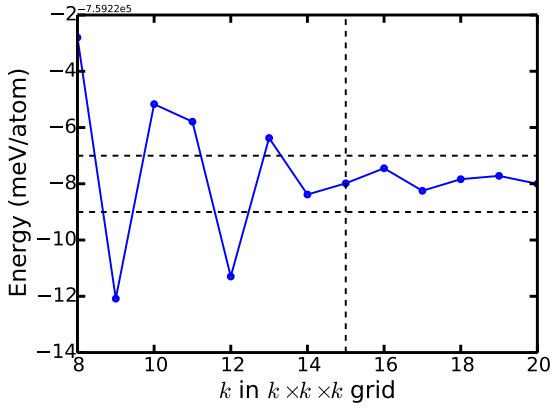
```
import numpy as np
calat = 1.73
k1_array = np.arange(8,21)
k3_array = np.ceil(k1_array/calat).astype(int)
```

k_1	8	9	10	11	12	13	14	15	16	17	18	19	20
k_3	5	6	6	7	7	8	9	9	10	10	11	11	12

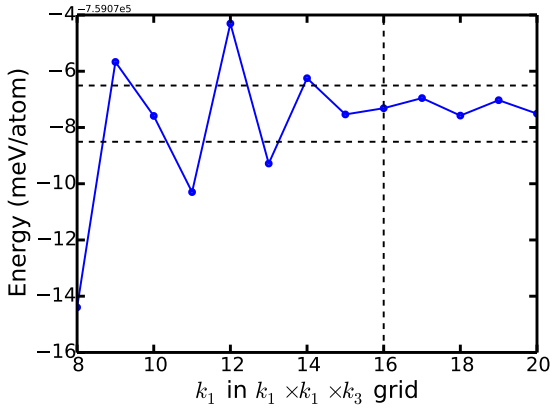
Convergence test results:

- bcc Fe converges at $15 \times 15 \times 15$ k-point grid.
- fcc Fe converges at $16 \times 16 \times 10$ k-point grid.

Use the converged k-mesh for the following calculations.



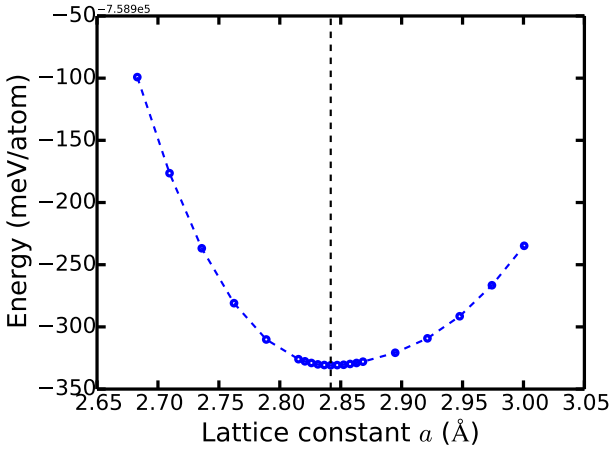
(a) bcc Fe



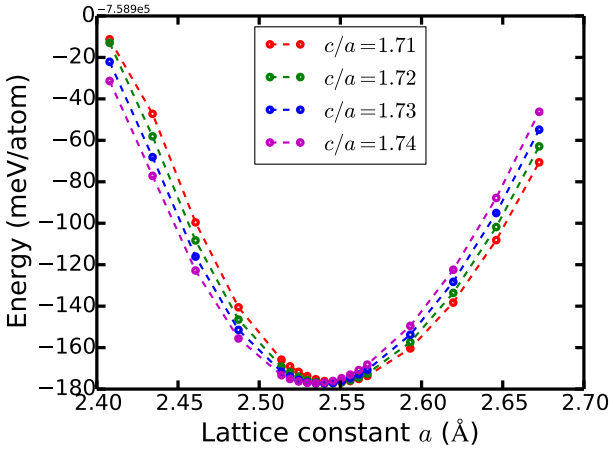
(b) hcp Fe

1

Calculate and plot the ground state energy of bcc and hcp Fe near the equilibrium lattice constant. For bcc Fe, the equilibrium lattice constant $a_0 = 2.842$ Å $= 5.37$ a.u. For hcp Fe, the equilibrium lattice constant $a_0 = 2.540$ Å $= 4.80$ a.u., and $c/a = 1.73$. Note the energy differences between different ratios are small near a_0.



