



First-Principles Determination of Lattice Parameters and Computational Elucidation of the Stable Lattice Structure of Palladium (Pd)

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The lattice parameters of a solid-state material are important they determine its external properties such as coefficients of thermal expansion, transparency, etc. The computational determination of these lattice parameters/lattice constants have been widely used in order to determine the stable crystal configurations of certain materials. The current work used these principles in the elucidation of the stable lattice configuration of Palladium (Pd), Self-Consistent Field calculations predict that the element will adopt a face-centered cubic (FCC) configuration with a lattice constant (a) of 3.95 Å, with cohesive energy calculations for the system yielding a value of 3.71 eV. These are in close agreement with values obtained through literature.

1. Introduction

It is known that many solids do not exist as a random arrangement of atoms and molecules, save for a few exceptions. And in this respect, it has been observed that there are only a few possible ways for regular arrangements to exist. The regularity of crystals can be accurately described by a very small arrangement of atoms and molecules; this very small arrangement, repeated many times in three dimensions, can tell a lot about the properties of a solid [1].

Solids that have some regular, three-dimensional order are called crystals, which are basically three-dimensional repetitions of small groups of molecules, ions or atoms called the unit cell [2], ultimately forming what is known as a crystal lattice. These unit cells are mathematically defined elements that yield the spatial configuration of the crystal lattice, and are described by lattice vectors as shown:

$$\mathbf{r} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

Here, n_1 , n_2 , and n_3 are integers. a , b , and c are the three fundamental translation vectors. The integer numbers n_1 , n_2 , n_3 yield the lattice points of the crystal. The translation vectors a , b , and c , generate the elementary cell, which in turn builds up the crystal lattice by its spatially periodic repetition [3].

Of the seven crystal systems known, the simplest one is known as the cubic system. It is separated into three lattice configurations (also known as Bravais lattices), depending on whether the unit cell has species only at the corners (*simple or primitive cubic*); at the corners and the center of the unit cell (*body-centered cubic*); or at the

faces of the unit cell (*face-centered cubic*), as illustrated in Figure 1.

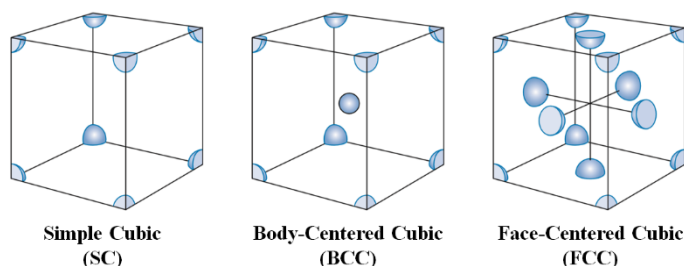


Figure 1. The three Bravais lattices of the cubic crystal system. [1]

The cubic unit cell has all edges of the same length, and collectively they are known as the lattice constant for the lattice structure, denoted by a , or can also be called as lattice parameters that can be measured for a particular crystal structure [4]. As it turns out, precise knowledge of the lattice parameters and the crystal structure of materials is important in solid-state investigations. For example, such data have been of great help in developing satisfactory concepts of bonding energies in crystalline solids. Further, precise lattice parameter measurements are useful in determining solid solubility limits of one component in another, coefficients of thermal expansion, true densities of materials, cleavage, electronic band structure, and optical transparency [5].

For this particular activity, Self-Consistent Field calculations were made for the total energies of the three different cubic crystal bravais lattices of Palladium (Pd) metal as a function of their lattice constants. The lattice constant at which the energy minimum is obtained will denote the stable lattice constant for that particular structure, and the structure that contains the smaller energy minimum among the three bravais lattices will be considered as the stable crystal structure for the element. Insights are then made into the

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energies associated with the structure, as well as comparisons made to data obtained throughout literature (both experimental and computational in nature).

2. Results and Discussion

Self-Consistent Field computations were performed using Quantum Espresso to solve for the total energies associated with the three cubic bravais lattices for Palladium. These energies were calculated as a function of the lattice constant (α), with equal increments between lattice constants and then fine-tuning to get as close as possible to the energy minimum and an accurate value for α . The results of these calculations have been graphed and shown in Figure 2.

