

Lattice Constants and Stable Lattice Structures

Objectives:

In this activity, you will

- 1) calculate the lattice constants of a metal for cubic, bcc, and fcc structures
- 2) determine the most stable lattice structure of a metal
- 3) report the results in a write-up

Theory:

The calculation of the lattice parameters of crystal structures is an important first step in the DFT calculations of crystalline periodic structures. Metal atoms can arrange themselves in crystalline states that have a translational symmetry. Such periodic array in which the repeated units of the crystal are arranged is specified by the Bravais lattice. The units of the crystal may be single atoms, ions, molecules, or polymer strings of a solid. A three-dimensional Bravais lattice consists of all points with position vectors \mathbf{R} of the form

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

where n_i are any integers and \mathbf{a}_i are primitive vectors that span the lattice.

The most common crystal structures for metals are the face-centered cubic (fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp) structures. Most transition metals take the fcc structures, with the exceptions of Fe, Mo, and W (taking the bcc structures), and Co and Ru (hcp structures). The lattice vectors for these structures are

fcc structure:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{y} + \hat{z}) \quad \mathbf{a}_2 = \frac{a}{2}(\hat{z} + \hat{x}) \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y})$$

bcc structure:

$$\mathbf{a}_1 = a\hat{x} \quad \mathbf{a}_2 = a\hat{y} \quad \mathbf{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$$

where a is the lattice constant and each unit has a single atom.

For hcp structure, the lattice vectors are:

$$\mathbf{a}_1 = a\hat{x} \quad \mathbf{a}_2 = \frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}\hat{y} \quad \mathbf{a}_3 = c\hat{z}$$

In this structure, the first two lattice vectors generate a triangular lattice in the xy plane, while the third vector places the triangular nets a distance c above the first one. The hcp structure is generated by interpenetrating simple hexagonal Bravais lattices, displaced from one another by $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$. For an ideal hcp structure, the c/a ratio is $\sqrt{8/3}$ or 1.633. These structures are shown in Fig. 2.1.

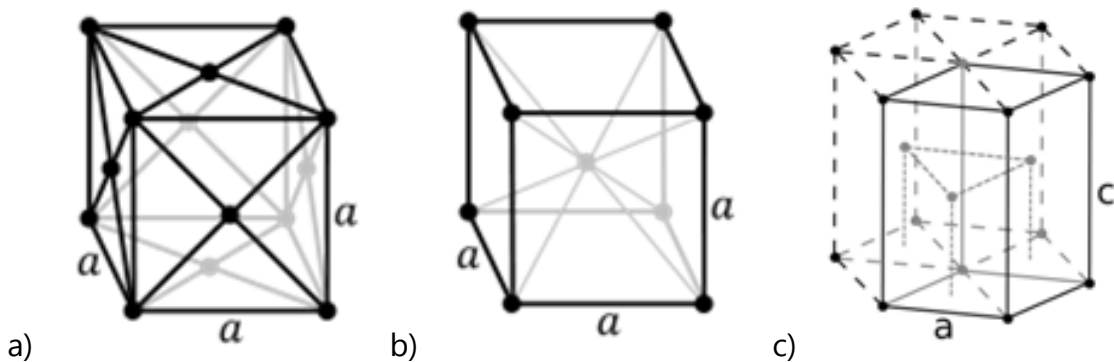


Figure 2.1: The most common crystal structures for metals: a) face centered cubic (fcc), b) body centered cubic (bcc), and c) hexagonal close-packed (hcp) structures. (Figure taken from K.W. Kolasinski, *Surface Science: Foundations of Catalysis and Nanoscience*, 2nd Ed., John Wiley & Sons, Ltd. 2008)

Another important structure is the diamond structure, which is assumed by some group IV elements such as C, Si, and Ge. It consists of two interpenetrating fcc Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter of the length of the diagonal. It can be regarded as fcc lattice with two-point basis at

$$\mathbf{0}, \quad \frac{a}{4}(\hat{x} + \hat{y} + \hat{z})$$

In practical DFT calculations for simple cubic (sc), fcc, and bcc structures, it is easy to model the crystal structure using a cubic supercell of length a defined by lattice vectors:

$$\mathbf{a}_1 = a(1,0,0), \mathbf{a}_2 = a(0,1,0), \mathbf{a}_3 = a(0,0,1)$$

Using this supercell, one possible coordinate/s of atom/s for each structure is as follows:

sc: (0,0,0)

fcc: (0,0,0); (0, 0.5, 0.5); (0.5, 0, 0.5); (0.5, 0.5, 0)

bcc: (0, 0, 0); (0.5, 0.5, 0.5)

On the other hand, for a supercell defined by lattice vectors for the hcp structure:

$$\mathbf{a}_1 = a(1,0,0), \mathbf{a}_2 = a\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right), \mathbf{a}_3 = a(0,0,\frac{c}{a})$$

The coordinates of the atoms can be: (0,0,0); $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$.