(a) bcc Fe



(b) hcp Fe

2

In thermodynamics, pressure is defined as:

$$p = -\frac{\partial U}{\partial V},$$

where U is the internal energy and V is the volume. The internal energy is the total energy from DFT calculation. On the E-V plot, the pressure on certain point can be calculated from the slope of the tangent line at that point.

The Gibbs free energy change is given by

$$\Delta G = \Delta U + p\Delta V - T\Delta S,$$

where T is the temperature, ΔS is the entropy change. The contribution of entropy is relatively small comparing with the other terms in solids. Therefore,

$$\Delta G = \Delta U + p\Delta V.$$

The phase transition occurs when the 2 phases have the same Gibbs free energy ($\Delta G = 0$). Even with a difference in internal (total) energy, 2 structures can have the same Gibbs free energy as long as they satisfy the following condition:

$$\Delta U = -p\Delta V.$$

For this case, on the E-V plot, the 2 points on different curves share a common tangent line as the phase transition pressure is unique.

The cell volume can be calculated from lattice parameters with the following equations:

$$V_{\text{bcc}} = a^3, V_{\text{hcp}} = \frac{\sqrt{3}}{2}\left(\frac{c}{a}\right)a^3$$

Plot the energy of bcc and hcp Fe against cell volume. For the hcp structure, the choice of c/a has no effect on the E-V curve. All the curves from different c/a will merge into one curve on the E-V plot. (tested)

To find the common tangent line, first fit each curve to a 4-degree polynomial

$$y(x) = ax^4 + bx^3 + cx^2 + dx + e,$$

The derivative of the above function is given by:

$$y'(x) = 4ax^3 + 3bx^2 + 2cx + d.$$

The equation of the tangent line passing through an arbitrary point $(x_0, y(x_0))$ on the curve is given by:

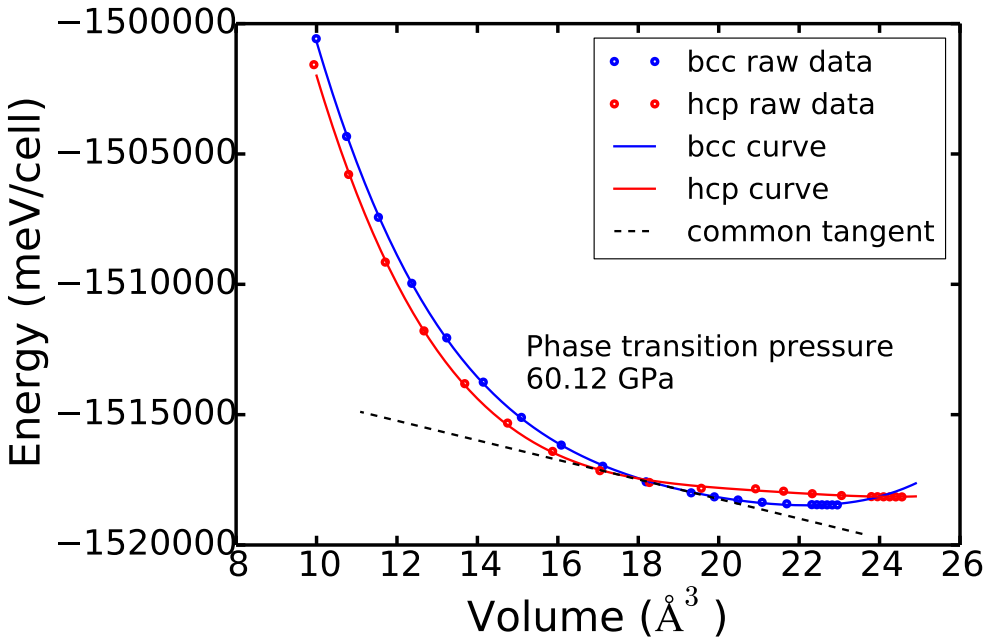
$$\begin{aligned} y - y(x_0) &= y'(x_0)(x - x_0) \\ y &= y'(x_0)x - y'(x_0)x_0 + y(x_0) \end{aligned}$$

The common tangent line passing through 2 points of tangency $(x_1, y_1(x_1))$ and $(x_2, y_2(x_2))$ on different curves should have the same slope and intercept. Therefore,

$$\begin{cases} y_1'(x_1) = y_2'(x_2) \\ -y_1'(x_1)x_1 + y_1(x_1) = -y_2'(x_2)x_2 + y_2(x_2) \end{cases}$$

Solve the equations to get the coordinates of the 2 points of tangency to get the common tangent line.