The stable lattice constants for the three bravais lattices are 2.60 Å, 3.15 Å and 3.95 Å for the simple cubic, body-centered cubic and face-centered cubic configurations, respectively. The increase in α_{stable} between the structures can be rationalized by the interactions of the atoms by virtue of number of atom equivalents in each specific unit cell. The number of atom equivalents increases going from simple cubic to body-centered and then to face-centered, having 1, 2 and 4 atom equivalents respectively.

To elucidate the naturally preferred structural configuration of Palladium, these energy minimums must be looked at in much closer detail. In order to do this, the cohesive energy minimums for each bravais lattice must

be compared at their respective stable lattice constants. The total energy of the system can be attributed to two things, the cohesive energy, E_{coh} , as well as the chemical potential, μ . That is:

$$E_{\text{tot}} = E_{\text{coh}} + n\mu$$

where n is the number of atomic equivalents inside the particular unit cell. By rearranging, the equation, the cohesive energies can be readily calculated for. The chemical potential, μ , for Palladium is simply the total energy on a per atom determined from each unit cell structure at the energy minimum. For palladium, the smallest chemical potential value comes from the face-centered cubic configuration at -331.0675 Ry per equivalent atom. This value will serve as the value of μ in the calculation of the required minimum energies. These results for these calculations are summarized in Table 1, and graphically illustrated in Figure 3.

Table 1.

Calculated values for minimum total energy, E_{totalmin} , and minimum cohesive energy, E_{cohmin} for each of the bravais structures. FCC structure gave smallest chemical potential for these systems and was used as the value of μ .

Cubic Bravais Lattice	α_{stable} (Å)	Equivalent Atoms	E_{totalmin} (Ry)	Chemical Potential, μ	E_{cohmin} (Ry)
SC	2.60	1	-331.049	-331.0450	0.0175
BCC	3.15	2	-662.132	-331.0670	0.0011
FCC	3.95	4	-1324.266	-331.0675	0.0000