Here, the positions of the atoms are in fractional coordinates of the lattice vectors. A sensible approach to determine the lattice constant a (or both a and c/a for hcp structure) is to calculate the total energy (or more meaningfully, the cohesive energy) of the material as a function of the lattice constant. The shape of curve is parabolic, with a single minimum at a value of the equilibrium lattice constant.

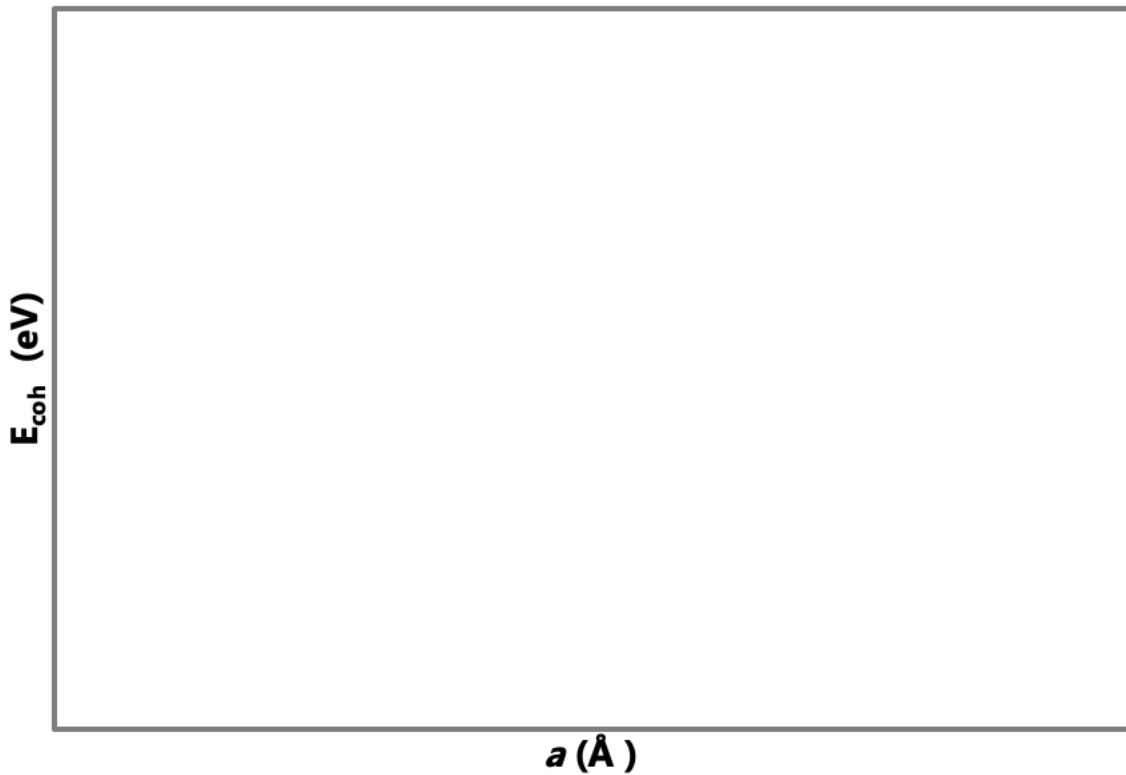
Computational Model:

DFT calculations will be implemented using Quantum Espresso with exchange-correlation term described using the generalized gradient approximation (GGA) based on Perdew-Burke-Ernzerhof (PBE) functional. The interaction between ions and electrons will be described using the projector augmented wave (PAW) method. Plane wave basis sets will be employed with an energy cut-off of 400 eV. The surface Brillouin zone integrations will be performed on a grid of 4×4×4 Monkhorst-Pack k-points using Methfessel-Paxton smearing of $\sigma=0.2$ eV.

Method:

- 1) Calculate the total energy *per atom* (E_{tot}/n) of a metal assigned to you in the cubic, bcc, and fcc, structures as a function of the lattice constant a . (For an extra challenge, you can also do the same for the hcp structure, i.e., calculate the total energy per atom as a function of the lattice constant a , for different c/a ratios. This is optional.)

Graph 1: Cohesive energy (E_{coh}) vs lattice constant a for different crystal structures.



1) What are the minimum (most stable) lattice constants and cohesive energies for the sc, bcc, and fcc structures of the metal assigned to you? Compare your results with those reported in literature and discuss the possible discrepancies, if any.

2) Based on graph 1, what is the most stable crystal structure of the metal assigned to you among the crystal structures that you considered in this activity? Does it agree with experiments?

Conclusion:
