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Abstract

Nowadays, different material like: lithium, silicon, germanium and tin are under investigation as possible anode materials for Lithium ion batteries (LIBs.) The function of anode in LIB is to accommodate the lithium ion and then release them. For this, anode material should react reversibly with lithium ions (Wang, Luo et al. 2012). We will study the behavior of 4H – SiC with lithium in this thesis.

Out of 250 polytypes of SiC, we chose 4H – SiC because it is widely used and has wide band gap. To understand the interaction of Lithium atom with SiC, the mechanism to insert lithium in to Silicon Carbide must be studied at atomic level. First- principle simulation is the way through which one can achieve this understanding. Here, first-principle calculation of different concentration of lithium in SiC has been studied. Formation energies of various combination of lithium in SiC have been calculated and compared.

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Abbreviations

SiC	= Silicon carbide
LIBs	= Lithium-ion batteries
BZ	= Brillion Zone
DFT	= Density Functional Theory
LDA	= Local Density Approximation
GGA	= Generalized Gradient Approximation
HF	= Hartree-Fock
SCF	= Self-Consistent Field
XC	= Exchange-Correlation
KS	= Kohn Sham

Chapter – 1

1.1 Introduction

Modern lifestyle has become more convenient and enjoyable due to the invention of electronic vehicle and portable electronic devices such as a laptop, cellphones, digital cameras, and so on (Wang, Luo et al. 2012). Rechargeable lithium-ion batteries are used in running such electronic gadgets. The research for lithium ion battery is being popular worldwide because of the following advantages: (<http://www.protochips.com>)

1. They have a high energy density
2. No memory effect and
3. Low standby energy drain

The demand for Li-ion batteries is increasing day by day. Proper selection of anode material can increase the energy density of such batteries. Nowadays, new electrode materials have been intensively studied in order to improve the energy density and meet the increasing demand for next-generation Li-ion batteries. (Wang, Luo et al. 2012). A semiconductor with a high band gap, SiC, is widely studied as an alternative anode material. SiC-based nano-structures and their cyclic performance have studied by some of the researchers to find alternative anode material. For example, nano cubic SiC, prepared by CVC (chemical vapor deposition) method delivers a reversible lithium deposition capacity of about 1200 mAh g⁻¹ over 200 cycles (Sri Devi Kumari, Jeyakumar et al. 2013).

Compositions of Silicon-carbon are studied intensively as an anode material of Li-ion batteries because silicon carbide (SiC) has a wide band gap, high electric breakdown field, high mobility, high thermal conductivity and they are mechanically stable (Zirkelbach, Stritzker et al. 2010). Silicon component of SiC helps to increase the capacity and Carbon component behaves as a strong active electrode. Though SiC is electrochemically inert for lithiation, it has been shown that surface graphitization converts doped SiC in to electrochemically active for lithium (Lipson, Chattopadhyay et al. 2012). This is why SiC is considered as a possible anode material for a next-generation Li-ion battery.

We want to investigate the incorporation and the diffusion behavior of Li into Cubic and hexagonal SiC and try to understand the observed enhancement effect. Experiments suggest that the carbon-rich subsurface reconstruction or the development of defects in the bulk during high-temperature processing may facilitate Li diffusion in SiC.

There are more than 250 Polymorphs of Silicon carbide. Among these 250 structures, some of the major SiC polytypes of SiC, are stated below (Yazdi, Iakimov et al. 2016).

