Copper Clusters

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Contents

Chapter 1

This Documentation

This document contains information of the lowest energetic structures of the copper clusters Cu_{55}, Cu_{78}, Cu_{101}, Cu_{124} and Cu_{147}.

The naming system for these clusters are in the form of A-B-C, where A, B and C are integers.

- The clusters with lower energies (for a particular trial, described by B) will have a lower A classication and the clusters with higher energies will have a higher A classication. Some integers of A are not included as they are mearly isomers of given clusters.
- B and C are a classification which allow Geoffrey to find the clusters from the genetic algorithm used to generate them. B is the genetic algorithm trial the cluster was obtained from and C is the formal name of the cluster.

The name of the cluster in the form of A-B-C are given as subsections in this report. The XYZ files for each cluster reported here will also be provided with the name A-B-C.xyz.

Chapter 2

Experimental

The proceedure for simulation one "trial" of the genetic algorithm used to obtain Cu_{55}, Cu_{78}, Cu_{101}, Cu_{124} and Cu_{147} clusters is described below:

A population of 20 copper clusters (either Cu_{55}, Cu_{78}, Cu_{101}, Cu_{124} and Cu_{147}) was created. Each cluster was formed by randomly placing Cu atoms within a unit cell and locally minimising it using the BFGS optimiser, where the energy of the cluster was described by the Gupta potential with Gupta parameters provided by Darby *et al.* [1]

The population was subjected to the genetic algorithm. In the genetic algorithm, 16 offspring were created from the clusters in the population. These 16 offspring were created either by the weighed cut and splice method of mating or starting from scratch and randomly placing Cu atoms within a blank unit cell (as was done to initialise the population). The offspring were further locally minimised using the BFGS optimiser where the energy to minimised was described by the Gupta potential. A modified population was created from the 20 lowest energy clusters from the 20 clusters in the original population and the 16 offspring from the current generation. This is typically called "Natural Selection" in the genetic algorithm. This new population was called the first "generation".

This process of generating generations by creating offspring and performing natural selection on the population was repeated 625 times. The genetic algorithm ended when either 625 generations were performed or if all the clusters in the population were of the exact same energy to two decimal places.

- Five trial of the generation were performed from each type of Cu cluster. The results of the history of each trial were compared by energy and cluster structure.
- These results were also compared with the original Birmingham Parallel Genetic Algorithm [3, 2], a genetic algorithm created by the Johnston group at the University of Birmingham, to see if both algorithms obtained the same lowest energy structure for Cu_{55}, Cu_{78}, Cu_{101}, Cu_{124} and Cu_{147}.
- For this algorithm, a population of 20 copper cluster was also created. However only one offspring was created at each generation and 10,000 generations of the genetic algorithm were performed and obtained. This alsgorithm used the same mating and mutation methods and "natural selection proceedure.

Chapter 3

Results

3.1 Low Energy Structures of the Cu_{55} Cluster

3.1.1 DFT Verification

Figure 3.1 shows the energy of the 26 lowest energy Cu_{55} structures compared to the lowest energetic structure (LES) where the energy of the structures are desribed by the Gupta Potential (yellow dots). These structure were further optimised by DFT using the PBE (blue dots) and PBEsol functionals (red dots).

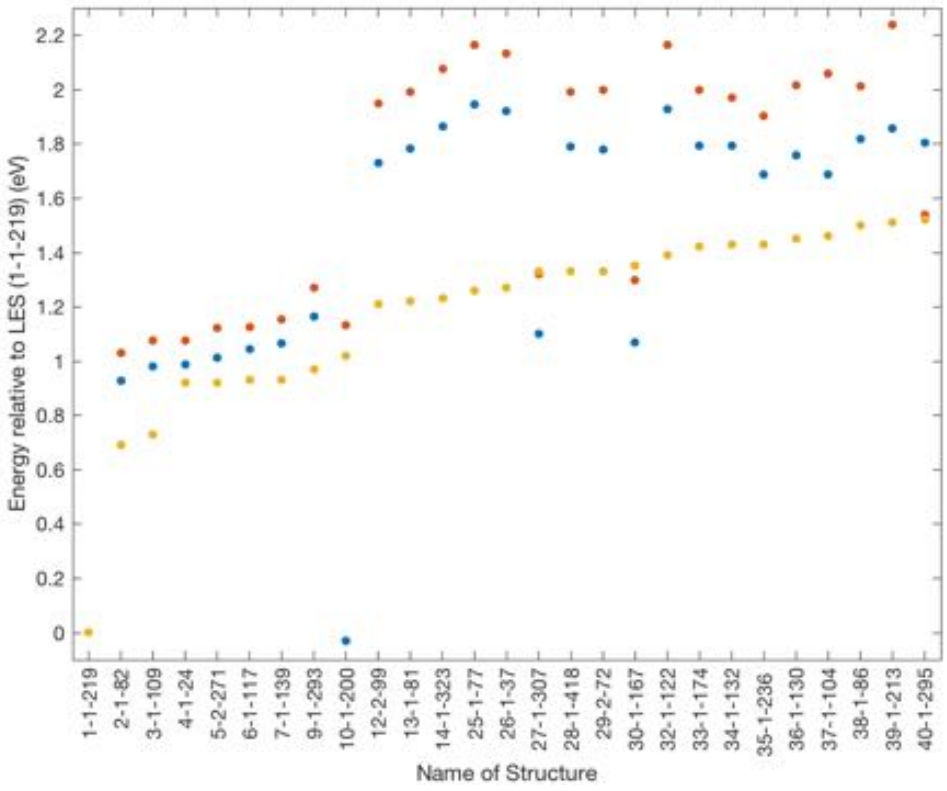


Figure 3.1: The energies of the 26 lowest energetic Cu_{55} structures compared to the LES obtained by the Genetic Algorithm (Energies described by the Gupta Potential) (yellow dots) and DFT-verification results, described by PBE (blue dots) and PBEsol (red dots).

3.1.2 1-1-219

- The lowest energetic structure of Cu_{55} is known to have a perfect icosahedral structure (Figure 3.2) [1] .

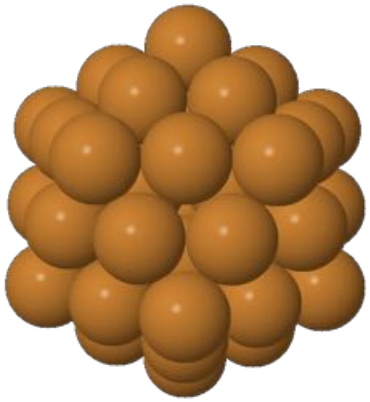


Figure 3.2: Energy = -163.21 eV = $E_{Cu_{55}Ico}$; Average Energy per Atom = -2.96746 eV/Atom (5dp); (1-1-219)

3.1.3 2-1-82

- 5 fold corner atom is moved

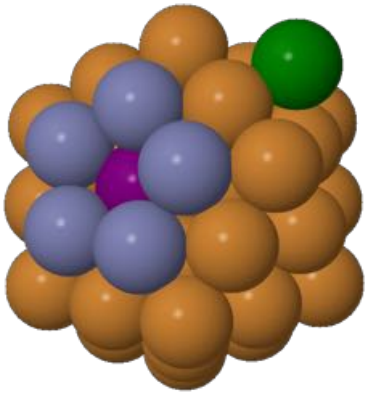


Figure 3.3: Energy = $E_{Cu_{55}Ico}$ + 0.69 eV; (2-1-82)

3.1.4 3-1-109

- 5 fold corner atom is moved

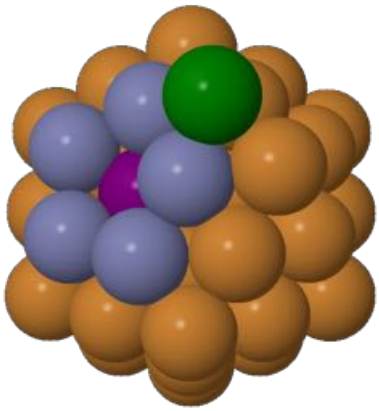


Figure 3.4: Energy = $E_{Cu_{55}Ico}$ + 0.73 eV; (3-1-109)

3.1.5 4-1-24

- Rosette and 6 fold corners present.

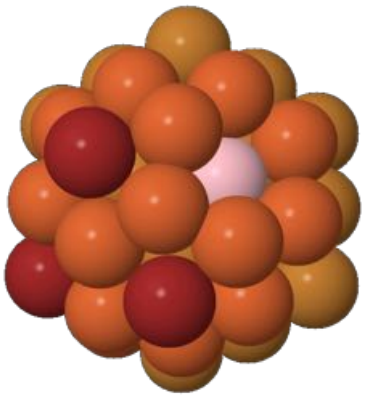


Figure 3.5: red around orange = 6 fold vertex, pink = centre of rosette. Energy = $E_{Cu_{55}Ico}$ + 0.92 eV; (5-1-24)

3.1.6 5-2-271

- Rosette and 6 fold corners present.

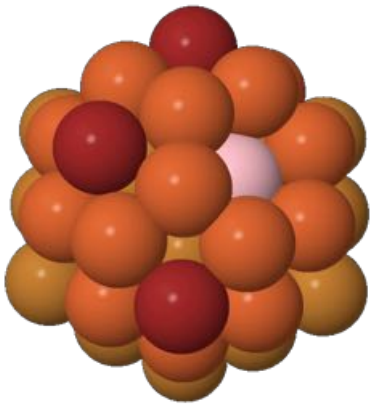


Figure 3.6: red around orange = 6 fold vertex, pink = centre of rosette. Energy = $E_{Cu_{55}Ico}$ + 0.92 eV; (2-271)

3.1.7 6-1-117

- 5 fold vertex vacancy and 6 fold corners present.

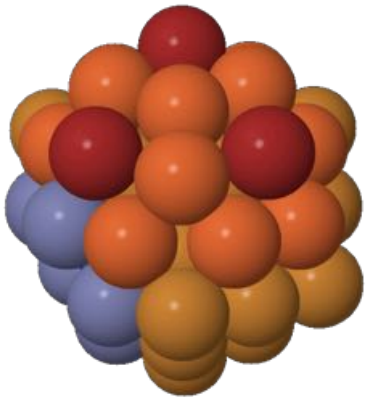


Figure 3.7: Energy = $E_{Cu_{55}Ico}$ + 0.93 eV; (6-1-117)

3.1.8 7-1-139

- 5 fold vertex vacancy and 6 fold corners present.

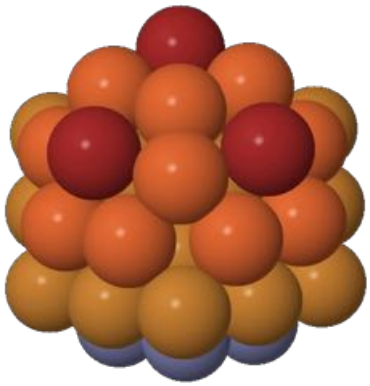
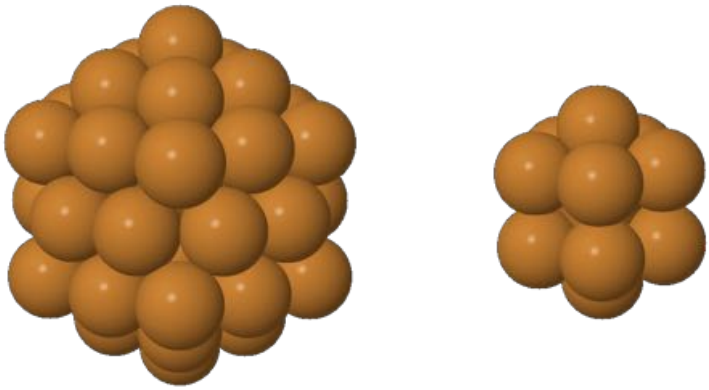


Figure 3.8: Energy = $E_{Cu_{55}Ico}$ + 0.93 eV; (7-1-139)

3.1.9 9-1-293 - The Twisted top Icosahedron

- The next lowest energy is a perfect isocahedron which is twisted along one of the C_5 axis by 36° (Figure 3.9a). This costs 0.97 eV.
- Can see that the bulk system has also been rotated in the same way (Figure 3.9b).



(a) Rotated Icosahedral Cu_{55} (b) Centre of Rotated Icosahedral Cu_{55}

Figure 3.9: Energy = $E_{Cu_{55}Ico}$ + 0.97 eV = $E_{Cu_{55}TwIco}$; (9-1-293)

3.1.10 10-1-200

- Contains a face with a five 6-fold vertice system as shown in Figure 3.10.
- The face of the opposite pole shown in Figure 3.10 is of a icosahedron.

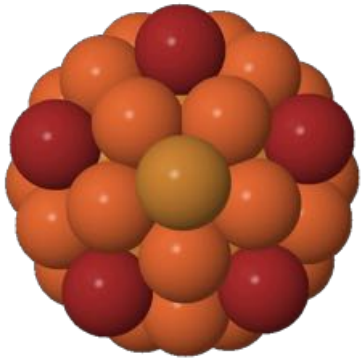


Figure 3.10: Energy = $E_{Cu_{55}Ico}$ + 1.02 eV; (10-1-200)

3.1.11 12-2-99

- Two 5 fold vertex vacancy present and a Cu dimer on surface of cluster.

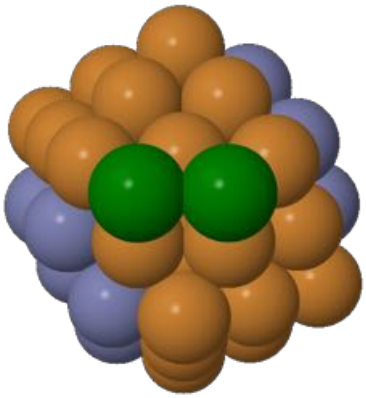


Figure 3.11: Energy = $E_{Cu_{55}Ico}$ + 1.21 eV; (13-2-99)

3.1.12 13-1-81

- Two 5 fold vertex vacancy present and a Cu dimer on surface of cluster.

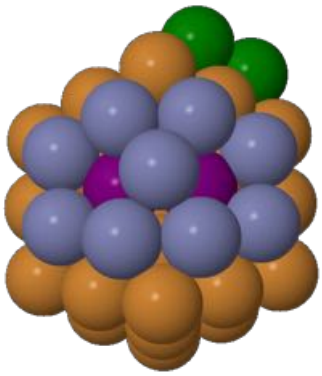


Figure 3.12: Energy = $E_{Cu_{55}Ico}$ + 1.22 eV; (12-1-81)

3.1.13 14-1-323

- Two 5 fold vertex vacancy present and a Cu dimer on surface of cluster.

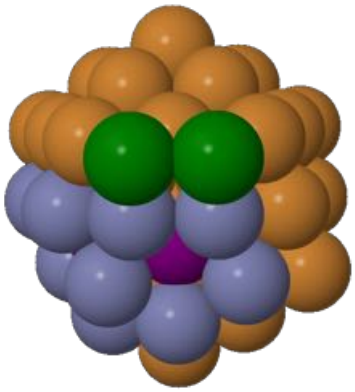


Figure 3.13: Energy = $E_{Cu_{55}Ico}$ + 1.23 eV; (14-1-323)

3.1.14 25-1-77

- Two 5 fold vertex vacancy present and a Cu dimer on surface of cluster.

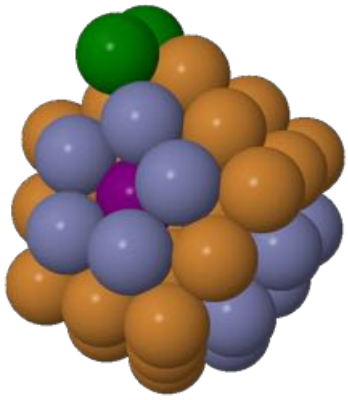


Figure 3.14: Energy = $E_{Cu_{55}Ico}$ + 1.26 eV; (25-1-77)

3.1.15 26-1-37

- Two 5 fold vertex vacancy present and a Cu dimer on surface of cluster.

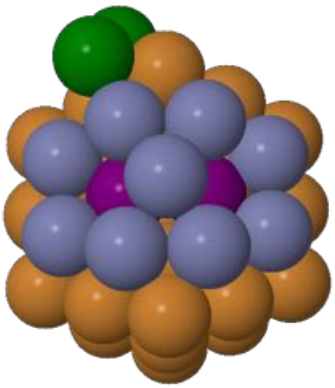


Figure 3.15: Energy = $E_{Cu_{55}Ico}$ + 1.27 eV; (26-1-37)

3.1.16 27-1-307

- An atom is moved an edge between two 5 fold corners.

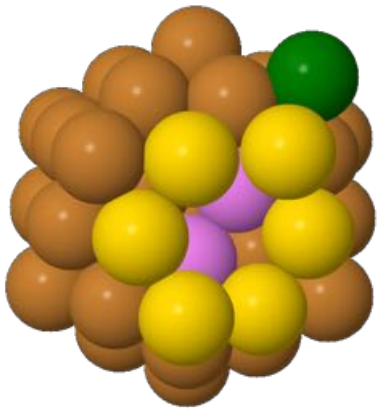


Figure 3.16: Energy = $E_{Cu_{55}Ico}$ + 1.33 eV; (27-1-307)

3.1.17 28-1-418

- Two 5 fold vertex vacancy present.

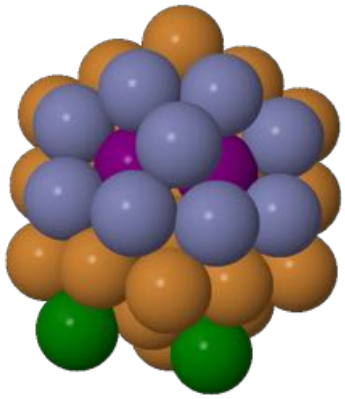


Figure 3.17: Energy = $E_{Cu_{55}Ico}$ + 1.33 eV; (28-1-418)

3.1.18 29-2-72

- Two 5 fold vertex vacancy present.

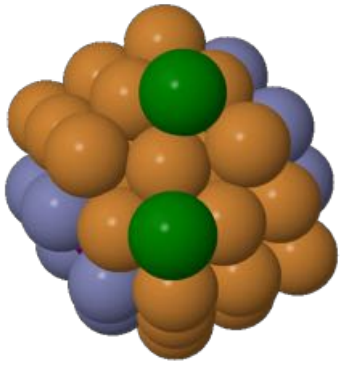
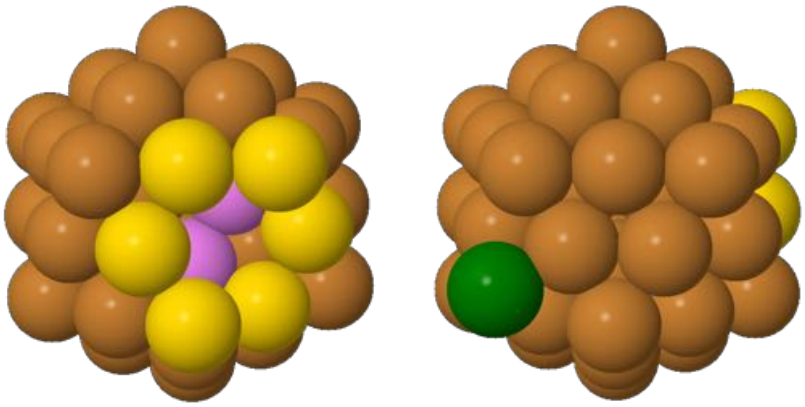


Figure 3.18: Energy = $E_{Cu_{55}Ico}$ + 1.34 eV; (29-2-72)

3.1.19 30-1-167

- An atom is moved an edge between two 5 fold corners. Moved atom placed on a face.



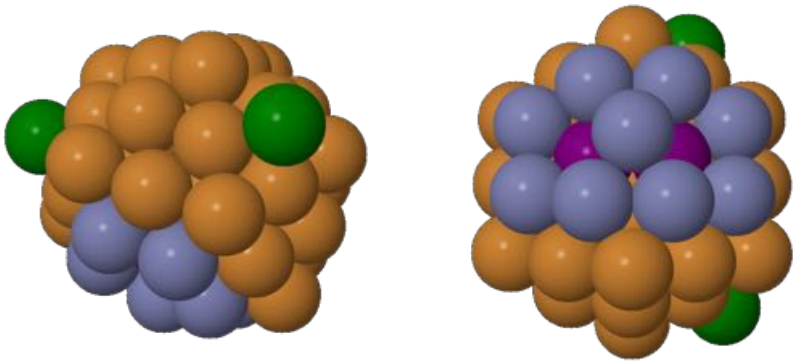
(a) (b)

Figure 3.19: Energy = $E_{Cu_{55}Ico}$ + 1.35 eV; (30-1-167)

3.1.20 32-1-122

Sorry not a good picture

- Two 5 fold vertex vacancy present.



(a) (b)

Figure 3.20: Energy = $E_{Cu_{55}Ico}$ + 1.39 eV; (32-1-122)

3.1.21 33-1-174

- 5 fold corner and rosette present.

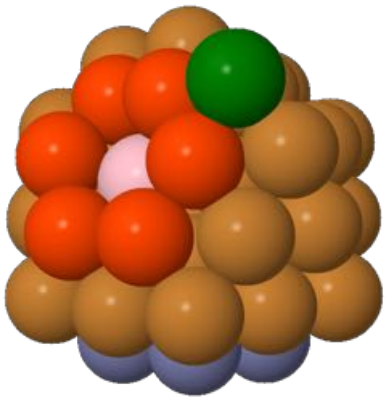


Figure 3.21: Energy = $E_{Cu_{55}Ico}$ + 1.42 eV; (33-1-174)

3.1.22 34-1-132

- 5 fold corner, rosette and two 6 fold corners present

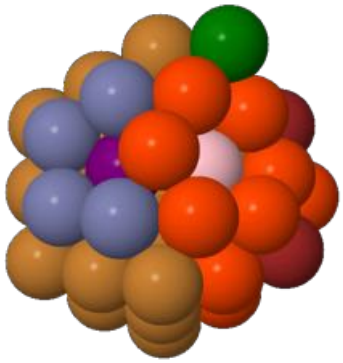


Figure 3.22: Energy = $E_{Cu_{55}Ico}$ + 1.43 eV; (34-1-132)

3.1.23 35-1-236

- Rosette and two 6 fold corners present

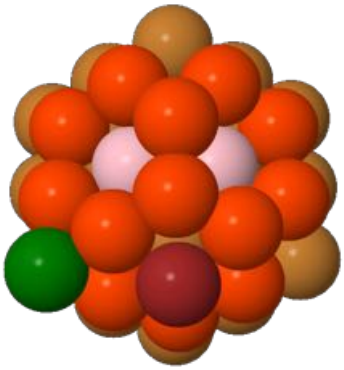


Figure 3.23: Energy = $E_{Cu_{55}Ico}$ + 1.43 eV; (35-1-236)

3.1.24 36-1-130

- two 5 fold vertex vacancies and two 6 fold corners present.

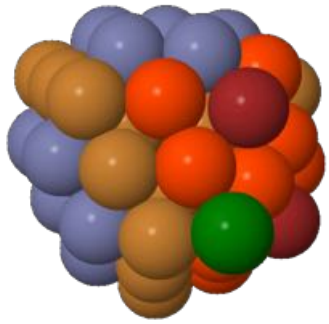


Figure 3.24: Energy = $E_{Cu_{55}Ico}$ + 1.45 eV; (36-1-130)

3.1.25 37-1-104

- One 5 fold vertex vacancy, one rosette and two 6 fold corners present.

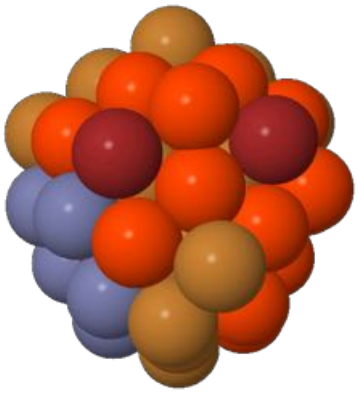
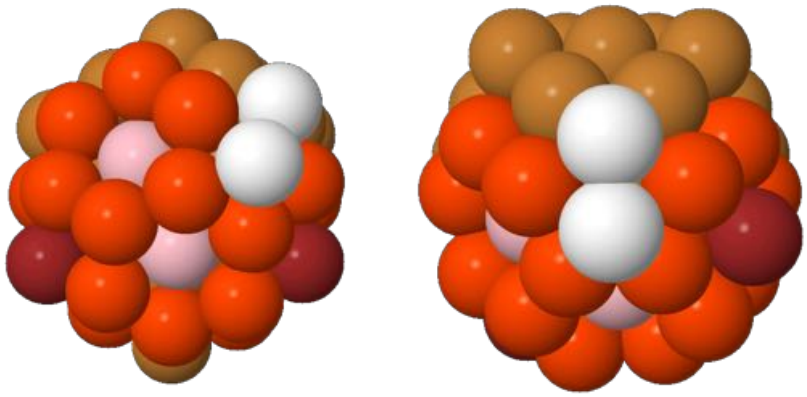


Figure 3.25: Energy = $E_{Cu_{55}Ico}$ + 1.46 eV; (37-1-104)

3.1.26 38-1-86

- Two rosette and two 6 fold corners precent
- The white atoms indicate two neighbouring 5 fold corners on the cluster.

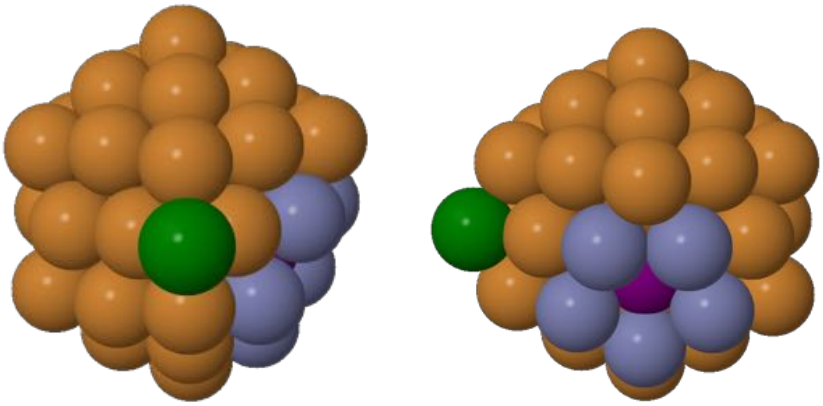


(a) (b) White = The neighbouring 5 fold vertices

Figure 3.26: Energy = $E_{Cu_{55}Ico}$ + 1.50 eV; (38-1-86)

3.1.27 39-1-213

- Move a 5 fold corner to an edge of a twisted isocahedron from Figure 3.9a. This cost less energy than to move a 5 fold corner for a perfect icosahedron. However we are moving the atom to a different type of face.



(a) (b)

Figure 3.27: Energy = $E_{Cu_{55}Ico}$ + 1.51 eV = $E_{Cu_{55}TwIco}$ + 0.54 eV; (39-1-213)

3.1.28 40-1-295

- An atom is moved an edge between two 5 fold corners.

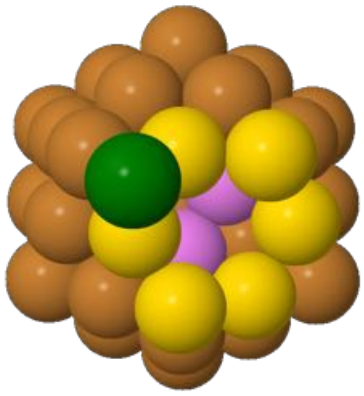


Figure 3.28: Energy = $E_{Cu_{55}Ico}$ + 1.52 eV; (40-1-295)

3.2 Low Energy Structures of the Cu_{78} Cluster

3.2.1 DFT Verification

Figure 3.29 shows the energy of the 18 lowest energy Cu_{78} structures compared to the lowest energetic structure (LES) where the energy of the structures are desribed by the Gupta Potential (yellow dots). These structure were further optimised by DFT using the PBE (blue dots) and PBEsol functionals (red dots). Points to note:

- The genetic algorithm (where the energy of the structure is defined by the Gupta potential) found that 3-4-14 was the lowest energy structure (LES) for Cu_{78}.
- However DFT calculations (using the PBEsol functional) found that 15-3-3629 was the LES for Cu_{78}.

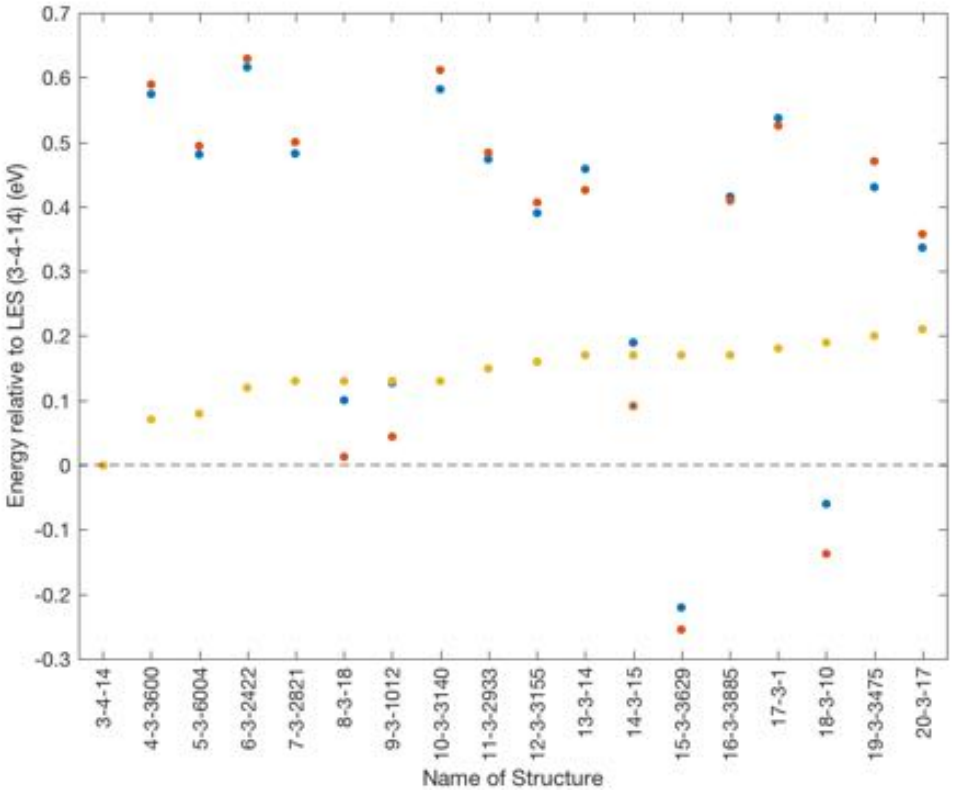


Figure 3.29: The energies of the 18 lowest energetic Cu_{78} structures compared to the LES obtained by the Genetic Algorithm (Energies described by the Gupta Potential) (yellow dots) and DFT-verification results, described by PBE (blue dots) and PBEsol (red dots).

3.2.2 3-4-14

- The lowest energetic structure of Cu_{78} has a centre motif of a perfect icosahedron Cu_{55} cluster which is additionally covered by shell of Cu atoms (Figure 3.30). This shell has the form of a perfect icosahedron.
- The shell of this structure of Cu_{78} is symmetrical.

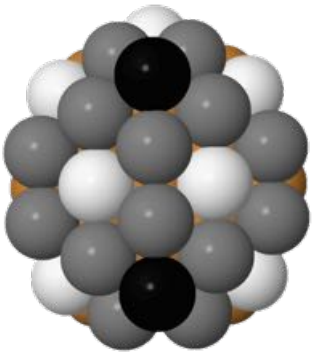
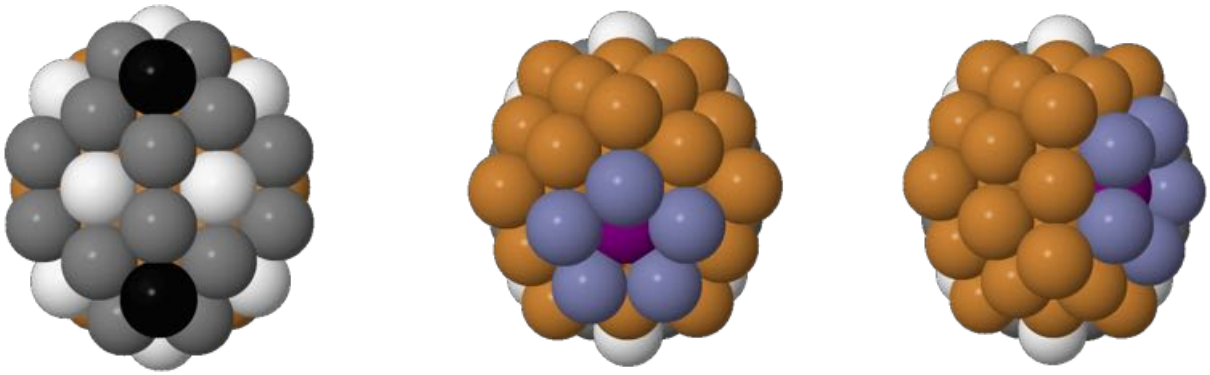


Figure 3.30: black = 5 fold corner on the shell, grey = edge on the shell, white = face of shell. Energy = -234.81 eV = $E_{Cu_{78}LES}$; Average Energy per Atom = -3.01038 eV/Atom (5dp); (3-4-14)

- Other higher energy forms are of this structure but with different defects.

3.2.3 4-3-3600 and 5-3-6004

- The next energetic cluster involves moving a 5 fold corner from the inner isocahedron and moving it to the shell (Figure 3.31).



(a) Shell of modifed structure. (4-3-3600). black = 5 fold corner, grey = edge of a perfect icosahedral, white = face of a perfect icosahedral.

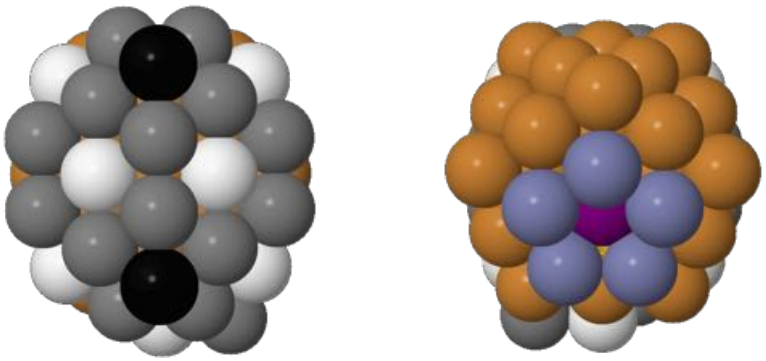
(b) Inner structure of one modifed Cu_{78} structure. Energy = $E_{Cu_{78}LES}$ + 0.07 eV; (4-3-3600)

(c) Inner structure of another differently modifed Cu_{78} structure. Different corner is used. Energy = $E_{Cu_{78}LES}$ + 0.08 eV; (5-3-6004)

Figure 3.31

3.2.4 6-3-2422

- Similar to 4-3-3600 and 5-3-6004.
- Does not matter if you move the 5-fold corner to a face or an edge of the outer shell (Figure 3.32).
- These are energetically equivalent structures.



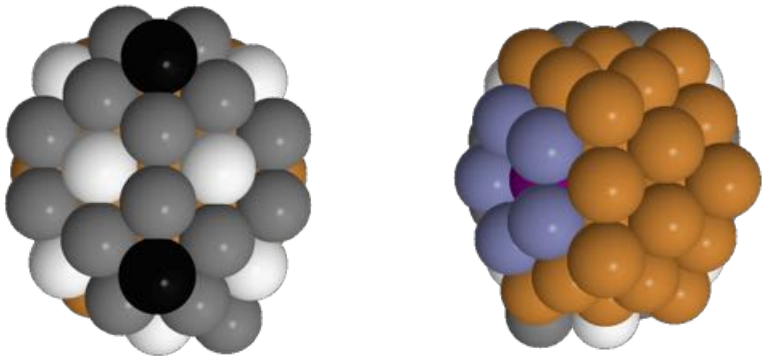
(a) black = 5 fold corner, grey = edge of a perfect icosahedral, white = face of a perfect icosahedral.

(b)

Figure 3.32: Energy = $E_{Cu_{78}LES}$ + 0.12 eV; (6-3-2422)

3.2.5 7-3-2821

- Similar to 4-3-3600 and 5-3-6004.
- Does not matter if you move the 5-fold corner to a face or an edge of the outer shell (Figure 3.33).
- These are energetically equivalent structures.



(a) black = 5 fold corner, grey = edge of a perfect icosahedral, white = face of a perfect icosahedral.

(b)

Figure 3.33: Energy = $E_{Cu_{78}LES}$ + 0.12 eV; (7-3-2821)

3.2.6 8-3-18

- The top and bottom (in red and green) have the same structure as the corner sections of a icosahedron. These sections have been shifted so they are not exactly at opposite poles of the structure.

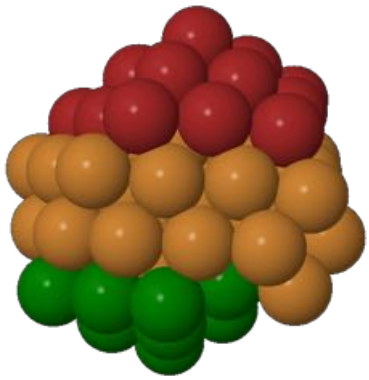


Figure 3.34: Red = One pole of an icosahedron, Green = Another pole of an isocahedron. Energy = $E_{Cu_{78}LES}$ + 0.13 eV; (9-3-1012)

3.2.7 9-3-1012

- We also see structures where the location of the top and bottom corner sections of a icosahedron are shifted, i.e. do not line up along a pole (Figure 3.35). These are more energetic than forming a perfect isocahedron by 0.13 eV.

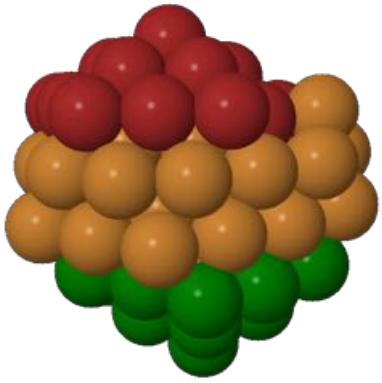
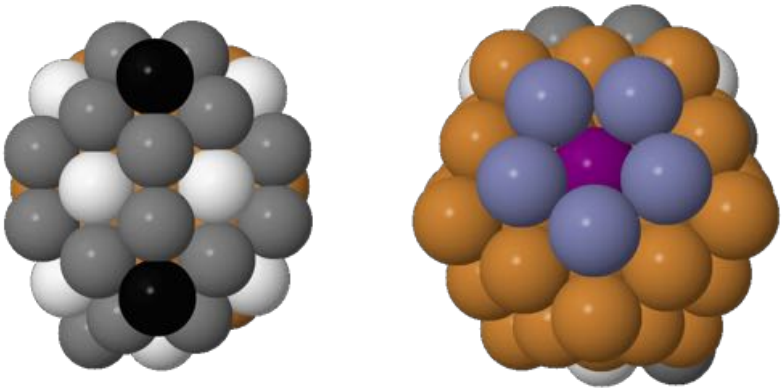


Figure 3.35: Red = One pole of an icosahedron, Green = Another pole of an isocahedron. Energy = $E_{Cu_{78}LES}$ + 0.13 eV; (9-3-1012)

3.2.8 10-3-3140

- 5 fold vertex on the inner icosahedron of the structure and moved to the shell.



(a) (b)

Figure 3.36: Red = One pole of an icosahedron, Green = Another pole of an isocahedron. Energy = $E_{Cu_{78}LES}$ + 0.13 eV; (9-3-1012)

3.2.9 11-3-2933

- A more energetic motif to form is to move a 5 fold corner from the shell to a edge (Figure 3.37).
- This is more energetic than moving a 5 fold corner from the inner icosahedral by 0.07 eV.
- Energetically better to distort the inner isocahedron than the outer shell.

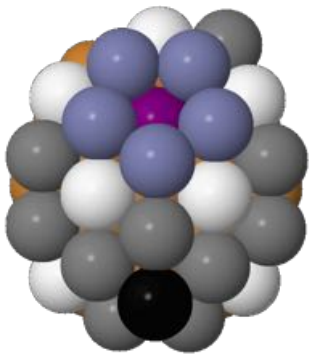
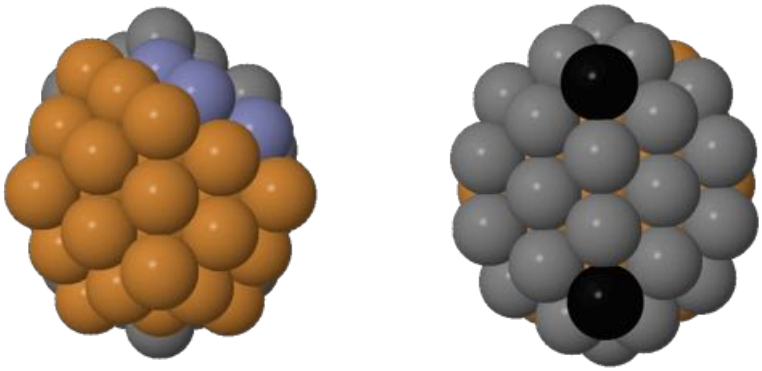


Figure 3.37: Energy = $E_{Cu_{78}LES}$ + 0.15 eV; (11-3-2933)

3.2.10 12-3-3155

- A 5 fold corner atom from the inner isocahedron has moved to the outer shell.

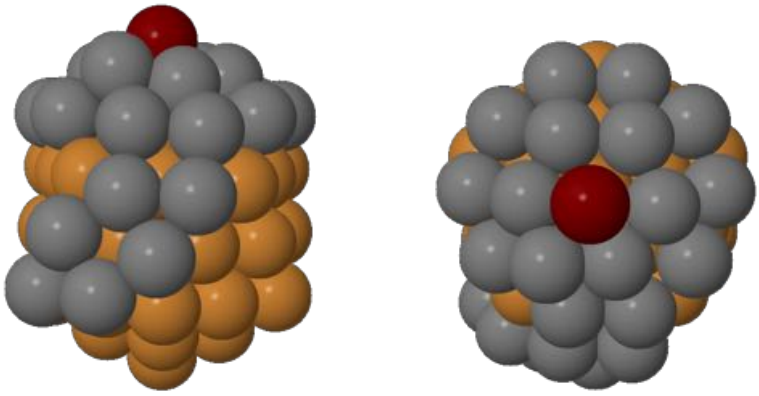


(a) (b)

Figure 3.38: Energy = $E_{Cu_{78}LES}$ + 0.16 eV; (12-3-3155)

3.2.11 13-3-14

- Contains a inner icosahedron with extra Cu atoms around the icosahedron.
- These extra Cu atoms around the icosahedron have formed a 6 fold vertex.
- Looks a bit like Jebediah Springfield's (from the Simpsons) hat.

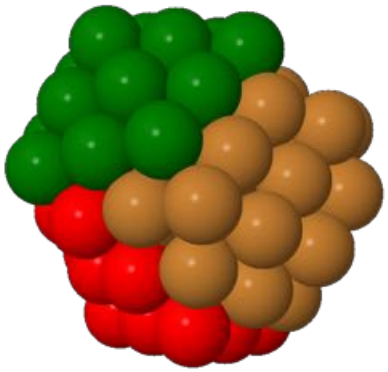


(a) (b)

Figure 3.39: Grey = these extra Cu atoms around the icosahedron. Red = a distorted 6-fold vertex. Energy = E_{Cu_8LES} + 0.17 eV; (13-3-14)

3.2.12 14-3-15

- Contains two icosahedron "tops" half sandwiching a group of amorphrous Cu atoms

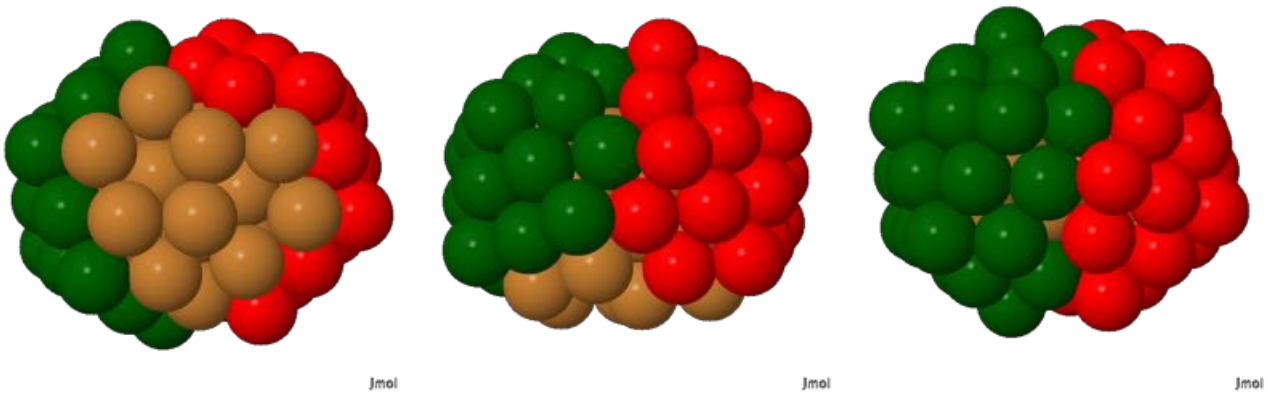


(a) Cluster 14-3-15

Figure 3.40: Red = One of the icosahedron "tops"; Green = Another of the icosahedron "tops". Energy = E_{Cu_8LES} + 0.17 eV; (14-3-15)

3.2.13 15-3-3629

- Contains two icosahedron "tops" half sandwiching a group of amorphrous Cu atoms

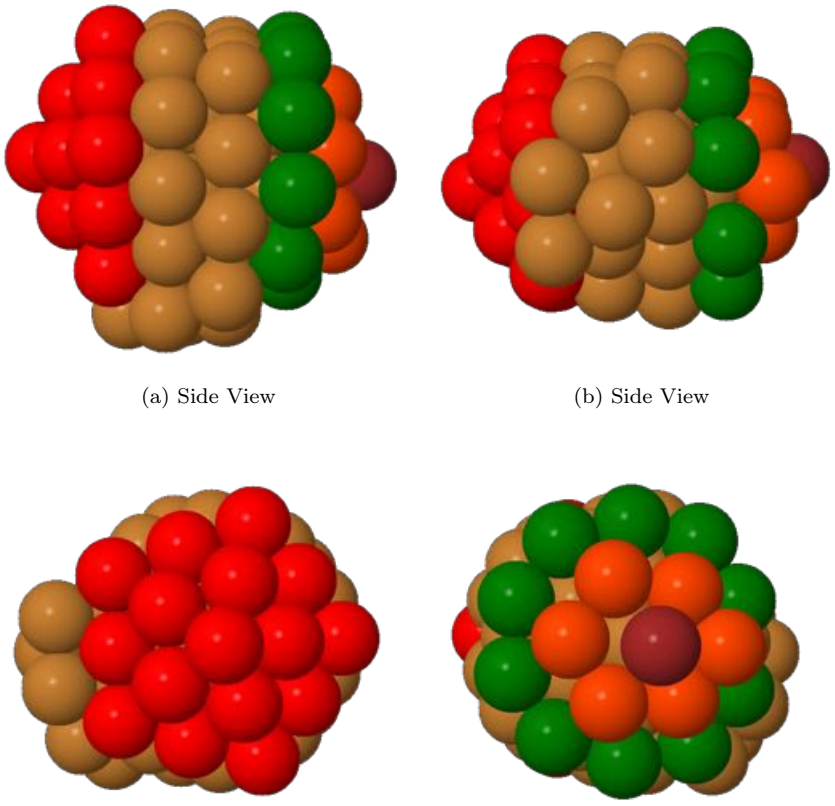


(a) (b) (c)

Figure 3.41: Red = One of the icosahedron "tops"; Green = Another of the icosahedron "tops". Energy = $E_{Cu_{78}LES}$ + 0.17 eV; (15-3-3629)

3.2.14 16-3-3885

- This is like structures 14-3-15 and 15-3-3629, containing two icosahedron-like "tops" half sandwiching an order array of Cu atoms about the belly of the structure.
- One of the icosahedron-like faces contains a 6 fold vertex.



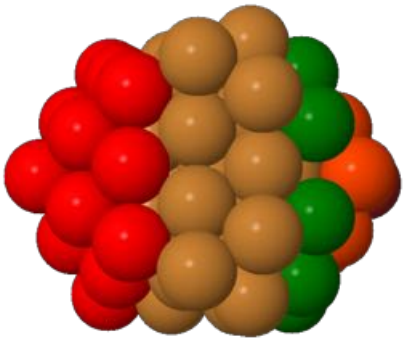
(a) Side View (b) Side View

(c) Top face (d) Bottom face. Dark Red = 6 fold vertex

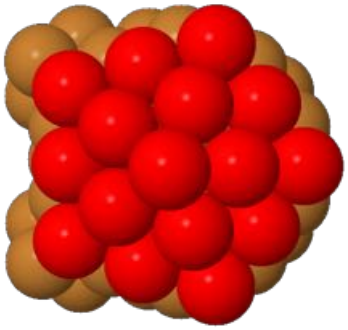
Figure 3.42: Red = One of the icosahedron "tops"; Green = Another of the icosahedron "tops". Energy = $E_{Cu_{78}LES}$ + 0.17 eV; (16-3-3885)

3.2.15 17-3-1

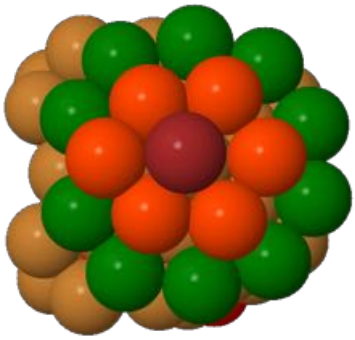
- This is like structures 14-3-15 and 15-3-3629, containing two icosahedron-like "tops" half sandwiching an order array of Cu atoms about the belly of the structure.
- One of the icosahedron-like faces contains a 6 fold vertex.
- It also contains two wing-like sets of Cu atoms on the surface of the cluster (not coloured in sorry about slightly visible in Figure 3.43a and observable around the belt of the cluster in Figures 3.43b and 3.43c).



(a)



(b) Top face

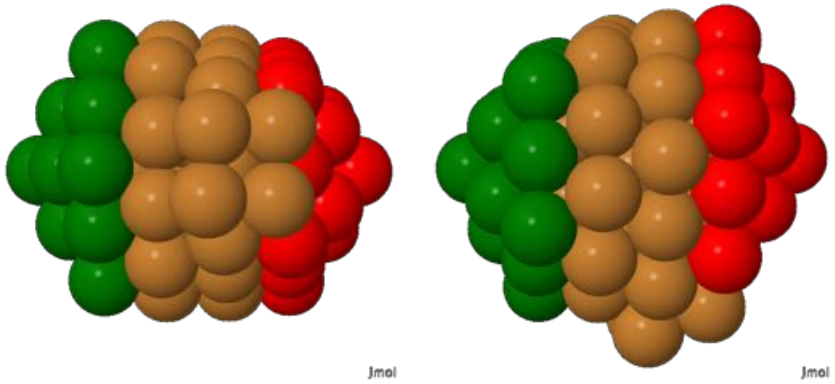


(c) Bottom face. Dark Red = 6 fold vertex

Figure 3.43: Red = One of the icosahedron "tops"; Green = Another of the icosahedron "tops". Energy = $E_{Cu_7 8 LES}$ + 0.18 eV; (17-3-1)

3.2.16 18-3-10

- This is like structures 14-3-15 and 15-3-3629, containing two icosahedron-like "tops" half sandwiching an order array of Cu atoms about the belly of the structure.

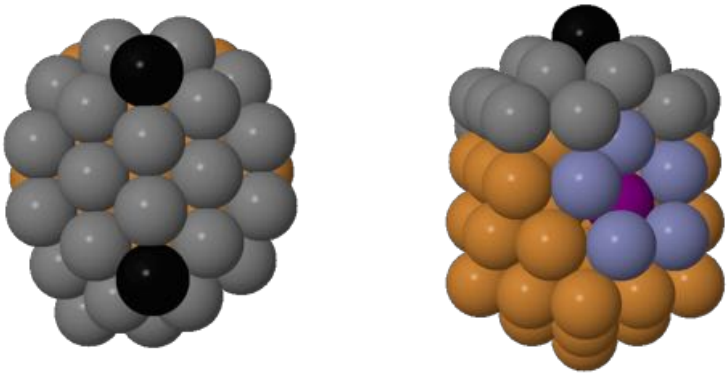


(a) Bottom View (b) Side View

Figure 3.44: Red = One of the icosahedron "tops"; Green = Another of the icosahedron "tops". Energy = $E_{Cu_7 8 LES}$ + 0.19 eV; (18-3-10)

3.2.17 19-3-3475

- The general structure is an elongated like icosahedron.
- A 5 fold corner atom from the inner isocahedron has moved to the outer shell.

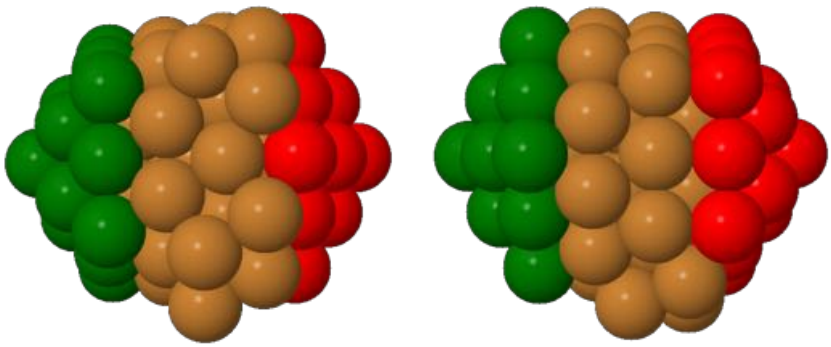


(a) (b)

Figure 3.45: Energy = $E_{Cu_7 8 LES}$ + 0.20 eV; (19-3-3475)

3.2.18 20-3-17

- This is like structures 14-3-15 and 15-3-3629, containing two icosahedron-like "tops" half sandwiching an order array of Cu atoms about the belly of the structure.



(a) (b)

Figure 3.46: Red = One of the icosahedron "tops"; Green = Another of the icosahedron "tops". Energy = $E_{Cu_{78}LES}$ + 0.21 eV; (19-3-3475)

3.3 Low Energy Structures of the Cu_{101} Cluster

3.3.1 DFT Verification

Figure 3.47 shows the energy of the 26 lowest energy Cu_{101} structures compared to the lowest energetic structure (LES) where the energy of the structures are described by the Gupta Potential (yellow dots). These structure were further optimised by DFT using the PBE (blue dots) and PBEsol functionals (red dots). Points to note:

- The genetic algorithm (where the energy of the structure is defined by the Gupta potential) found that dec231 was the lowest energy structure (LES) for Cu_{101}.
- However DFT calculations (using the PBEsol functional) found that 8-3-2764 was the LES for Cu_{101}.
- DFT calculations (using the PBE functional) found that 8-3-2764 was the LES for Cu_{101}. The next lowest structure as calculated by PBE was 1-3-1558. The relative energy compared to dec231 for 8-3-2764 was -1.30 eV and for 1-3-1558 was -1.29 eV.

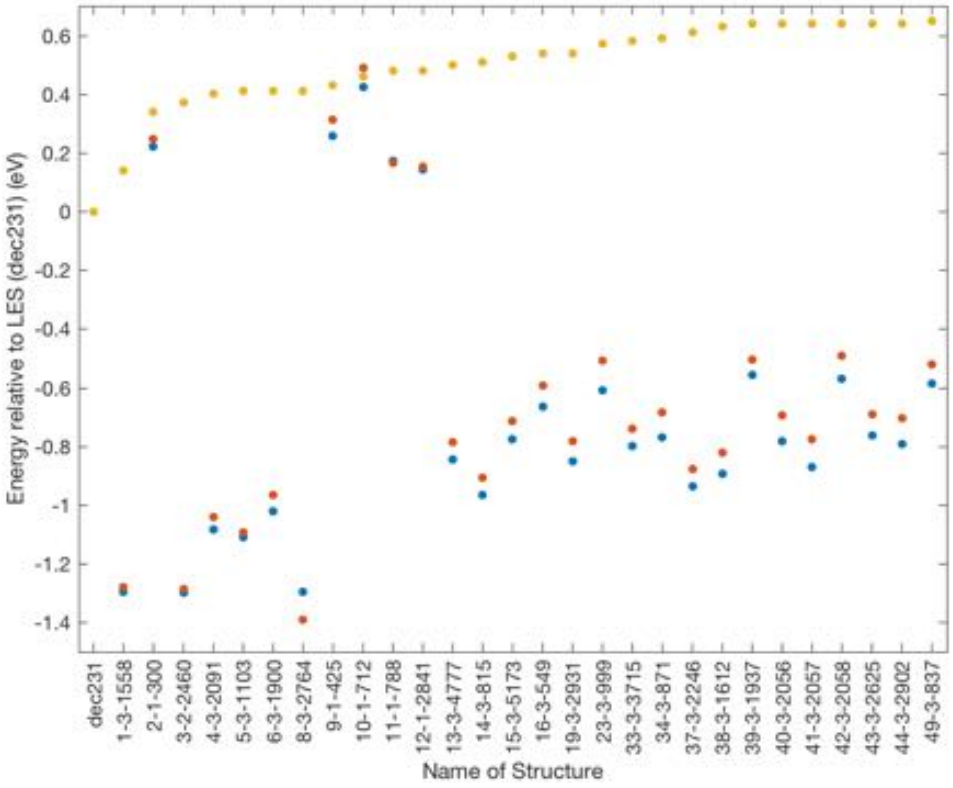
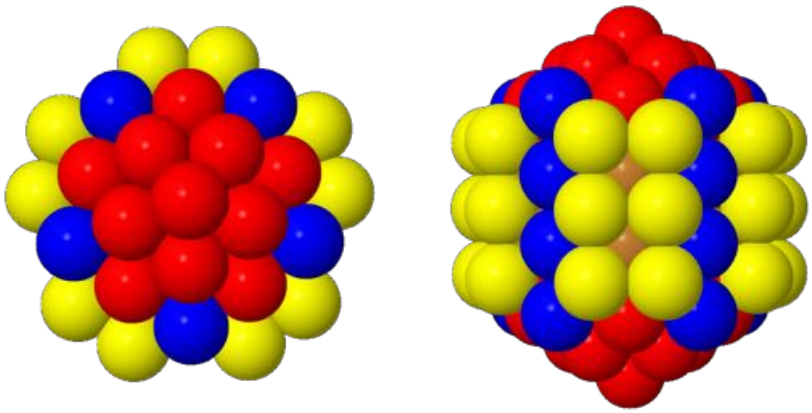


Figure 3.47: The energies of the 26 lowest energetic Cu_{101} structures compared to the LES obtained by the Genetic Algorithm (Energies described by the Gupta Potential) (yellow dots) and DFT-verification results, described by PBE (blue dots) and PBEsol (red dots).

3.3.2 Decahedron (2,3,1)

- This structure is a (p=2,q=3,r=1) decahedron, where
  - p: Number of atoms on the (100) facets perpendicular to the five fold axis.
  - q: Number of atoms on the (100) facets parallel to the five fold axis.
  - r: Depth of the Marks re-entrence at the pentagon corners.
- This cluster was not found using the Genetic Algorithm.

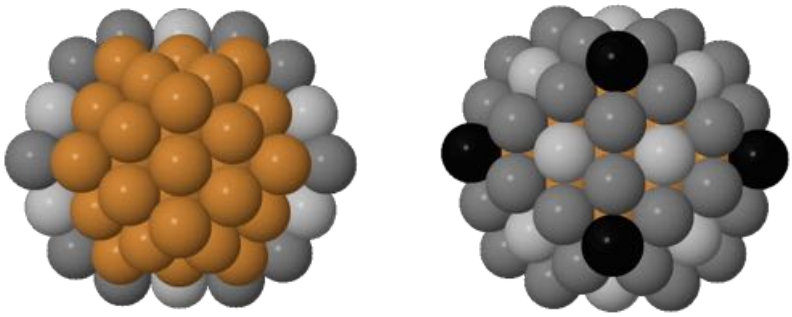


(a) Top View (b) Side View

Figure 3.48: Red = Top of a decahedron; Yellow = (100) faces about the body of the decahedron; Blue = column of atoms inbetween the (100) faces (the Marks re-entrence) . Energy = -309.29 = $E_{Cu_{101}LES}$; Average Energy per Atom = -3.06089 eV/Atom (5dp) (1-3-1558)

3.3.3 1-3-1558

- The lowest energetic structure of Cu_{101} has a centre motif of a perfect icosahedron Cu_{55} cluster which is additionally covered by a shell of Cu atoms (Figure 3.49). This shell has the form of a perfect icosahedron.
- The shell of this structure of Cu_{101} is symmetrical.
- This is the lowest energetic structure (LES) as obtained by the Genetic Algorithm.



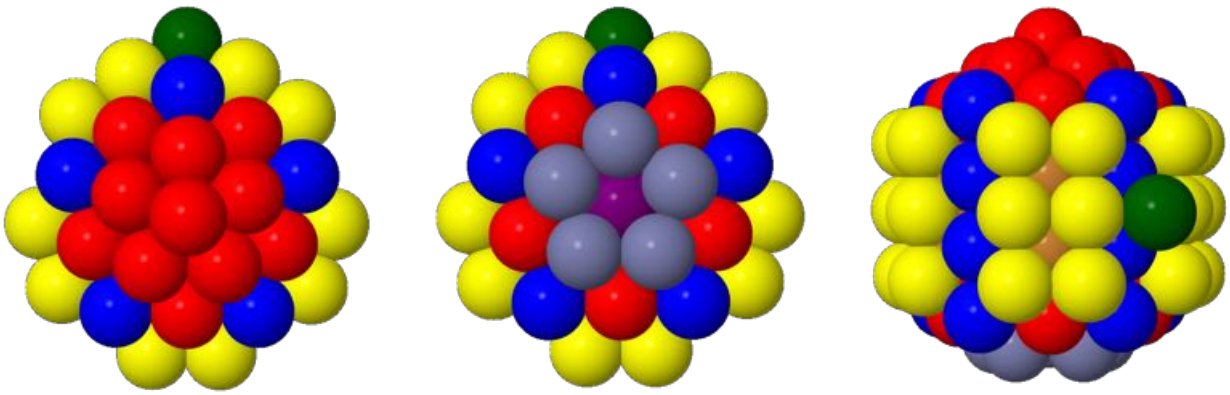
(a) (b)

Figure 3.49: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell. Energy = -309.15 eV = $E_{Cu_{101}LES}$ + 0.14 eV; Average Energy per Atom = -3.06089 eV/Atom (5dp) (1-3-1558)

- Other higher energy forms are of this structure but with different defects.

3.3.4 2-1-300

- This structure is a (p=2,q=3,r=1) decahedron, where
  - p: Number of atoms on the (100) facets perpendicular to the five fold axis.
  - q: Number of atoms on the (100) facets parallel to the five fold axis.
  - r: Depth of the Marks re-entrence at the pentagon corners.
- One Cu atom has be removed from a 5 fold corner and placed on a Marks re-entrence face (between two (100) faces).
- This forms a 5 fold vertex vacancy as well.

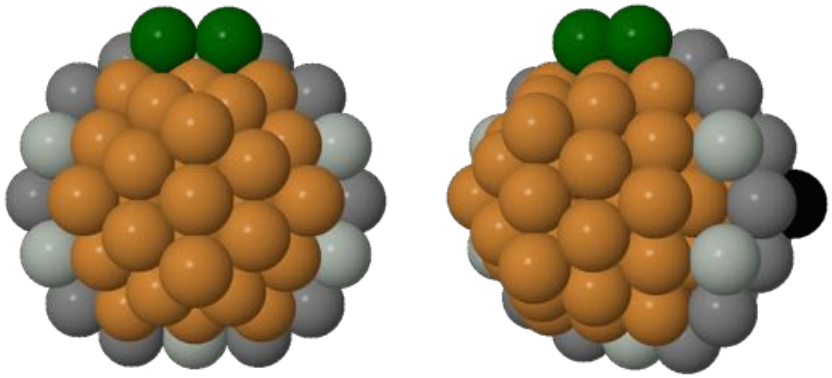


(a) (b) (c)

Figure 3.50: Red = Top of a decahedron; Yellow = (100) faces about the body of the decahedron; Blue = column of atoms inbetween the (100) faces (the Marks re-entrence); Purple = a 5-fold vertex vacancy; Dark green = displaced Cu atom; Energy = $E_{Cu_{101}LES}$ + 0.34 eV; (2-3-2019)

3.3.5 3-2-2460

- Here two Cu atoms have been displaced (dark green) from corners of the lining of the outer shell (as can be seen in Figure 3.51b).
- Compared to 4-3-2019, we get a stabilisation from grouping the two corner Cu atoms.



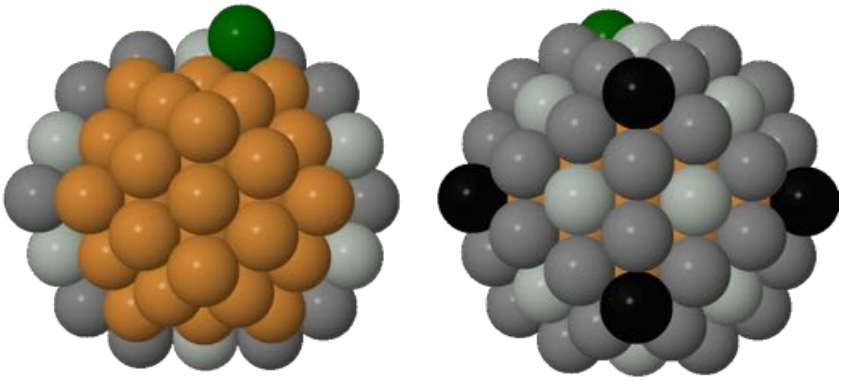
(a)

(b) The corner of the lining of the shell has been removed.

Figure 3.51: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Dark green = A displaced Cu Atom. Energy = $E_{Cu_{101}LES}$ + 0.37 eV; (3-2-2460)

3.3.6 4-3-2091

- A corner Cu atom of the lining of the shell is moved to another area next to the shell.
- Note that this structure is similar to 3-2-2460 except only one Cu atom has been displaced in this structure.
- More energetic to keep a Cu atom on the corner of the lining of the shell compared to 3-2-2460.



(a) (b)

Figure 3.52: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Dark green = A displaced Cu Atom. Energy = $E_{Cu_{101}LES}$ + 0.40 eV; (4-3-2019)

3.3.7 5-3-1103

- A corner Cu atom of the lining of the shell is moved to another area next to the shell.

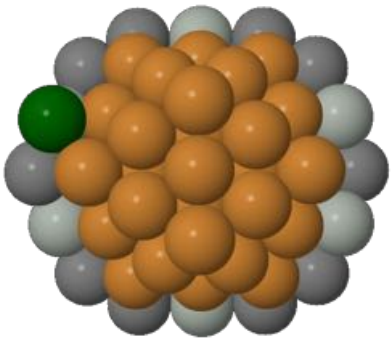


Figure 3.53: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom.Energy = $E_{Cu_{101}LES}$ + 0.41 eV; (5-3-1103)

3.3.8 6-3-1900

- A corner Cu atom of the lining of the shell is moved to another area next to the shell.
- An isomer of 5-3-1103

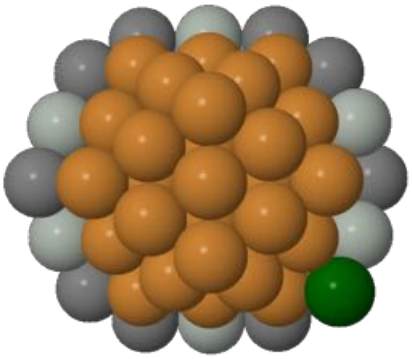
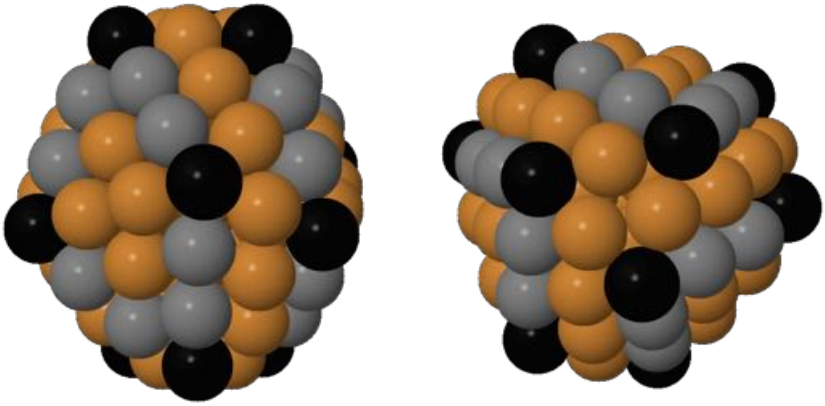


Figure 3.54: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom.Energy = $E_{Cu_{101}LES}$ + 0.41 eV; (6-3-1900)

3.3.9 8-3-2764

- This is a new shape which contains a C_3 axis and looks like a rugby ball.
- Appologies for current color scheme.



(a) Side View (b) C_3 View

Figure 3.55: Black = a 5 fold corner; Grey, the outline of a diamond shape. Energy = $E_{Cu_{101}LES}$ + 0.41 eV; (8-3-2764)

3.3.10 9-1-425

- Very similar to structure 2-1-300.
- Displaced Cu atom (dark green) is located on a different part of the Marks re-entrence compared to structure 2-1-300.

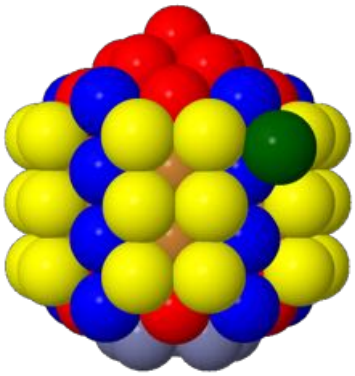


Figure 3.56: Red = Top of a decahedron; Yellow = (100) faces about the body of the decahedron; Blue = column of atoms inbetween the (100) faces (the Marks re-entrence); Purple = a 5-fold vertex vacancy; Dark green = displaced Cu atom; Energy = $E_{Cu_{101}LES}$ + 0.43 eV; (9-1-425)

3.3.11 10-1-712

- Very similar to structure 2-1-300.
- Two displaced Cu atom (dark green) is located on the Marks re-entrence.
- This creates two 5-fold vertex vacancies at each end of the decahedron.

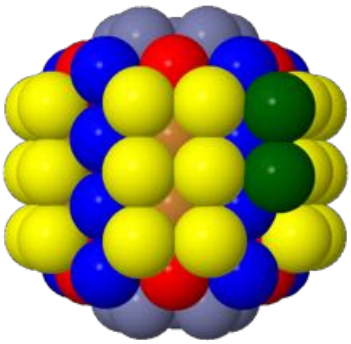
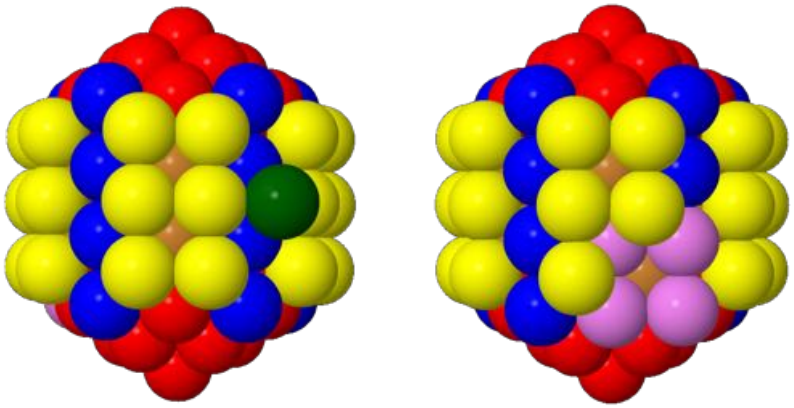


Figure 3.57: Red = Top of a decahedron; Yellow = (100) faces about the body of the decahedron; Blue = column of atoms inbetween the (100) faces (the Marks re-entrence); Purple = a 5-fold vertex vacancy; Dark green = displaced Cu atom; Energy = $E_{Cu_{101}LES}$ + 0.46 eV; (10-1-712)

3.3.12 11-1-788

- Very similar to structure 2-1-300.
- A Cu atom (Dark green) has moved from a (100) face to the Marks re-entrence.
- This forms a vacant (100) site (pink).



(a) (b)

Figure 3.58: Red = Top of a decahedron; Yellow = (100) faces about the body of the decahedron; Blue = column of atoms inbetween the (100) faces (the Marks re-entrence); Purple = a 5-fold vertex vacancy; Dark green = displaced Cu atom; Pink = an exposed (100) face. Energy = $E_{Cu_{101}LES}$ + 0.48 eV; (11-1-788)

3.3.13 12-1-2841

- Very similar to structure 2-1-300.
- A Cu atom (Dark green) has moved from a (100) face to the Marks re-entrence.
- This forms a vacant (100) site (pink).
- Similar to 10-1-788, however the vacant (100) site is in a different location.

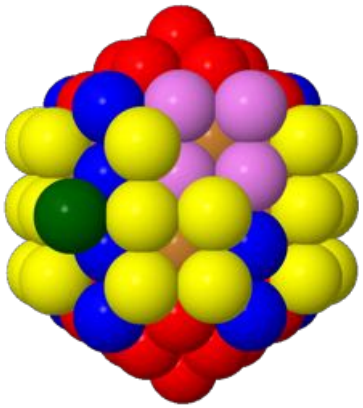


Figure 3.59: Red = Top of a decahedron; Yellow = (100) faces about the body of the decahedron; Blue = column of atoms inbetween the (100) faces (the Marks re-entrence); Purple = a 5-fold vertex vacancy; Dark green = displaced Cu atom; Pink = an exposed (100) face. Energy = $E_{Cu_{101}LES}$ + 0.48 eV; (12-1-2841)

3.3.14 13-3-4777

- An atom of the lining of the shell has also been moved to another area of the shell lining.
- A 5 fold corner of the inner icosahedron is removed and placed at the edge of the outer shell.
- This cost energy to remove this Cu atom from a 5 fold vertex compared to a corner of the lining of the shell (comparing with 3-2-2460 and 4-3-2019)

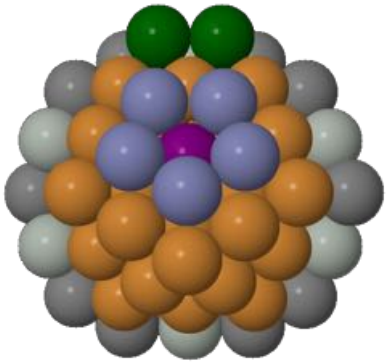


Figure 3.60: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy.Energy = $E_{Cu_{101}LES}$ + 0.50 eV; (13-3-4777)

3.3.15 14-3-815

- Two atoms of the lining of the shell has also been moved to another area of the shell lining.
- A 5 fold corner of the inner icosahedron is removed and placed at the edge of the outer shell.

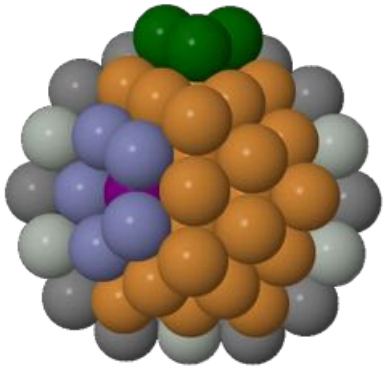


Figure 3.61: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{101}LES}$ + 0.51 eV; (14-3-815)

3.3.16 15-3-5173

- Here only a 5 fold corner of the inner icosahedron has been removed and placed at the edge of the outer shell.

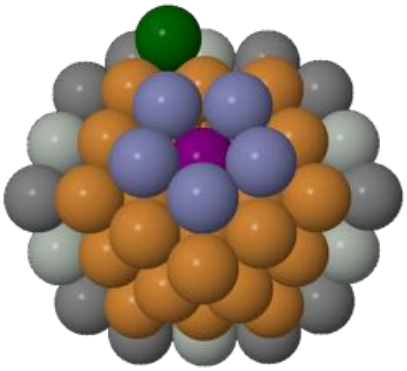


Figure 3.62: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{101}LES}$ + 0.53 eV; (15-3-5173)

3.3.17 16-3-549

- A 5 fold corner of the inner icosahedron is removed and placed at the edge of the outer shell.

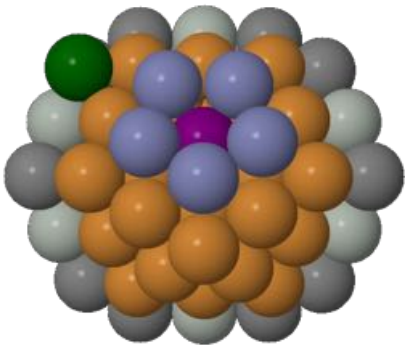
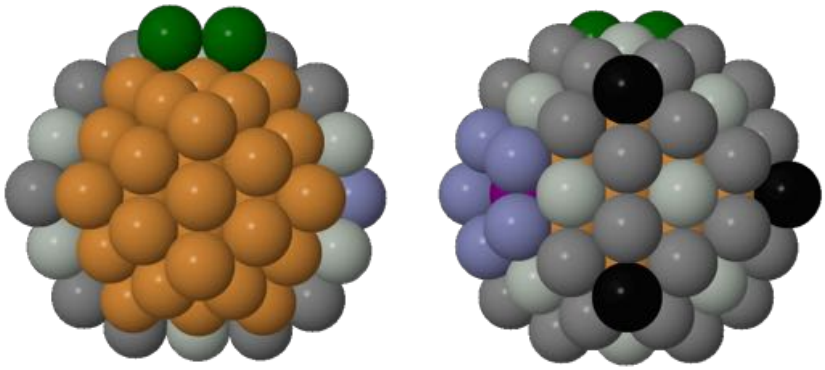


Figure 3.63: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy.Energy = $E_{Cu_{101}LES}$ + 0.54 eV; (16-3-549)

3.3.18 19-3-2931

- The corner of the outer shell is removed and placed at the edge of the outer shell.
- An atom of the lining of the shell has also been moved to another area of the shell lining.
- More energetic to move a 5 fold corner Cu atom from the shell than from the inner icosahedron (compared to 13-3-4777)

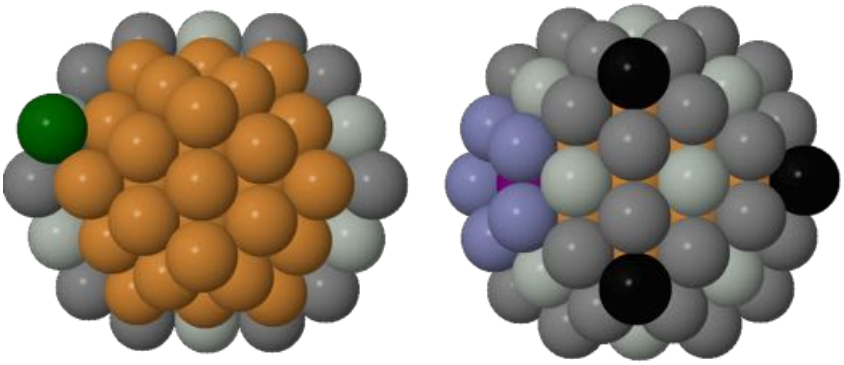


(a) (b)

Figure 3.64: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy.Energy = $E_{Cu_{101}LES}$ + 0.54 eV; (19-3-2931)

3.3.19 23-3-999

- The corner of the outer shell is removed and placed at the edge of the outer shell.
- More energetic to move a 5 fold corner Cu atom from the shell than from the inner icosahedron (compared to 15-3-5173)



(a) (b)

Figure 3.65: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy.Energy = $E_{Cu_{101}LES}$ + 0.57 eV; (17-3-999)

3.3.20 33-3-3715

- A corner of the inner icosahedron and an atom from the lining of the outer shell have been moved.
- The 5 fold corner which results lies next to the lining of the shell.

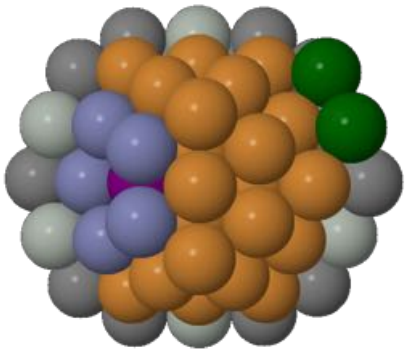


Figure 3.66: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{101}LES}$ + 0.58 eV; (33-3-3715)

3.3.21 34-3-871

- The lining of the outer shell has been rearranged.

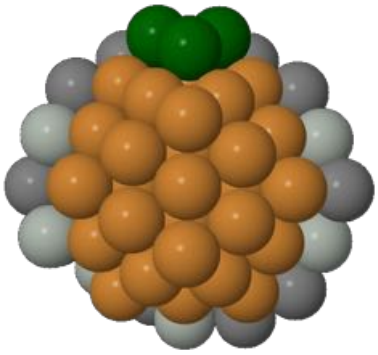


Figure 3.67: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Energy = $E_{Cu_{101}LES}$ + 0.59 eV; (34-3-871)

3.3.22 37-3-2246

- The lining of the outer shell has been rearranged.

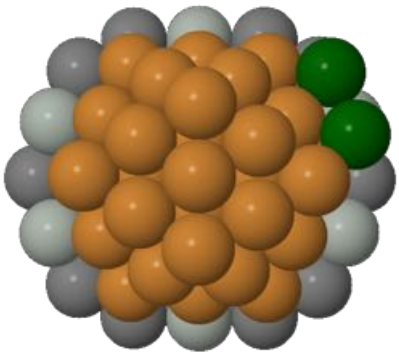


Figure 3.68: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Energy = $E_{Cu_{101}LES}$ + 0.61 eV; (37-3-2246)

3.3.23 38-3-1612

- The lining of the outer shell has been rearranged.

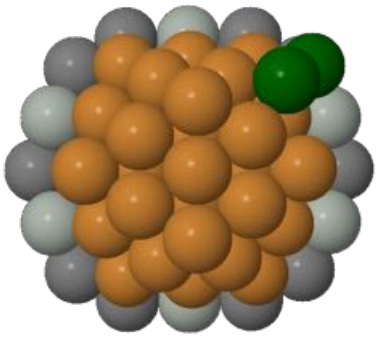
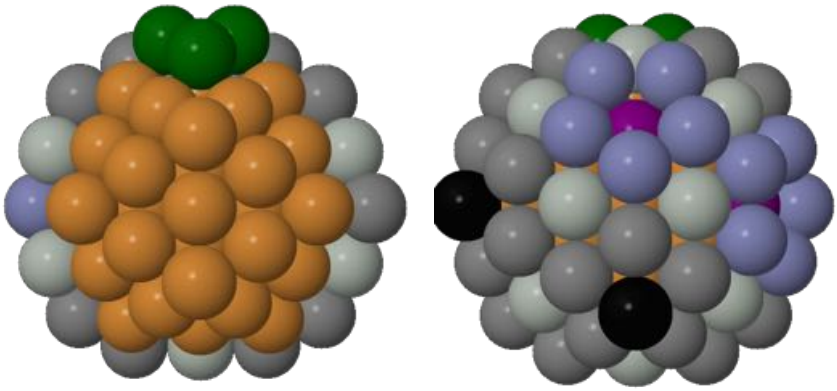


Figure 3.69: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom.Energy = $E_{Cu_{101}LES}$ + 0.63 eV; (38-3-1612)

3.3.24 39-3-1937

- An atom from the outer shell has been rearranged.
- Two atoms from the 5 fold corners of the outer shell have been moved to the lining of the outer shell.



(a) (b)

Figure 3.70: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{101}LES}$ + 0.64 eV; (39-3-1937)

3.3.25 40-3-2056

- The lining of the outer shell has been rearranged.

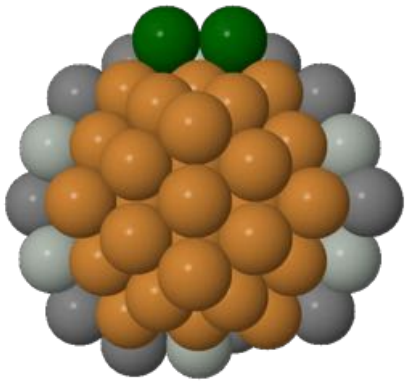


Figure 3.71: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Energy = $E_{Cu_{101}LES}$ + 0.64 eV; (40-3-2056)

3.3.26 41-3-2057

- The lining of the outer shell has been rearranged.

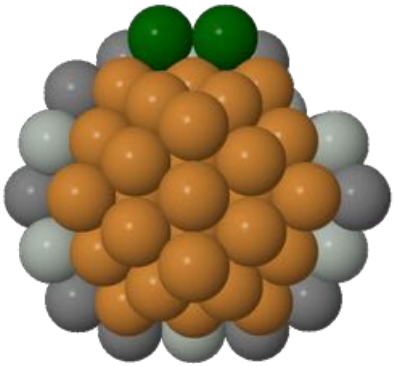


Figure 3.72: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Energy = $E_{Cu_{101}LES}$ + 0.64 eV; (41-3-2057)

3.3.27 42-3-2058

- Two atoms from the 5 fold corners of the inner ocisahedron have moved in the lining of the outer shell.

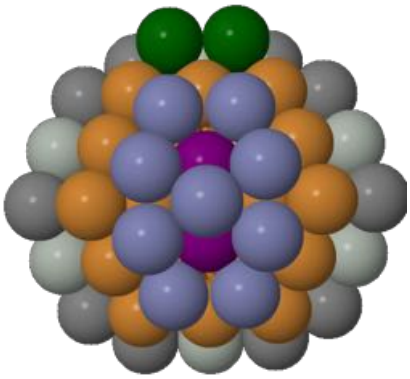


Figure 3.73: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{101}LES}$ + 0.64 eV; (42-3-2058)

3.3.28 43-3-2625

- The lining of the outer shell has been rearranged.

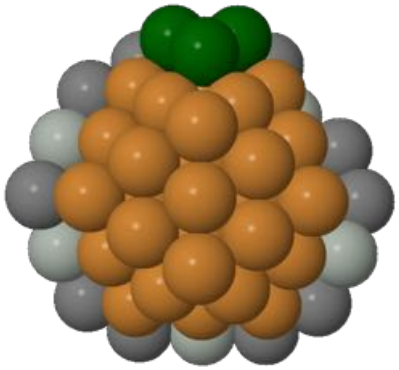


Figure 3.74: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Energy = $E_{Cu_{101}LES}$ + 0.64 eV; (43-3-2625)

3.3.29 44-3-2902

- The lining of the outer shell has been rearranged.

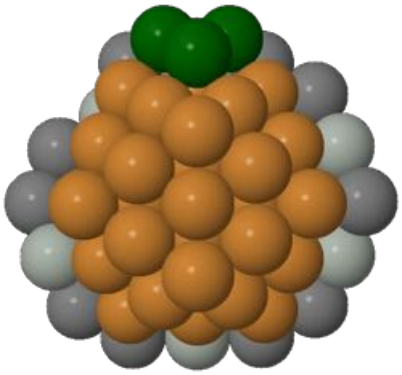


Figure 3.75: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Energy = $E_{Cu_{101}LES}$ + 0.64 eV; (44-3-2902)

3.3.30 49-3-837

- An atom from the lining of the outer shell has been rearranged.
- Two atoms from the 5 fold corners of the inner icosahedron have moved in the lining of the outer shell.

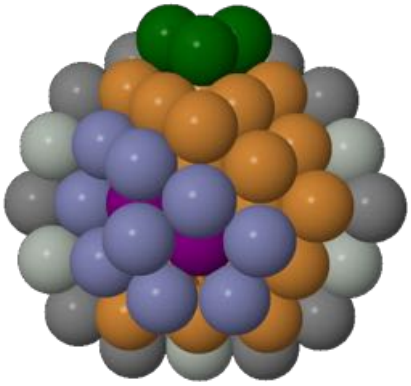


Figure 3.76: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{101}LES}$ + 0.65 eV; (49-3-837)

3.4 Low Energy Structures of the Cu_{124} Cluster

3.4.1 DFT Verification

Figure 3.77 (blue dots) shows the energy of the 12 lowest energy Cu_{124} structures compared to the lowest energetic structure (LES) where the energy of the structures are desribed by the Gupta Potential (yellow dots). These structure were further optimised by DFT using the PBE (blue dots) and PBEsol functionals (red dots). Points to note:

- The genetic algorithm (where the energy of the structure is defined by the Gupta potential) found that 1-3-7457 was the lowest energy structure (LES) for Cu_{124}.
- DFT calculations (using the PBE and PBEsol functional) found that 1-3-7457 was the LES for Cu_{124} as well.

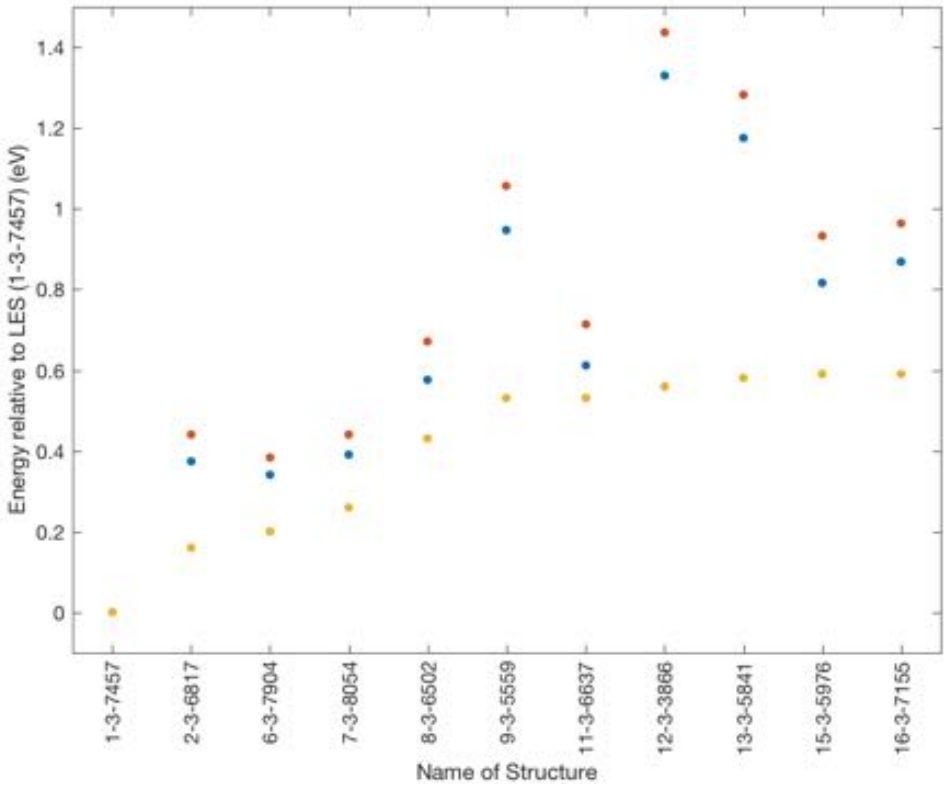
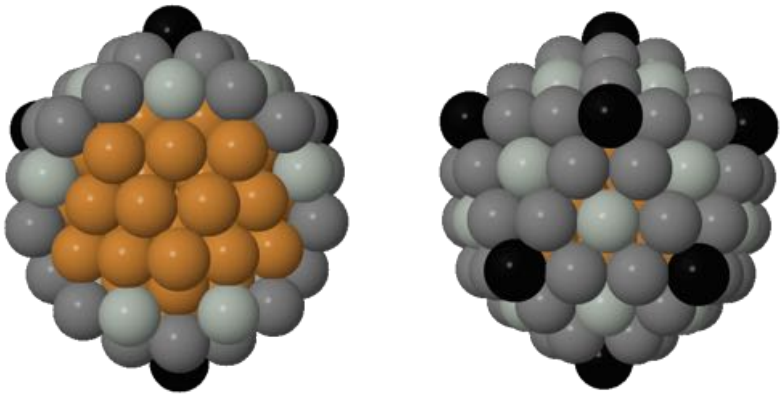


Figure 3.77: The energies of the 12 lowest energetic Cu_{124} structures compared to the LES obtained by the Genetic Algorithm (Energies described by the Gupta Potential) (yellow dots) and DFT-verification results, described by PBE (blue dots) and PBEsol (red dots).

3.4.2 1-3-7457

- The lowest energy structure for Cu_{124}.
- Has a inner icosahedron which is covered by a partial Cu shell.

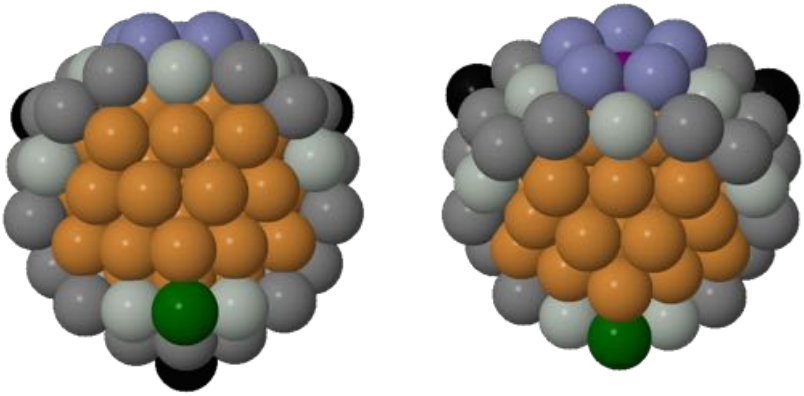


(a) (b)

Figure 3.78: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell. Energy = -383.90 eV = $E_{Cu_{124}LES}$; Average Energy per Atom = -3.09598 eV/Atom (5dp) (1-3-7457)

3.4.3 2-3-6817

- A five fold vertex atom is removed and placed in the lining of the shell.
- This produces a five fold vertex vacancy.

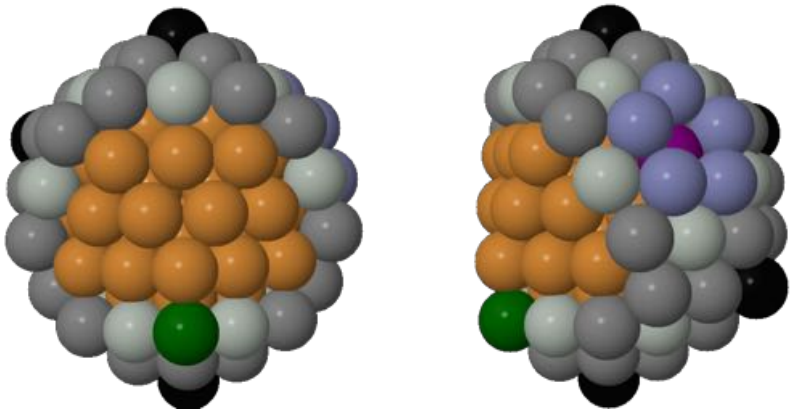


(a) (b)

Figure 3.79: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.16 eV. (2-3-6817)

3.4.4 6-3-7904

- A five fold vertex atom is removed and placed in the lining of the shell.
- This produces a five fold vertex vacancy.
- Differs from 2-3-6817 in the position of the 5 fold vertex on the shell.



(a) (b)

Figure 3.80: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.20 eV. (6-3-7904)

3.4.5 7-3-8054

- Lining of the shell have been rearranged.

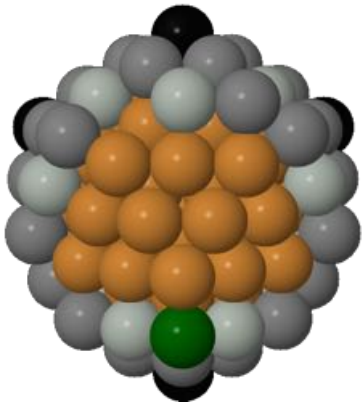


Figure 3.81: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Energy = $E_{Cu_{124}LES}$+ 0.26 eV. (7-3-8054)

3.4.6 8-3-6502

- A five fold vertex atom is removed and placed in the lining of the shell.
- This produces a five fold vertex vacancy.
- Placement of darkgreen Cu atom different from 2-3-6817

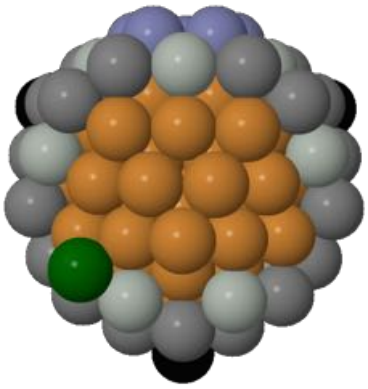


Figure 3.82: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.43 eV. (8-3-6502)

3.4.7 9-3-5559

- Three five fold vertex atoms are removed and placed in the lining of the shell.
- The shell lining of 9-3-5559 is unlike what we have seen in the lower energy Cu_{124} structures.

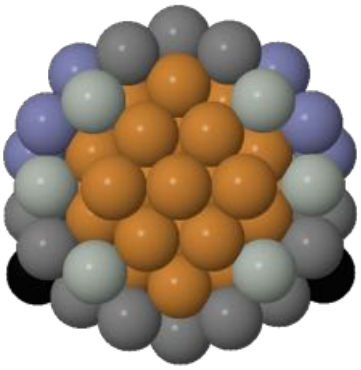


Figure 3.83: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.53 eV. (9-3-5559)

3.4.8 11-3-6637

- A five fold vertex atom is removed and placed in the lining of the shell.
- This produces a five fold vertex vacancy.
- Similar to 2-3-6817 with atom rearrangement.

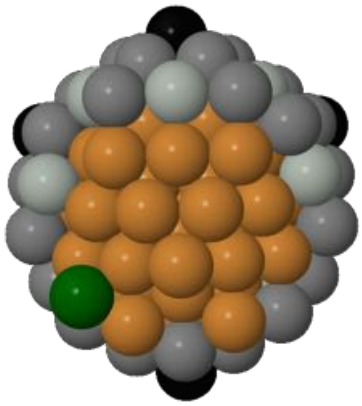
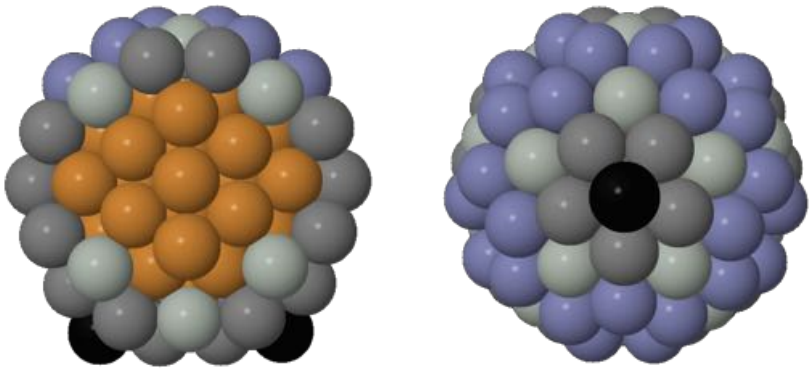


Figure 3.84: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom. Energy = $E_{Cu_{124}LES}$+ 0.53 eV. (11-3-6637)

3.4.9 12-3-3866

- 5 five fold vertex atoms are removed and placed in the lining of the shell.
- This produces a five fold vertex vacancy.
- Similar to 9-3-5559 with atom rearrangement.

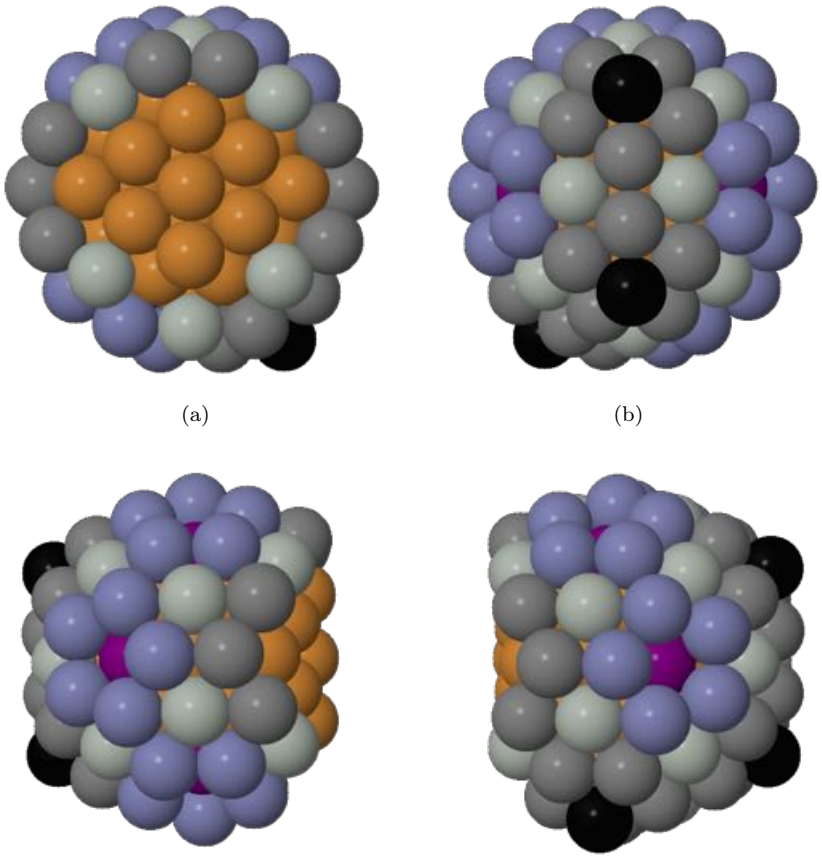


(a) (b)

Figure 3.85: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.58 eV. (12-3-3866)

3.4.10 13-3-5841

- 5 five fold vertex atoms are removed and placed in the lining of the shell.
- This produces a five fold vertex vacancy.
- Similar to 12-3-3866 with atom rearrangement.



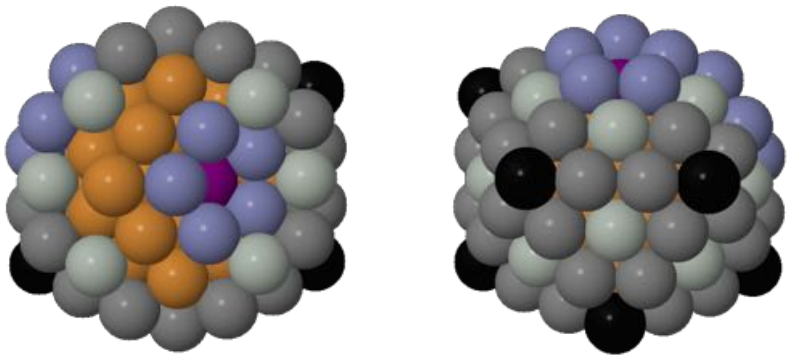
(a) (b)

(c) (d)

Figure 3.86: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.58 eV. (13-3-5841)

3.4.11 15-3-5976

- 3 five fold vertex atoms are removed and placed in the lining of the shell.
- One of these five fold vertices which is from the exposed area of the inner icosahedron.
- This produces a 3 fold vertex vacancy.
- Similar to 12-3-3866 with atom rearrangement.



(a) (b)

Figure 3.87: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.59 eV. (15-3-5976)

3.4.12 16-3-7155

- 3 five fold vertex atoms are removed and placed in the lining of the shell.
- One of these five fold vertices which is from the exposed area of the inner icosahedron.
- This produces a 3 fold vertex vacancy.

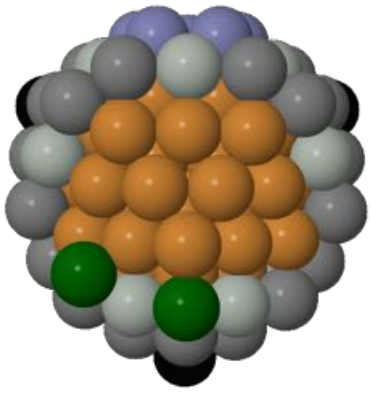


Figure 3.88: Black = 5 fold corner on the shell; Grey = edge on the shell; Pale grey = face of shell; Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{124}LES}$+ 0.59 eV. (16-3-7155)

3.5 Low Energy Structures of the Cu_{147} Cluster

3.5.1 DFT Verification

Figure 3.89 (blue dots) shows the energy of the 36 lowest energy Cu_{147} structures compared to the lowest energetic structure (LES) where the energy of the structures are desribed by the Gupta Potential (yellow dots). These structure were further optimised by DFT using the PBE (blue dots) and PBEsol functional (red dots).

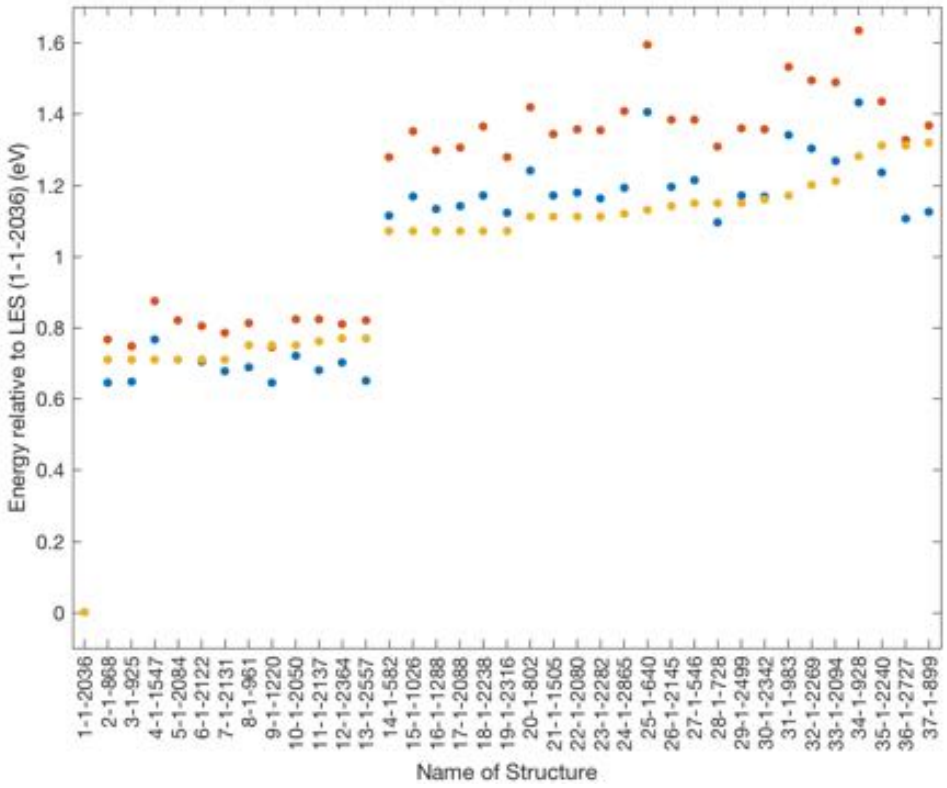


Figure 3.89: The energies of the 36 lowest energetic Cu_{147} structures compared to the LES obtained by the Genetic Algorithm (Energies described by the Gupta Potential) (yellow dots) and DFT-verification results, described by PBE (blue dots) and PBEsol (red dots).

3.5.2 1-1-2036

- This is the lowest energy structure of Cu_{147} as found, where the energy of the system is based on the Gupta Potential.
- Is a perfect Icosahedron

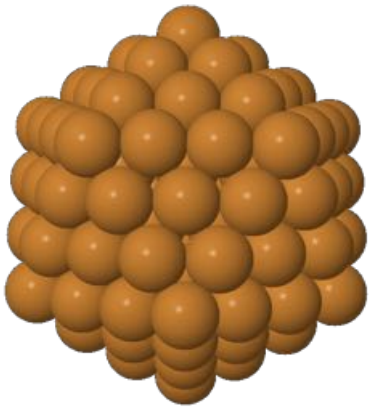


Figure 3.90: Energy = -460.47 eV = $E_{Cu_{147}LES}$; Average Energy per Atom = -3.13248 eV/Atom (5dp) (1-1-2036)

3.5.3 2-1-868

- A five fold vertex atoms are removed and placed on a face.
- Creates a five fold vertex vacancy.

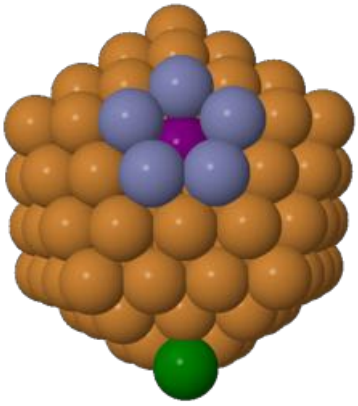


Figure 3.91: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy $E_{Cu_{147}LES}$+ 0.71 eV; (2-1-868)

3.5.4 3-1-925

- A five fold vertex atoms are removed and placed on a face.
- Creates a five fold vertex vacancy.
- Similar to 2-1-686

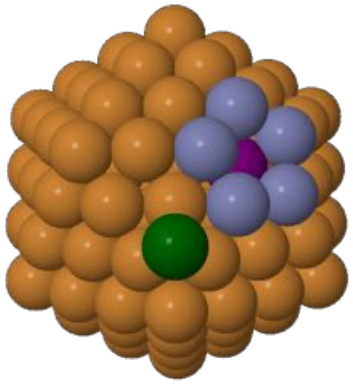


Figure 3.92: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy $E_{Cu_{147}LES}$+ 0.71 eV; (3-1-925)

3.5.5 4-1-1547

- A five fold vertex atoms are removed and placed on a face.
- Creates a five fold vertex vacancy.
- Similar to 2-1-686

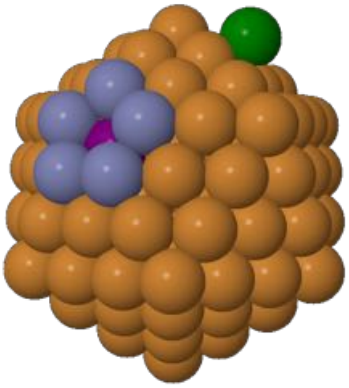


Figure 3.93: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy $E_{Cu_{147}LES}$+ 0.71 eV; (4-1-1547)

3.5.6 5-1-2084

- A five fold vertex atoms are removed and placed on a face.
- Creates a five fold vertex vacancy.
- Similar to 2-1-686

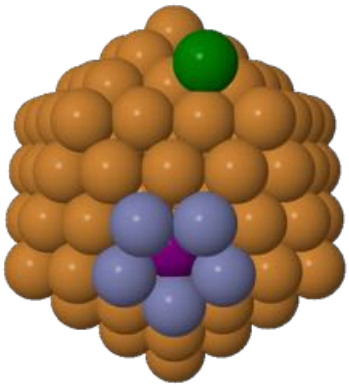


Figure 3.94: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy $E_{Cu_{147}LES}$+ 0.71 eV; (5-1-2084)

3.5.7 6-1-2122

- A five fold vertex atoms are removed and placed on a face.
- Creates a five fold vertex vacancy.
- Similar to 2-1-686

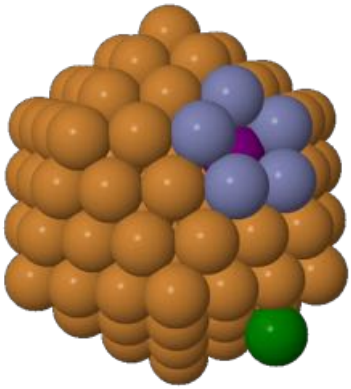


Figure 3.95: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy $E_{Cu_{147}LES}$+ 0.71 eV; (6-1-2122)

3.5.8 7-1-2131

- A five fold vertex atoms are removed and placed on a face.
- Creates a five fold vertex vacancy.
- Similar to 2-1-686

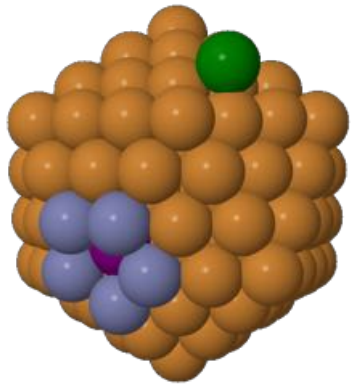


Figure 3.96: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy $E_{Cu_{147}LES}$+ 0.71 eV; (7-1-2131)

3.5.9 8-1-961

- A five fold vertex atoms are removed and placed on an edge.
- Creates a five fold vertex vacancy.

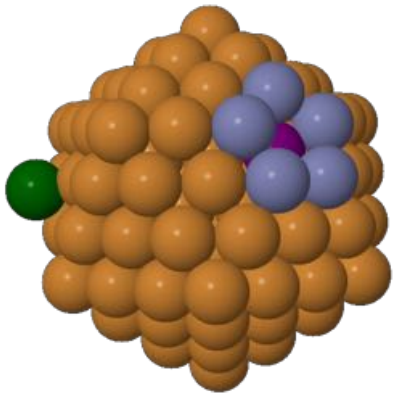


Figure 3.97: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy $E_{Cu_{147}LES}$+ 0.75 eV; (8-1-961)

3.5.10 9-1-1220

- A five fold vertex atoms are removed and placed on an edge.
- Creates a five fold vertex vacancy.
- Similar to 8-1-961

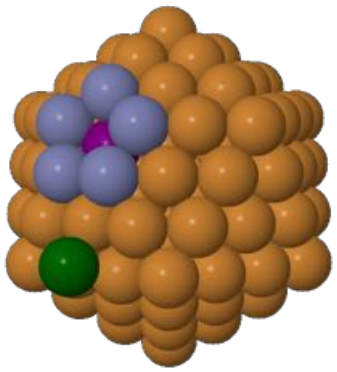


Figure 3.98: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 0.75 eV; (9-1-1220)

3.5.11 10-1-2050

- A five fold vertex atoms are removed and placed on an edge.
- Creates a five fold vertex vacancy.
- Similar to 8-1-961

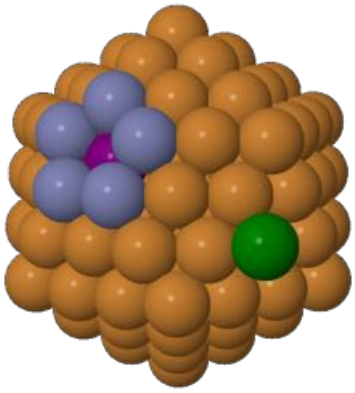


Figure 3.99: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 0.75 eV; (10-1-2050)

3.5.12 11-1-2137

- A five fold vertex atoms are removed and placed on a face next two the newly created five fold vertex vacancy.

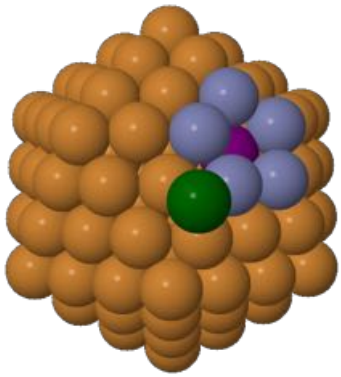


Figure 3.100: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 0.76 eV; (11-1-2137)

3.5.13 12-1-2364

- A five fold vertex atoms are removed and placed on a face next two the newly created five fold vertex vacancy .
- Similar to 11-1-2137

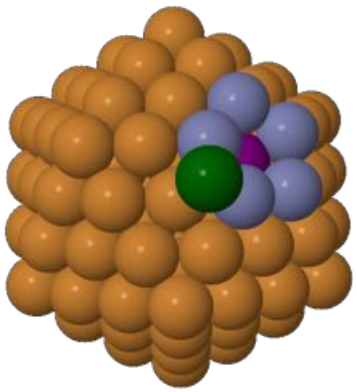


Figure 3.101: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 0.77 eV; (12-1-2364)

3.5.14 13-1-2557

- A five fold vertex atoms are removed and placed between an edge and a 5 fold vertex.
- This creates a five fold vertex vacancy.

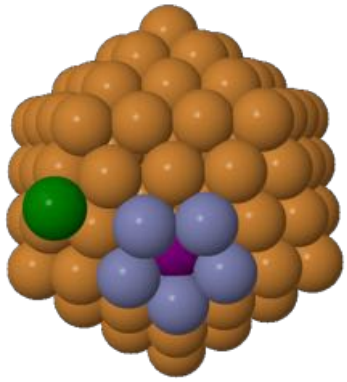


Figure 3.102: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 0.77 eV; (13-1-2557)

3.5.15 14-1-582

- 2 five fold vertex atoms are removed and placed on a face next to a newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.

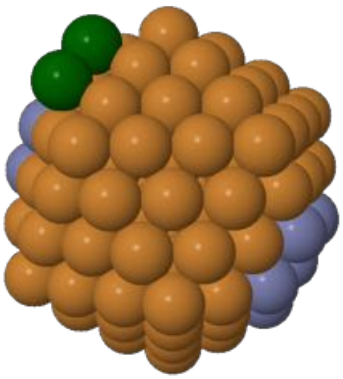


Figure 3.103: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.07 eV; (14-1-582)

3.5.16 15-1-1026

- 2 five fold vertex atoms are removed and placed on a face next to a newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 14-1-582

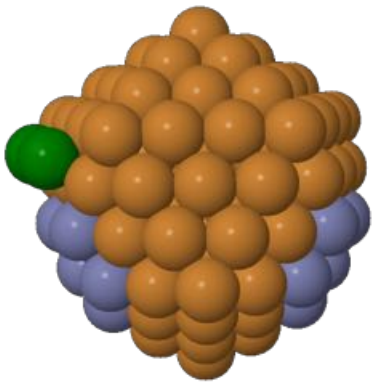


Figure 3.104: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.07 eV; (15-1-1026)

3.5.17 16-1-1288

- 2 five fold vertex atoms are removed and placed on a face next to a newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 14-1-582

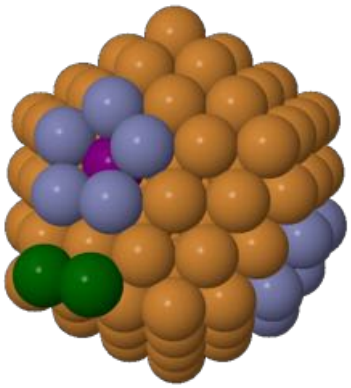


Figure 3.105: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.07 eV; (16-1-1288)

3.5.18 17-1-2088

- 2 five fold vertex atoms are removed and placed on a face next to a newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 14-1-582

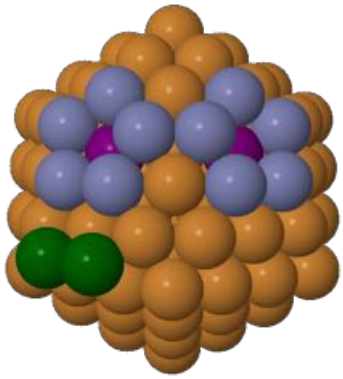


Figure 3.106: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.07 eV; (17-1-2088)

3.5.19 18-1-2238

- 2 five fold vertex atoms are removed and placed on a face next to a newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 14-1-582

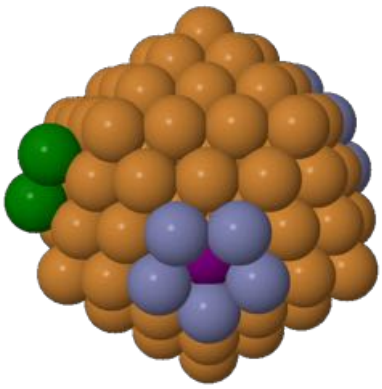


Figure 3.107: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.07 eV; (18-1-2238)

3.5.20 19-1-2316

- 2 five fold vertex atoms are removed and placed on a face next to a newly created five fold vertex vacancy.
- The vertices are very close to eachother
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 14-1-582

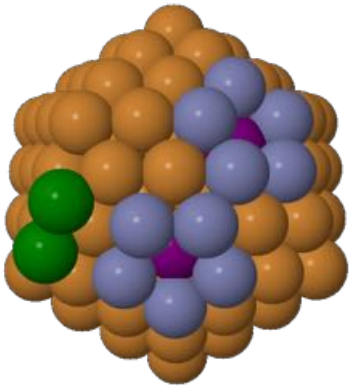


Figure 3.108: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.07 eV; (19-1-2316)

3.5.21 20-1-802

- 2 five fold vertex atoms are removed and placed on an face, very close to a five fold vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.

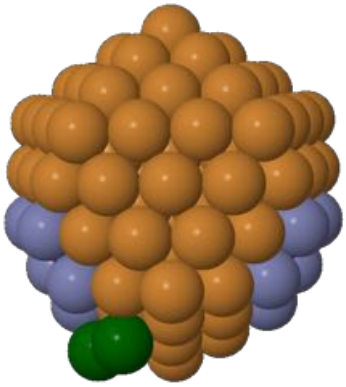


Figure 3.109: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.11 eV; (20-1-802)

3.5.22 21-1-1505

- 2 five fold vertex atoms are removed and placed on a face, very close to a five fold vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 20-1-802

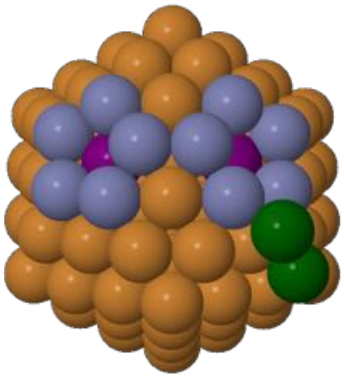


Figure 3.110: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.11 eV; (21-1-1505)

3.5.23 22-1-2080

- 2 five fold vertex atoms are removed and placed on an edge, very close to a both of the five fold vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 20-1-802

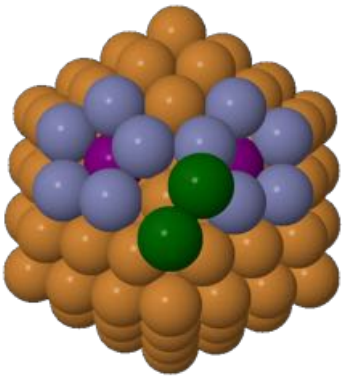


Figure 3.111: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.11 eV; (22-1-2080)

3.5.24 23-1-2282

- 2 five fold vertex atoms are removed and placed on a face, very close to a five fold vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Similar to 20-1-802

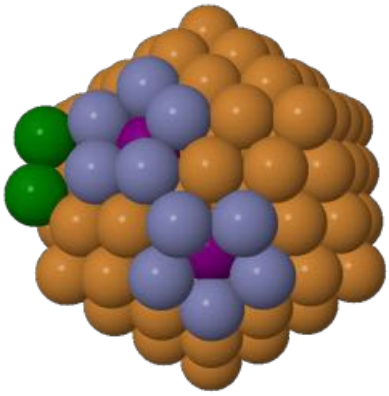


Figure 3.112: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.11 eV; (23-1-2282)

3.5.25 24-1-2865

- 2 five fold vertex atoms are removed and placed on an edge next to both of the five fold vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.

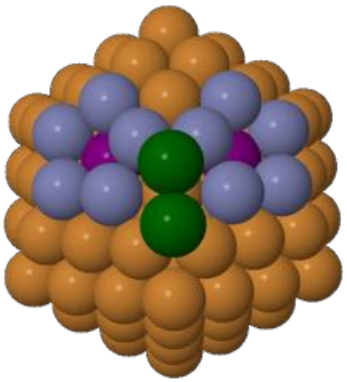
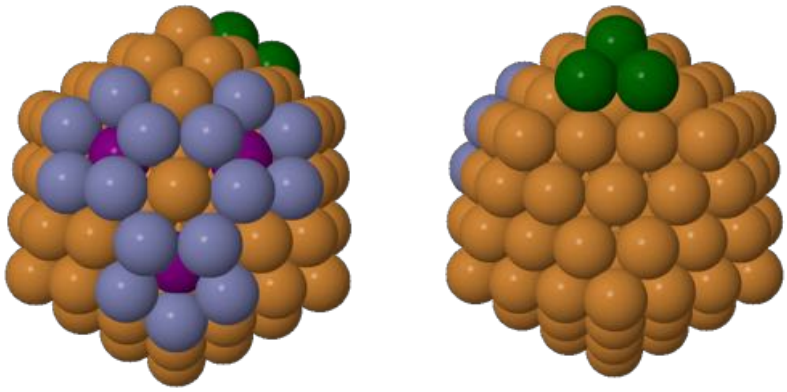


Figure 3.113: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.12 eV; (24-1-2865)

3.5.26 25-1-640

- 3 five fold vertex atoms are removed and placed on a face next two the newly created five fold vertex vacancy.
- The three displaced Cu atoms (dark green) form a trimer.



(a) (b)

Figure 3.114: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.13 eV; (25-1-640)

3.5.27 26-1-2145

- 2 five fold vertex atoms are removed and placed on a face next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- Dimer is on a edge of a five fold vertex vacancy

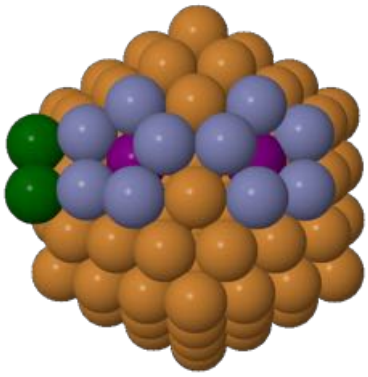


Figure 3.115: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.14 eV; (26-1-2145)

3.5.28 27-1-546

- 2 five fold vertex atoms are removed and placed on an edge next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- The dimer is located across the five fold vertex vacancies.

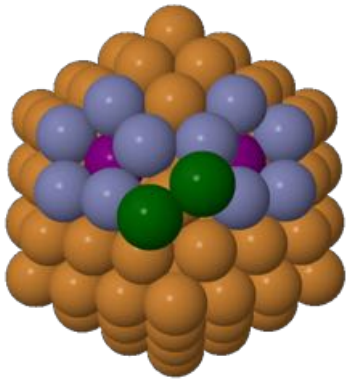


Figure 3.116: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.15 eV; (27-1-546)

3.5.29 28-1-728

- 2 five fold vertex atoms are removed and placed on an edge next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- The dimer is located across the five fold vertex vacancies.

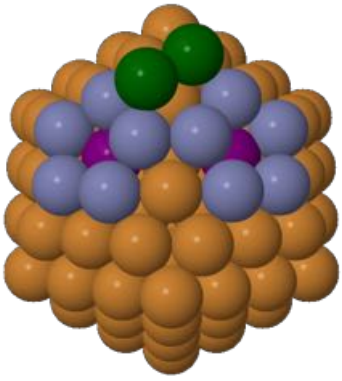


Figure 3.117: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.15 eV; (28-1-728)

3.5.30 29-1-2499

- 2 five fold vertex atoms are removed and placed on an edge next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- The dimer is located across the five fold vertex vacancies.

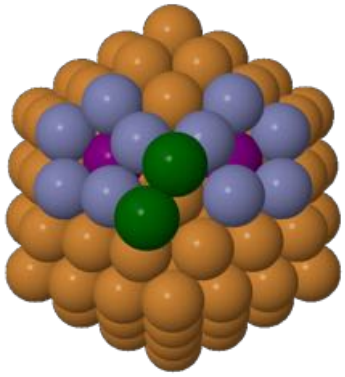


Figure 3.118: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.15 eV; (29-1-2499)

3.5.31 30-1-2342

- 2 five fold vertex atoms are removed and placed on an edge next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- The dimer is located across the five fold vertex vacancies.

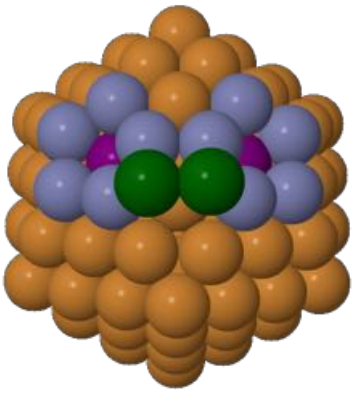
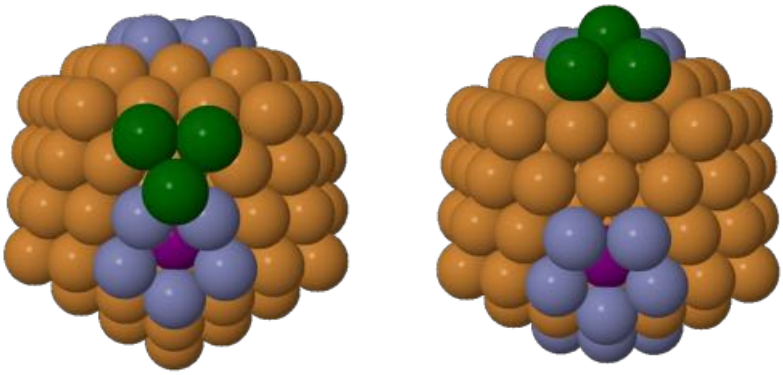


Figure 3.119: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.16 eV; (30-1-2342)

3.5.32 31-1-983

- Three five fold vertex atoms are removed and placed on a face next two the newly created five fold vertex vacancy.
- The three displaced Cu atoms (dark green) form a trimer on the surface.
- The trimer is located next to a five fold vertex vacancy.



(a) (b)

Figure 3.120: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.17 eV; (31-1-983)

3.5.33 32-1-2269

- 2 five fold vertex atoms are removed and placed on an edge next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- The dimer is located across the five fold vertex vacancies.

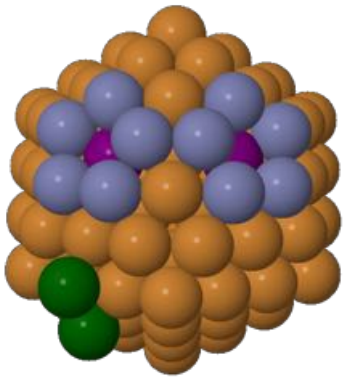


Figure 3.121: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.20 eV; (32-1-2269)

3.5.34 33-1-2094

- 2 five fold vertex atoms are removed and placed on an edge next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- The dimer is located across the five fold vertex vacancies.

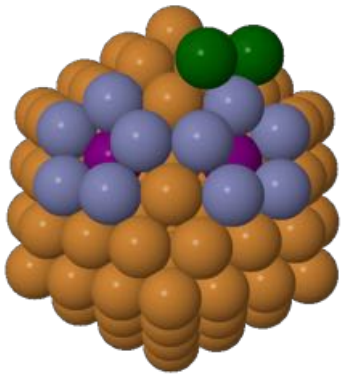
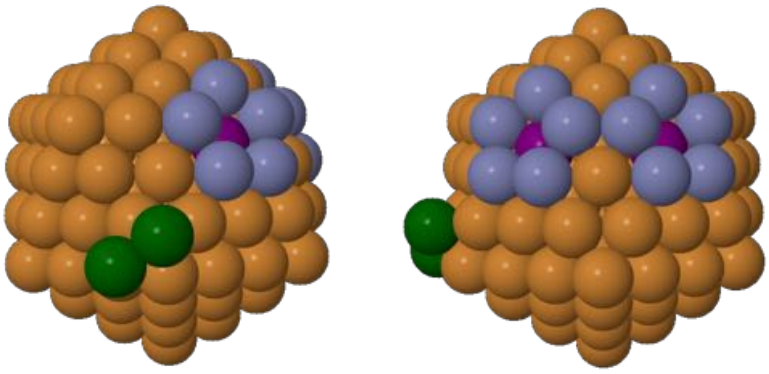


Figure 3.122: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.21 eV; (33-1-2094)

3.5.35 34-1-928

- 2 five fold vertex atoms are removed and placed on an edge next two the newly created five fold vertex vacancy.
- The two displaced Cu atoms (dark green) form a dimer on the surface.
- The dimer is located across the five fold vertex vacancies.



(a) (b)

Figure 3.123: Dark green = A displaced Cu Atom; Purple = a 5-fold vertex vacancy. Energy = $E_{Cu_{147}LES}$+ 1.28 eV; (34-1-928)

3.5.36 35-1-2240

- An atom is removed from an edge to form an edge vacancy.
- The removed atom is place on the surface of the structure.

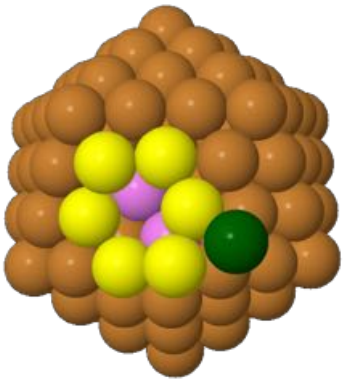


Figure 3.124: Dark green = A displaced Cu Atom; Yellow and Violet = Vacant edge site. Energy = $E_{Cu_{147}LES}$+ 1.31 eV; (35-1-2240)

3.5.37 36-1-2727

- An atom is removed from an edge to form an edge vacancy.
- The removed atom is place on the surface of the structure.

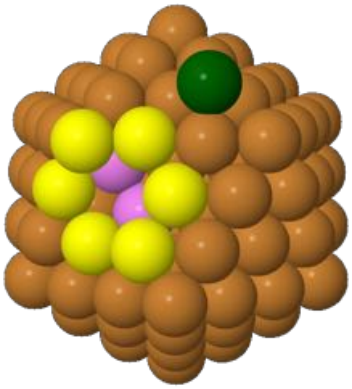


Figure 3.125: Dark green = A displaced Cu Atom; Yellow and Violet = Vacant edge site. Energy = $E_{Cu_{147}LES}$+ 1.31 eV; (36-1-2727)

3.5.38 37-1-899

- An atom is removed from an edge to form an edge vacancy.
- The removed atom is place on the surface of the structure.

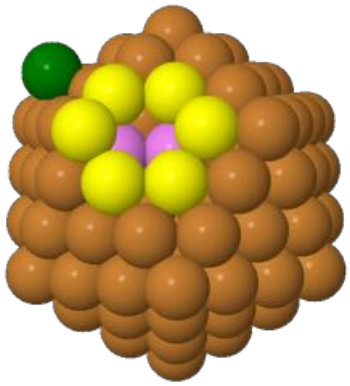


Figure 3.126: Dark green = A displaced Cu Atom; Yellow and Violet = Vacant edge site. Energy = $E_{Cu_{147}LES}$+ 1.32 eV; (37-1-899)

3.6 References

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[2] J. B. A. Davis and R. L. Johnston. Birmingham parallel genetic algorithm, 7 2015. https://bitbucket.org/JBADavis/bpga/.

[3] H. A. Hussein, J. B. A. Davis, and R. L. Johnston. DFT global optimisation of gas-phase and MgO-supported sub-nanometre AuPd clusters. *Physical Chemistry Chemical Physics*, 18:26133–26143, 2016.
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