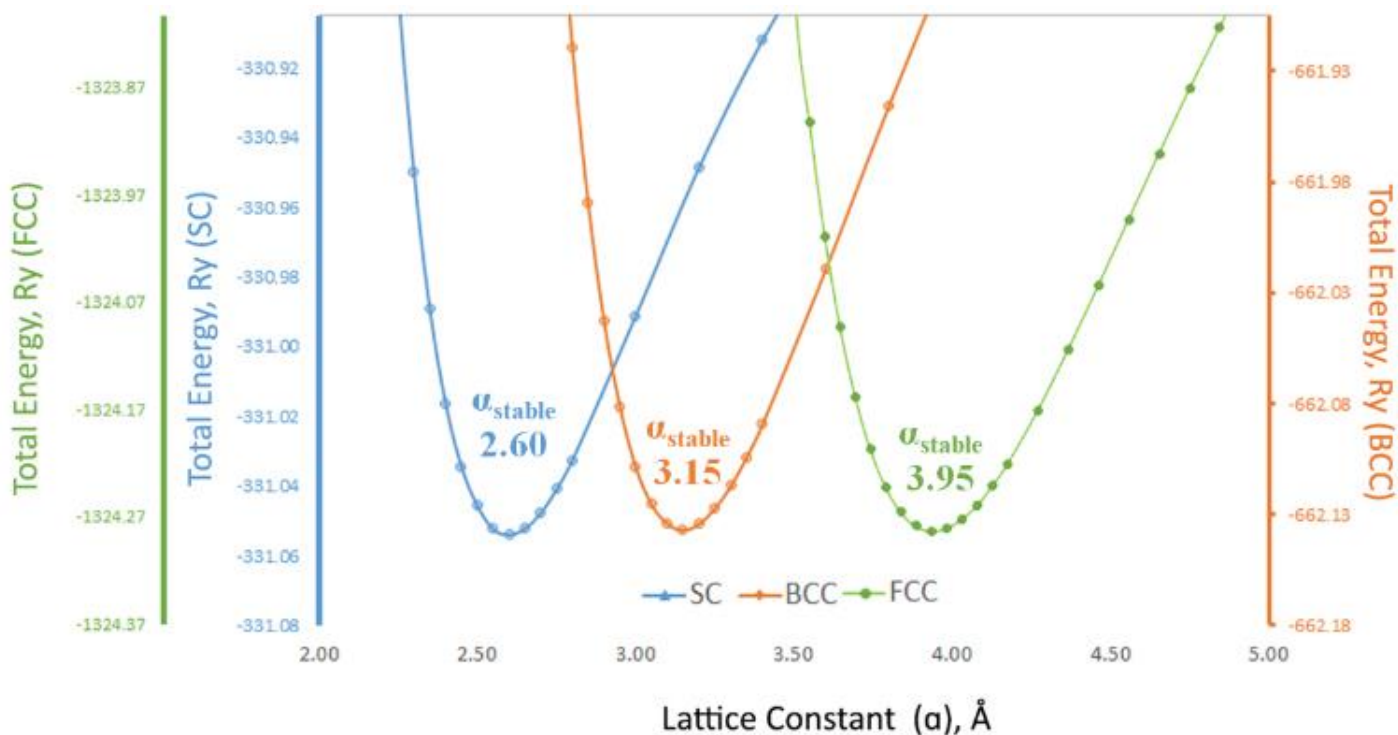


Figure 2. Plot of total energies of each cubic bravais lattice as a function of lattice constant, α . The stable lattice constants (that is, the most stable unit cell dimension given the nature of Palladium) are denoted by α_{stable} for each.

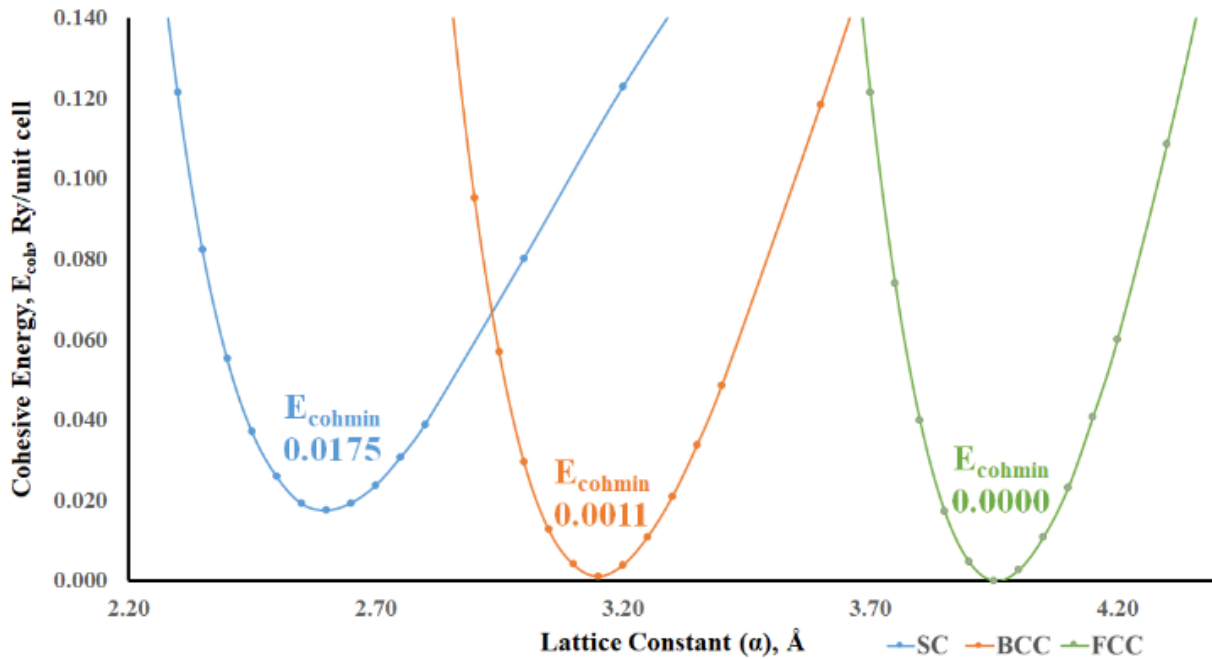


Figure 3. Plot of calculated cohesive energies of each of the bravais lattices as a function of lattice constant, a . The energy minimums of each structure are indicated (E_{cohmin}) and these results show the face-centered cubic configuration to have the smallest relative cohesive energy, and so this can then be deduced as the naturally preferred crystal structure for Palladium.