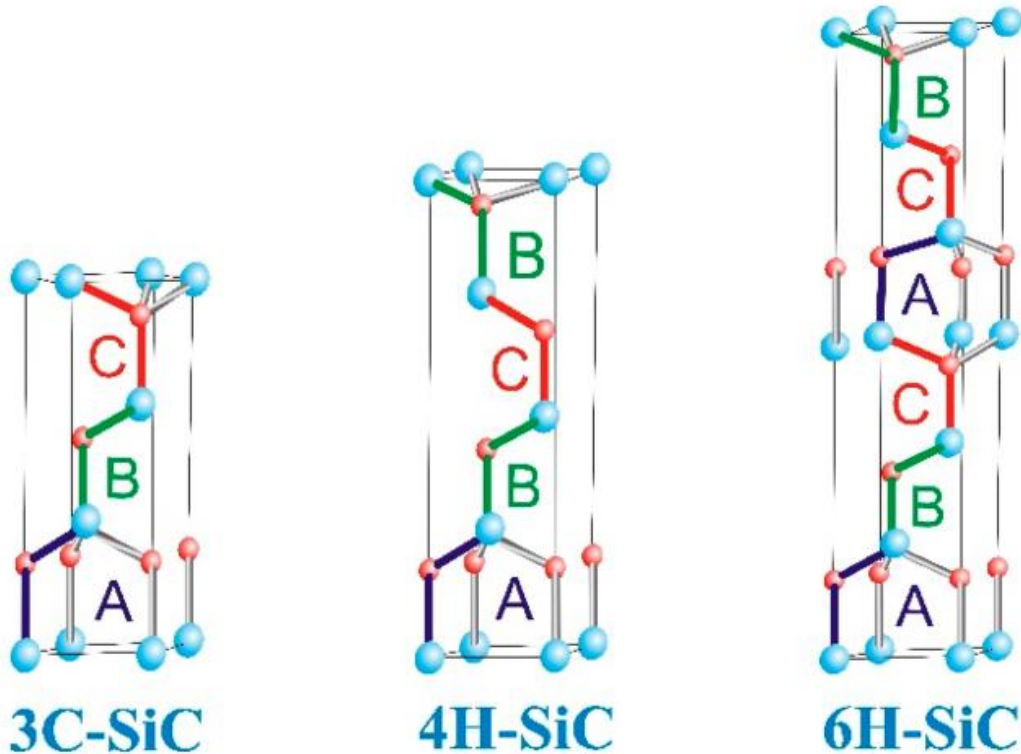


Fig 1.1: polytypes of SiC (taken from Yazdi, Iakimov et al. 2016)

There are three bilayer structure elements A, B and C. Elements A and B never changes the orientation of lattice whereas bilayer C changes the orientation of lattice by 60°. 3C-SiC is composed of elements ABC. 4H –SiC can be built from elements ABCB and 6H –SiC can be consists of elements ABCACB.

All the polytypes have their own advantages and properties. Out of them, we choose 4H- SiC because it is widely used in electronic devices and it has a wide band gap of 3.26 eV (Chow, Ramungul et al. 2004). Furthermore, it has both cubical and hexagonal structure and In between stacking layers of 4H SiC, there is an attractive interaction as a result structural stability is found to be maximized for the 4H SiC hexagonal structure. (Park, Cheong et al. 1994)

The total energy of various structures can be calculated by DFT self-consistent calculation. The important tool to determine the structure and to find the stability of compounds is Formation energy (Qianfan, Yi et al. 2013). Here, we have found the formation energy of various structures of 4H – SiC incorporated with lithium. From that calculation, we found that formation energy of lithium in carbon vacancy of SiC is more than formation energy of lithium in silicon vacancy of SiC. We also found the sum of individual formation energies of lithium in Silicon and lithium in Carbon vacancies is greater than the formation energy of two lithium atoms in Silicon and Carbon vacancies of SiC together.

Chapter – 2

Theoretical background

Theoretical description of density functional theory (DFT) has been described below. It doesn't include all the areas of DFT, but it includes the areas related to my thesis.