Thanks to NumPy and SciPy, I was able to solve them numerically without even knowing the equation of either curve. The source code is available at:



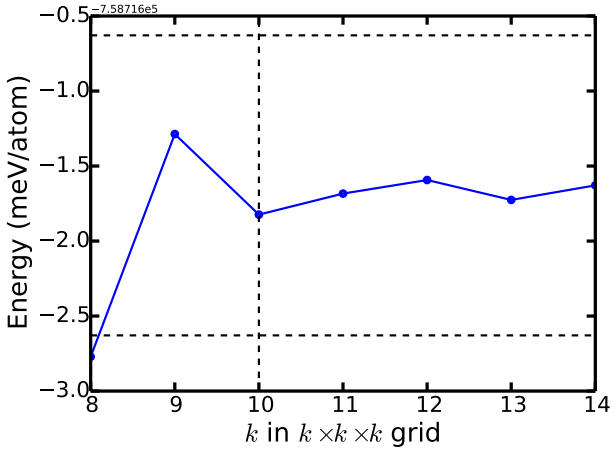
With the data of 2 tangent points, the pressure is calculated as:

$$p = -\frac{\Delta E}{\Delta V} = 60.12\,\text{GPa}$$

3

To calculate the total energy of bcc Fe in anti-ferromagnetic state, break the bcc symmetry to simple cubic cell with the 2 atoms having the opposite starting magnetization values (2 different species). Do a k-point convergence test using the lowest energy structure from ferromagnetic bcc Fe to get the converged total energy. The template is available at: https://github.com/adengz/nano266/blob/master/labs/lab3/Fe.sc.pw.in.template

The result shows that the total energy converges at at $10 \times 10 \times 10$ k-point grid.

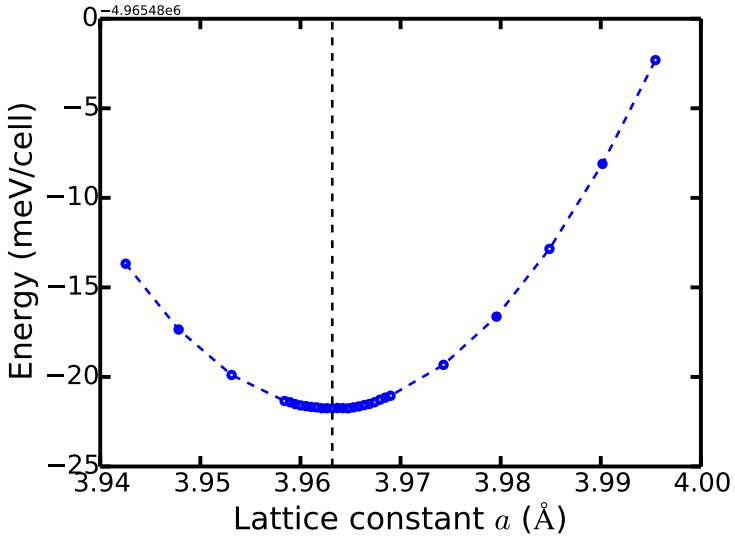


Compare the total energies between ferromagnetic and anti-ferromagnetic states using the converged total energies. The total energy of bcc Fe in ferromagnetic state is around 0.5 eV/atom lower than that in anti-ferromagnetic state.