As shown in Figure 3, the face-centered cubic configuration has the smallest relative minimum cohesive energy in comparison to the other two. This means that based on these energies, the face-centered cubic configuration shall be the structure where the Palladium atoms will be at their lowest relative energy per unit cell at a stable lattice constant of 3.95 Å, and this shows the natural inclination for Palladium to form a face-centered cubic crystal system.

The cohesive energies (E_{coh}) for each respective structure can be calculated by first calculating the total energy of an isolated Palladium atom when placed in a vacuum, represented computationally as a sole atom in the center of a large unit cell. SCF calculations gave a value of -330.7936 Ry for the Palladium atom, and then the following:

$$E_{\text{coh}} = E_{\text{total(structure)}} - E_{\text{total(isolated)}}$$

Where $E_{\text{total(structure)}}$ represents the calculated energy minimums of each bravais lattice at their stable lattice constants. These are summarized in Table 2, and results show

Table 2.

Calculated values for cohesive energy, E_{coh} , for each of the cubic lattice structures

Cubic Bravais Lattice	a_{stable} (Å)	$E_{\text{total(structure)}}$ (Ry)	$E_{\text{total(isolated)}}$ (Ry)	E_{coh} (Ry)	E_{coh} (eV)
SC	2.60	-331.0450		-0.2554	-3.475
BCC	3.15	-331.0670	-330.7936	-0.2724	-3.706
FCC	3.95	-331.0675		-0.2730	-3.714

that the computed value for the cohesive energy of the FCC structure is -3.714 eV. To validate the calculations made in this study, comparisons should be made to values that have been obtained, both computationally and experimentally, by other researchers in the past. Comparisons can be made in the summary presented in Table 3.

Table 3.

Comparison of computed values to literature values

Parameter	Computed Values	Literature Values	Source
Lattice Constant (a), Å	3.950	3.88 to 3.90	Watanabe (1963)
		3.962	Escano et al (2011)
		3.897	Arblaster (2012)
		3.951	Lovvik & Olsen (2002)
		3.889	Wei (1996)
		3.904	Wolf (1993)
		3.770	Lamber (1995)
		3.883	Hellawell (1954)
Cohesive Energy (E_{coh}), eV	3.710	3.942	Jona (2002)
		3.650	Lovvik & Olsen (2002)
		3.695	Hsu (1979)
		3.743	Owen (1933)

The results obtained from these calculations ultimately indicate that pure Palladium metal has a natural inclination to form the face-centered cubic crystal structure, as do most of the heavier transition metal elements. Studies have extensively shown that close packed face-centered structures are more stable any pair of central force interparticle interactions [17]. These results are also in agreement with

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computational and experimental values obtained by other researchers in the past ([6] to [16]), showing only a relatively small deviation from experimentally determined values through X-ray Diffraction (XRD). Of all the 4d transition metals, the electronic structure of palladium has probably been one of the most studied [18], and deviations in computationally obtained results are not uncommon because of the other considerations that need to be addressed in the calculations [19], for example, researchers finding that computed values for cohesive energy generally deviate from experimental values from 3 to 5 % dependent on spin polarization considerations [20].

3. Conclusion

For the current study, total energies were computed for the three cubic crystal bravais lattice configurations of pure Palladium as a function of lattice constant (α). This was achieved through Self-Consistent Field calculations done using the parameters as set in the Computational Model portion of this paper. The values obtained for stable lattice constants for the simple cubic, body-centered and face-centered configurations are 2.60 Å, 3.15 Å and 3.95 Å, respectively. Computationally obtained energy minimums at these lattice constants predict the element adopts a face-centered cubic (FCC) crystal lattice since the energy minimums can be related to relative structural stability. There is a close agreement between the values obtained in this study and literature values, only deviating by a small degree or so, which is not uncommon. This is indicative of the ability of DFT calculations in terms of the prediction of the stable structures of solid-state materials, which lends itself in application to a large variety of fields

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 x 4 x 4 Monkhorst-Pack k-points using Methfessel-Paxton smearing of $\sigma=0.2$ eV.

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