2.1 Schrödinger equation

The Schrödinger wave equation is the partial differential equation for the electron's wave function Ψ . It is used to find properties of a bound electron with the help of conservation of energy principle. A solution of this equation gives a quantum number, size, and orientation of electronic orbitals. The time-independent Schrödinger equation for a single non-relativistic particle is (Schrödinger 1926):

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi = E\psi \dots\dots\dots(2.1.1)$$

Here, $\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} JS$ is the reduced Planck constant

$m = 9.109 \times 10^{-31} kg$ is the mass of the electron,

∇^2 is the Laplacian (differential operator)

$V(r)$ is the potential energy

For hydrogen-like atom like H, He⁺, etc., we can easily solve the Schrödinger wave equation to get the wave function and hence the allowed energy states of the system. But for the multiple electrons system, it is difficult to solve Schrödinger equation. In order to solve this problem, we must apply some approximation to reduce the number of degree of freedom of the system. One of the most basic approximations is a Born-Oppenheimer approximation. This approximation helps to separate the motion of the nuclei and the motion of the electrons in the molecule. As a

result, this approximation breaks the molecular wave function into the electronic and nuclear component.

The time-independent, non-relativistic Schrödinger equation for multiple electrons interacting with multiple nuclei is: (D. S. Sholl and J. A. Steckel, 2009)

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(r_i) + \sum_{i=1}^N \sum_{j \neq i} U(r_i, r_j) \right] \psi = E\psi \quad \dots \dots \dots (2.1.2)$$

Here,

$U(r_i, r_j)$ the potential due to the interaction between an electron at position r_i and another at position r_j ,

$\Psi = \Psi(r_1, \dots, r_N)$ is the electronic wave function for all N electron and

E is the ground state energy of the electrons.

The first term in this bracket in this equation define the kinetic energy of each electron, the second term defines the interaction energy between each electron and the third term defines the collection of atomic nuclei and the interaction energy between different electrons.

2.2 Density functional theory

Density functional theory (DFT) is one of the standard computational tools in condensed matter physics, chemistry, and biochemistry to study the electronic structure of many-electron systems. It is called density functional theory because functional of electron density is used instead of the wave function to study properties of the many-body system. As electron density is used instead of the wave function, the multi-dimensional many-electron systems reduced to three dimensions; making the problem much easier. So, for the many-electron system, the density functional theory is one of the best methods to obtain an approximate solution to the Schrödinger equation (Density-Functional Theory by Paul W. Ayers, Weitao Yang, 2003).

2.3 Thomas–Fermi (TF) model

In 1920, Thomas and Fermi used electron density instead of the wave function to determine electronic energy. Only for the infinite nuclear charge, the model was correct. Though the model had limited accuracy, they introduced the new concept to solve the Schrödinger equation. The expression for Exchange-correlation energy:(Parr and Weitao 1987) (ref: W. Koch, M. C. Holthausen, “A Chemist’s Guide to Density Functional Theory”, Wiley-VCH: New York, 2000)

$$E[\rho] = C_F \int \rho^{5/3}(\vec{r}) d\vec{r} - Z \int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + C_X \int \rho^{4/3}(\vec{r}) d\vec{r} \quad \dots (2.3.1)$$

Here, the values of the constants C_F and C_X are of order unity

Z = number of electrons.

As this model used the approximate expression of kinetic energy and didn’t include a term for exchange energy of the atom, it didn’t follow one of the important results of Pauli Exclusion Principle and the accuracy of this model is limited. Later, in the Thomas-Fermi-Dirac theory (TFD), Dirac included the exchange energy term; still, the TFD was not successful because they didn’t take in to account the electron correlation. As a result, there were errors in exchange energy and kinetic energy and the TFD model became further inaccurate.

2.4 The Hohenberg–Kohn theorems

Density functional theory was developed on the basis of two mathematical theorems; they are called The Hohenberg-Kohn theorems. They deal on the systems of electrons affected by external potential. (Hohenberg and Kohn 1964):

Theorem 1: the external potential $V(\vec{r})$ is uniquely determined by the electron density $\rho(\vec{r})$.

Or

There are no two different external potentials $V(\vec{r})$ and $V'(\vec{r})$, which have the same electron density $\rho(\vec{r})$.