Q2

1

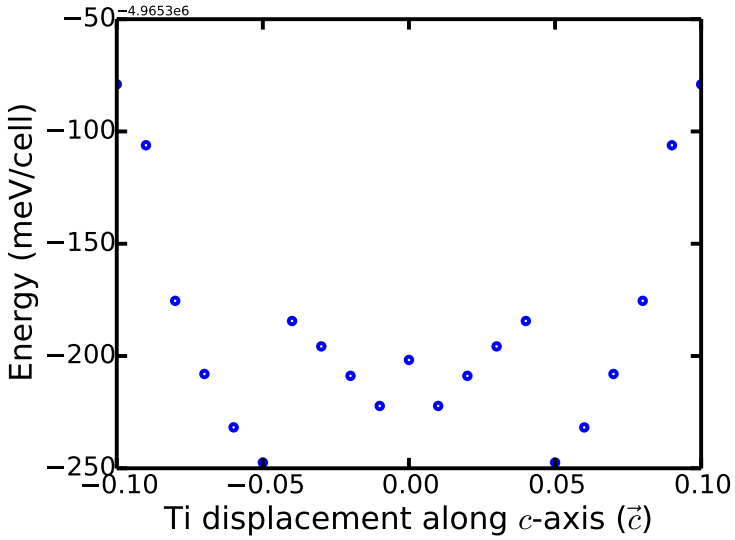
Calculate and plot the energy of cubic $PbTiO_3$ as a function of lattice parameter.



At equilibrium, the lattice parameter $a = 3.9632\,\text{Å} = 7.489\,\text{a.u.}$

2

Using the lattice constant at equilibrium, calculate and plot the energy as a function of the displacement of Ti along c-axis.



The total energy reaches minimum when the displacement of Ti is $\pm 0.05\vec{c}$. The energy difference between this configuration and the minimum-energy configuration from previous part is 45.71 meV/fu.

3

Perform the relaxation allowing Ti movement together with O using the configuration with Ti displacement of $0.05\vec{c}$.

The final atomic positions are listed in the following table.

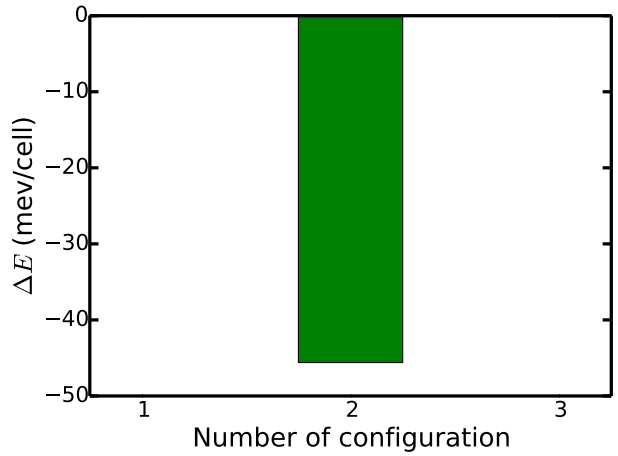
	x	y	z
Pb	0	0	0
Ti	0.5	0.5	0.504526412
O	0.5	0.5	-0.000608651
O	0.5	0	0.500988678
O	0	0.5	0.500988678

Record the final energy to compare the energy differences.

4

Using the lowest energy configuration obtained from part 1 as reference, plot the energy difference of the following $PbTiO_3$ configurations:

1. Ti at (0.5,0.5,0.5). Space group: $Pm\bar{3}m$
2. Ti at (0.5,0.5,0.55). Space group: $P4mm$
3. Ti at (0.5,0.5,0.504). Space group: $P4mm$



The most stable structure is the one with Ti coordinates of (0.5,0.5,0.55). (For the 3rd configuration, I believe the total energy converged to a local minimum)

In the lowest energy structure, the center of mass of positive charges (Pb^{2+}) does not coincide with the one of negative charges (TiO_4 tetrahedra). The non-polarized structure (with space group $Pm\bar{3}m$) tends to polarize due to the energy difference, which explains the spontaneous electric polarization, i.e., the ferroelectricity of $PbTiO_3$.

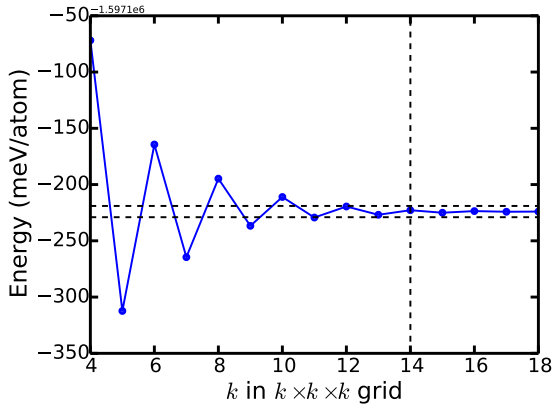
Q3

1

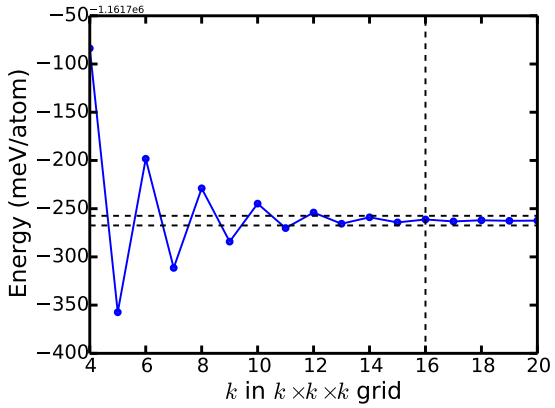
Calculate the ground state energy of Cu, Au and CuAu. The initial guess of lattice constants are listed in the following table.

Structure	a	
	unit: Å	unit: a.u.
fcc Cu	3.61505	6.83
fcc Au	4.17010	7.88
$L1_0$ CuAu	3.96900	7.50

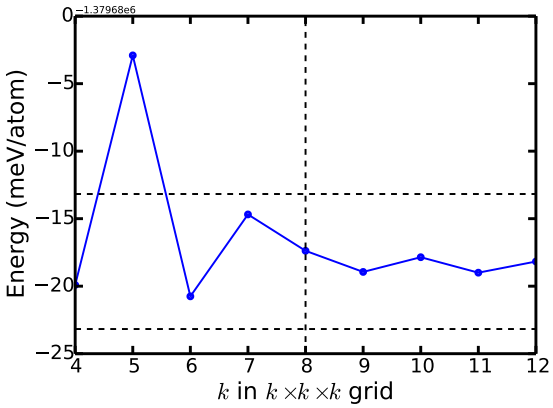
Perform the k-point convergence test for all structures to get converged total energies.



(a) Cu



(b) Au



(c) CuAu

Convergence test results:

- Cu converges at $14 \times 14 \times 14$ k-point grid. The lattice constant $a = 6.88$ a.u. for the relaxed structure.

- Au converges at $16 \times 16 \times 16$ k-point grid. The lattice constant $a = 7.88$ a.u. for the relaxed structure.
- CuAu converges at $8 \times 8 \times 8$ k-point grid.

Use the converged total energies for formation energy calculations.

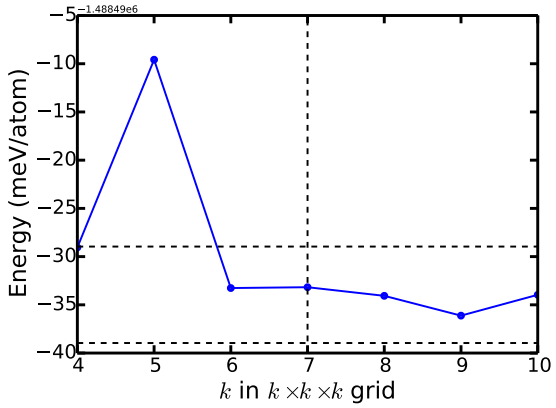
2

Calculate the formation energy of CuAu.

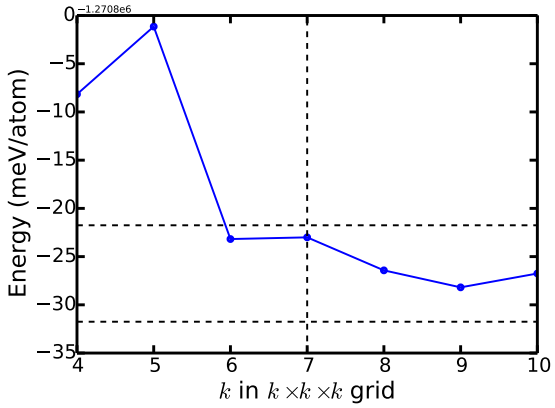
$$\begin{aligned}\Delta H_{\mathrm{f}}(\mathrm{Cu_{0.5}Au_{0.5}}) &= E(\mathrm{Cu_{0.5}Au_{0.5}}) - 0.5E(\mathrm{Cu}) - 0.5E(\mathrm{Au}) \\ &= -54.97\,\mathrm{meV/atom}\end{aligned}$$

3

Calculate the ground state energy of Cu_3Au and $CuAu_3$. The initial guess on lattice constants are predicted from the relaxed structure of fcc Cu and Au based on Vegard's law (7.13 a.u. for Cu_3Au and 7.63 a.u. for $CuAu_3$). The k-mesh choice should be similar to CuAu as all of them start from simple cubic structure with 4 atoms in the unit cell.



(a) Cu_3Au



(b) $CuAu_3$

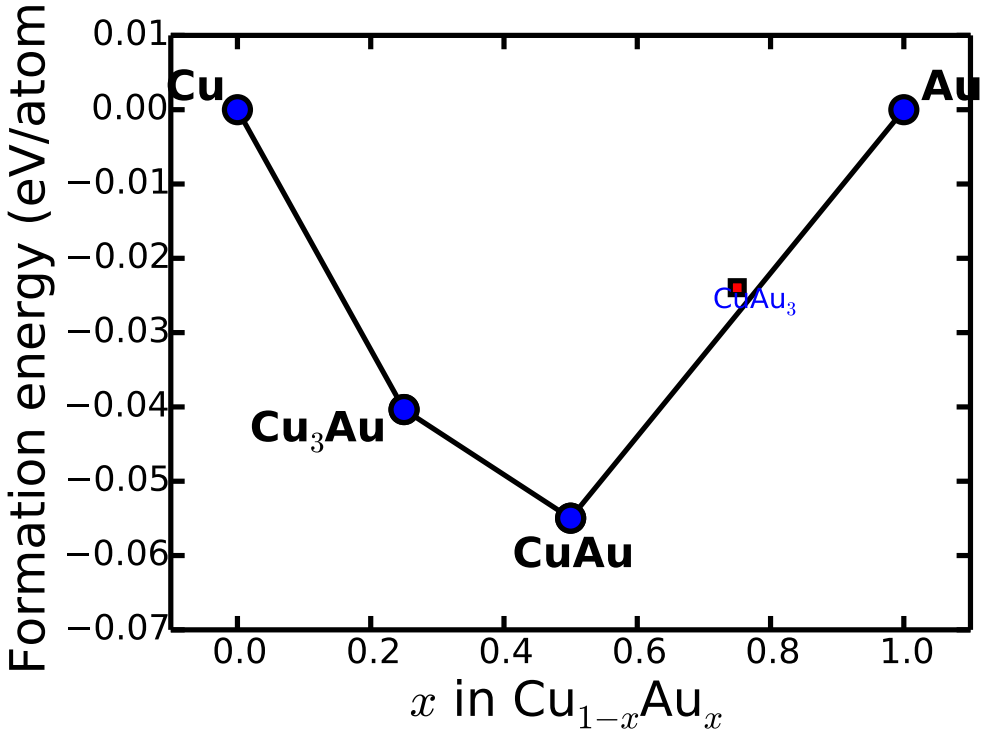
Both Cu_3Au and $CuAu_3$ converges at $7 \times 7 \times 7$ k-point grid. Use the converged total energies for formation energy calculations.

4

Calculate the formation energy of Cu_3Au and $CuAu_3$.

$$\begin{aligned}\Delta H_\mathrm{f}(\mathrm{Cu_{0.75}Au_{0.25}}) &= E(\mathrm{Cu_{0.75}Au_{0.25}}) - 0.75E(\mathrm{Cu}) - 0.25E(\mathrm{Au}) \\ &= -40.35\,\mathrm{meV/atom} \\ \Delta H_\mathrm{f}(\mathrm{Cu_{0.25}Au_{0.75}}) &= E(\mathrm{Cu_{0.25}Au_{0.75}}) - 0.25E(\mathrm{Cu}) - 0.75E(\mathrm{Au}) \\ &= -23.95\,\mathrm{meV/atom}\end{aligned}$$

Plot the formation energy as a function of x in $\mathrm{Cu}_{1-x}\mathrm{Au}_x$ using the phase diagram module in Pymatgen.



From the binary phase diagram, we can tell that $\mathrm{Cu_3Au}$ and CuAu are stable ordered intermetallic structures at 0 K. While the formation energy of $\mathrm{CuAu_3}$ is above the convex hull, indicating it's unstable at 0 K.