Proof: let us suppose we have two different external potentials $V(\vec{r})$ and $V'(\vec{r})$ have the same electron density $\rho(\vec{r})$. With these two potentials, we will have two different Hamiltonians, H and H' with the same ground state density and different Ψ and Ψ' . Now from the variational principle,

$$\begin{aligned} E_0 \langle \Psi' | H | \Psi' \rangle &= \langle \Psi' | H | \Psi' \rangle + \langle \Psi' | (H - H') | \Psi' \rangle \\ &= E_0' + \langle \Psi' | (V - V') | \Psi' \rangle \dots\dots\dots (2.4.1) \end{aligned}$$

Here, Ψ' is taken as a trial function for the H Hamiltonian and we used $\langle \Psi' | \Psi' \rangle = 1$

Again, If we take the Ψ as a trial function for the H' Hamiltonian, we get:

$$\begin{aligned} E_0' \langle \Psi | H' | \Psi \rangle &= \langle \Psi | H' | \Psi \rangle + \langle \Psi | (H' - H) | \Psi \rangle \\ &= E_0 + \langle \Psi | (V' - V) | \Psi \rangle \dots\dots\dots (2.4.2) \end{aligned}$$

Here, we used $\langle \Psi | \Psi \rangle = 1$

If we add two equations, we will get,

$$E_0 + E_0' < E_0' + E_0$$

This is contradiction. So, our assumption is wrong. This is sufficient to prove the first theorem.

Theorem 2: The exact ground state density gives the lowest total energy.

Proof: Suppose we have a trial density $\rho'(\mathbf{r})$. Then this density defines its own wave function Ψ' , and the expectation value of the true Hamiltonian satisfies the variational principle:

$$\langle \Psi' | H | \Psi' \rangle = T(\rho) + V_{ee}(\rho) + \int \rho(\vec{r})V(\vec{r})d\vec{r} = E[\rho'] \geq E_0[\rho_0] = \langle \Psi_0 | H | \Psi_0 \rangle \dots\dots\dots (2.3.3)$$

Where, $T(\rho)$ = Kinetic energy functional.

$V_{ee}(\mathbf{r})$ = Electron-electron functional.

$\int \rho(\vec{r})V(\vec{r})d\vec{r}$ = Nucleus – electron functional.

Thus, the correct density is the one that produces the minimum energy.

Kohn and sham developed further mathematical descriptions on energy functional, which is explained below.

2.5 Kohn – Shams equations

According to Hohenberg- Kohn theorem, ground state density can be used to calculate properties of the system. But the theorem doesn't give any method to find ground state density. Kohn and

Sham provide the way to find the ground state density. To derive the Kohn – Sham equations, ground state density as a functional of charge density is given by (Kohn and Sham 1965)

$$E[\rho(r)] = T[\rho(r)] + \int \rho(r)v(r)dr + E_{ee} \dots\dots\dots (2.5.1)$$

Here the first term represents kinetic energy,

The second term is for interaction with external potential and electron-nuclei interaction.

The third term gives the electron-electron interaction. The third term can be written as:

$$E_{ee}[\rho(r)] = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} drdr' + E_{xc}[\rho(r)] \dots\dots\dots (2.5.2)$$

On the right-hand side, the first term represents electron-electron electrostatic interaction and the second term gives exchange-correlation energy.

Kohn and Sham reintroduced wave functions Ψ_i to derive a set of a single particle as:

$$\rho(r) = \sum_{i=1}^n \psi_i^*(r)\psi_j(r) \dots\dots\dots (2.5.3)$$

Here n represents number of electrons.

Kinetic energy is expressed as:

$$T[\rho(r)] = -\frac{\hbar^2}{2m} \sum_i^n \langle \psi_i | \nabla^2 | \psi_i \rangle \dots\dots\dots (2.5.4)$$

As the wave function follow orthonormal condition i.e.

$$\int \psi_i^*(r)\psi_j(r)dr = \delta_{ij} \dots\dots\dots (2.5.5)$$

Functional of wave function can be defined as:

$$\Omega[\psi_i] = E[\rho(r)] - \sum_i \sum_j \epsilon_{ij} \int \psi_i^*(r)\psi_j(r)dr \dots\dots\dots (2.5.6)$$

To make the wave function orthonormal, Lagrange multipliers ϵ_{ij} is used.

If we minimize $\Omega[\psi_i]$ with respect to $\psi_i^*(r)$ we obtain the Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \dots\dots\dots (2.5.7)$$

Here, $v_{eff}(r) = v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}(r)$

The last term on the right-hand side is exchange-correlation potential energy with the expression,

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta \rho(r)}$$

To find the solution, the full system should be solved iteratively; the procedure for this SCF method is as follows (Qianfan, Yi et al. 2013, Shul'man and Posvyanskii 2014)

:

- I. Initial trial electron density $\rho(r)$ should be defined.
- II. To find Kohn-Sham orbitals $\psi_i(r)$, we should use this electron density to solve the Kohn-Sham equation.
- III. Calculate the electron density from step II, $\rho_{ks}(r) = 2 \sum_i \psi_i^*(r) \psi_i(r)$
- IV. We should repeat the process until the convergence is achieved, i.e. $|\rho_{ks}(r) - \rho(r)| < cc$, where $\rho(r)$ is the electron density used to solve Kohn-Sham equation, $\rho_{ks}(r)$ is resultant electron density from solution and cc is convergence criteria. After convergence is reached, final total energy is calculated from:

$$E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{xc}[\rho] - \int V_{xc}(r)\rho(r) dr \dots\dots\dots (2.5.8)$$

2.6. Exchange correlation functionals

One of the problems in DFT is the exact exchange functional and correlation functionals are unknown. Only for the free electron gases they are known. One of the widely used

approximations is Local density approximation (LDA). The functional is evaluated according to the formula below. (Kieron and O. 2013)

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r}) \epsilon_{xc}(\rho(\vec{r})) d\vec{r} \dots \dots \dots (2.6.1)$$

According to LDA, density is same at every place. Due to this, exchange energy can be underestimated and correlation energy can be overestimated. To correct this error, commonly electron density is expanded in terms of density gradient. This correction is called generalized gradient approximations (GGA) it has the following form

$$E_{xc}^{GGA}[\rho] = \int \rho(\vec{r}) \epsilon_{xc}(\rho(\vec{r}), \nabla(\rho)) d\vec{r} \dots \dots \dots (2.6.2)$$

We have used this exchange correlation term for our thesis.

2.7 Bloch theorem and K-space

Reference to this topic is from (N. W. Ashcroft and N. D. Mermin et al. 1976).

Atoms in the crystalline materials are arranged periodically as a result, the entire crystal can be studied with the help of study of one small unit cell. In DFT, supercell is used in terms of vectors that define cells and positions of atoms. Position vector gives the position of an atom with the help of three-dimensional Cartesian coordinates and lattice vectors.

Position vector $r = n_1 a_1 + n_2 a_2 + n_3 a_3$

Here, a_i are lattice vectors and n_i are integers.

According to Bloch theorem, for periodic potential, the solution of Schrödinger equation will be the sum of following term:

$$\phi_k(r) = u_k(r) e^{ik \cdot r} \dots \dots \dots (2.7.1)$$

Where,

$$u_k(r) = u_k(r + n_1 a_1 + n_2 a_2 + n_3 a_3), \text{ for all } n.$$

Here, $u_k(r)$ is periodic. From this we can see that using Bloch theorem; we can solve Schrödinger equation for each k vectors independently. The space occupied by k wave vectors is known as k -space. It is also known as reciprocal space. These reciprocal spaces are connected with real space with this formula (Monkhorst and Pack 1976)

:

$$b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}, \quad b_2 = 2\pi \frac{a_3 \times a_1}{a_2 \cdot (a_3 \times a_1)} \quad \text{and} \quad b_3 = 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)} \dots \dots \dots (2.7.2)$$

Here, $a_i \cdot b_j = 2\pi$ for $i = j$

$a_i \cdot b_j = 0$ for $i \neq j$

2.8. Pseudopotential

Usually coulomb potential due to core electrons are used in Schrodinger equation, which makes the equation complicated to solve. To get rid of this coulomb potential, the intricate effects of motion of non-valance electron or core electron of an atom and its nucleus are replaced by an effective potential called Pseudopotential (Schwerdtfeger, 2011).

In Pseudopotential, only the active valance electrons are considered and core electrons are not considered. Pseudo-wave function for valance electron is used and full potential caused by all electrons is not taken in to account to reduce the number of Fourier modes of Pseudopotential.

Usually, Norm-conserving pseudopotentials (Hamann, Schlüter et al. 1979) are used in plane-wave electronic structure codes nowadays.

It has the following form

$$V_{ps}(r) = \sum_l \sum_m \left| Y_{lm} \right\rangle V_{lm}(r) \langle Y_{lm} | \dots \dots \dots (2.8.1)$$

Where, $\left| Y_{lm} \right\rangle$ represents one particle wave function with angular momentum $\{l, m\}$. $V_{lm}(r)$ represents the pseudopotential act on projected component.

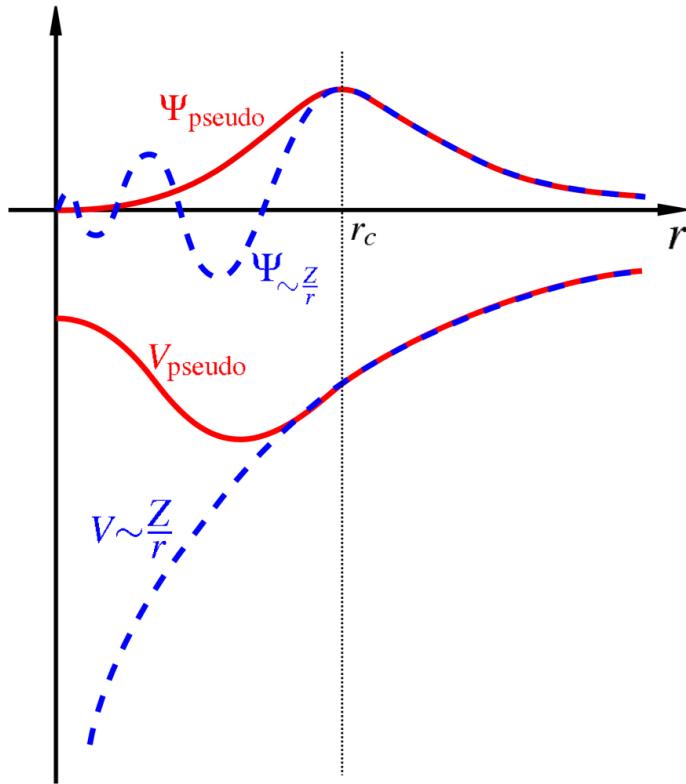


Fig 2.8.1: comparison between coulomb potential wavefunction and pseudopotential wavefunction.

This picture is taken from Wikipedia (wikipedia.org). This picture compares coulomb potential and pseudopotential wavefunction. The curves with red color are pseudopotential curves and the curves with blue color are coulomb potential wavefunction curve. After the cut off radius r_c , both pseudopotential wavefunction and coulomb potential wavefunction match.

Chapter –3

3.1 Methods

To solve non-relativistic Schrödinger equation or relativistic Dirac equation for number of electrons, Density Functional Theory (DFT) is used. In this thesis, we have done our calculation within the scope of DFT, with the use of plane wave self-consistent field (PWscf) code. To model an infinite hexagonal crystal containing 96 atoms, periodic boundary conditions were used. The following sequence was used to simulate the lithiation of SiC at room temperature. (V. L. Chevrier *et al*, 2009)

1. Insert a Lithium atom at the center of the largest spherical cavity.
2. Increase the size and scale coordinates.
3. Optimize the coordinates at a fixed volume.
4. Calculate the total energy.
5. Get back to step 1 with the same structure until the desired condition is reached.

The input structure for our calculation is presented below. This is silicon carbide in its 4H – SiC form.

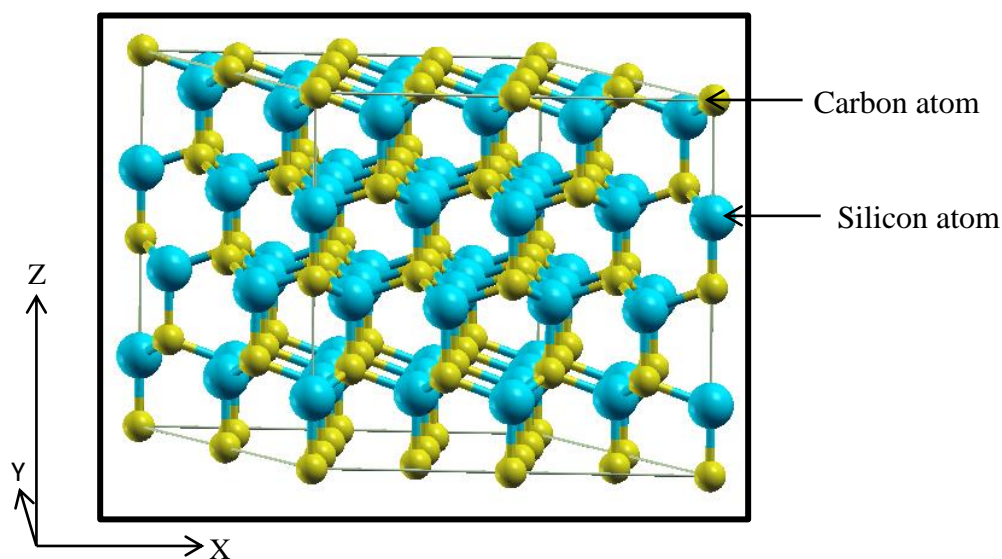


Fig 3.1.1. 4H – SiC silicon carbide structure

[Note: All the structures in this thesis will have the same orientation of coordinate axes.]

For the suitable values of cut off energy and k-points, Total energy for a different k-points and different cut of kinetic energy was calculated using Plane-Wave Self-Consistent Field (PWscf) method from quantum espresso. The table below shows the total energy (in Ry) for k-points (4*4*4), (2*2*2) and (1*1*1) with different cut-off energy 30, 40, 50, 60 and 70 Ry.

Cut-off energy (in Ry)	Total energy for k-point (4*4*4)	Total energy for k -point (2*2*2)	Total energy for k- point (1*1*1)
30	-926.4024	-926.4044	-926.3989
40	-927.2300	-927.2300	-927.2212
50	-927.2704	-927.2705	-927.2600
60	-927.2895	-927.2895	-927.0513
70	-927.3060	-927.3060	-927.2539

Table 3.1: variation of total energy for different K-points and cut-off energy

A graph is plotted between Total energy “in Ry” (Y-axis) and cutoff kinetic energy “in Ry” (X-axis) for different K values. This graph is presented below.

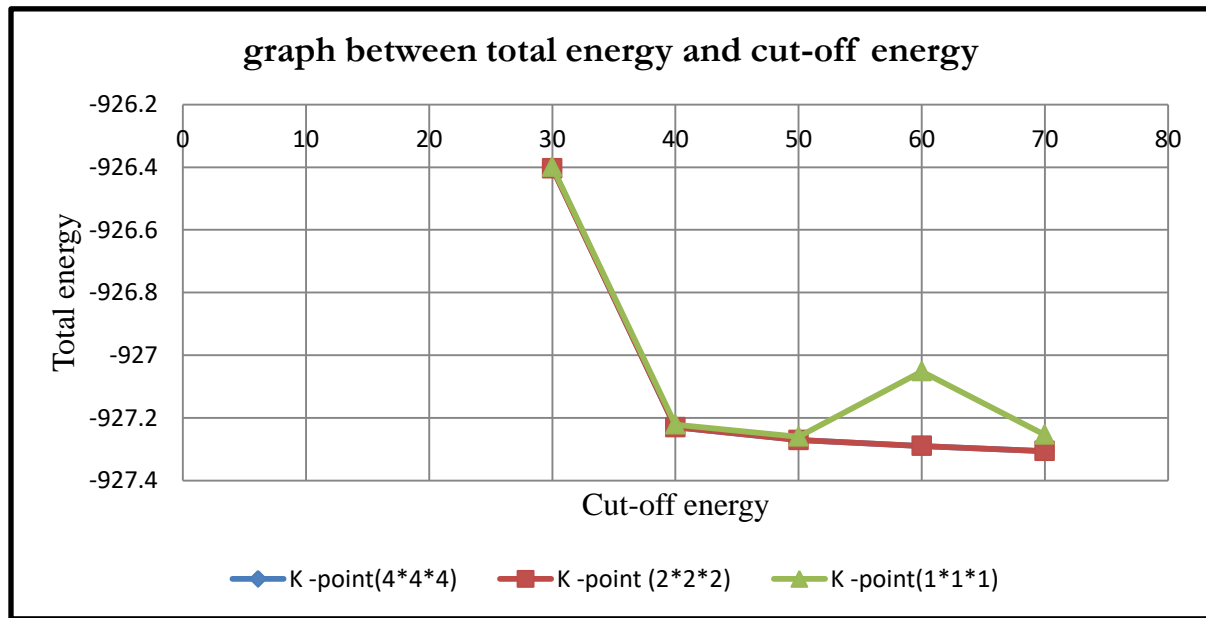


Fig 3.1.2: Graph between Total energy and plane wave cutoff energy for different K values.

In the graph we see that, for k-point (1*1*1), energy is not conserved with respect to increasing cut-off energy. But the energy is conserved for k-point (2*2*2) and for cut off energy 50 Ry. So we take k-point grid (2*2*2) and cut off energy 50 Ry to sample the Brillion zone. To explain exchange correlation term, The Perdew-Burke-Ernzerhof (pbe) pseudo potential was used (Paier, Hirschl et al. 2005).

With the suitable use of pseudo potentials, we ran the calculation to get convergence energy. We then removed silicon and carbon atom simultaneously to create the vacancy on the structure.

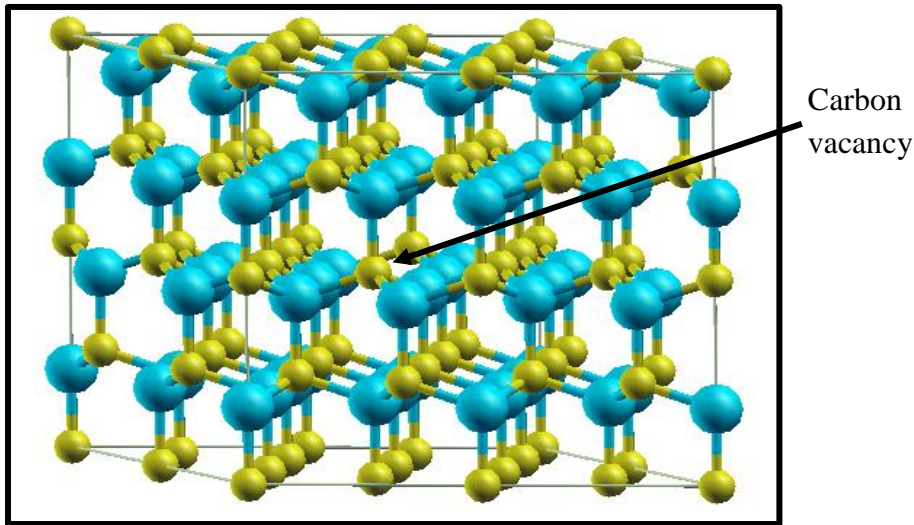


Fig 3.1.3: Carbon vacancy in 4H-SiC structure

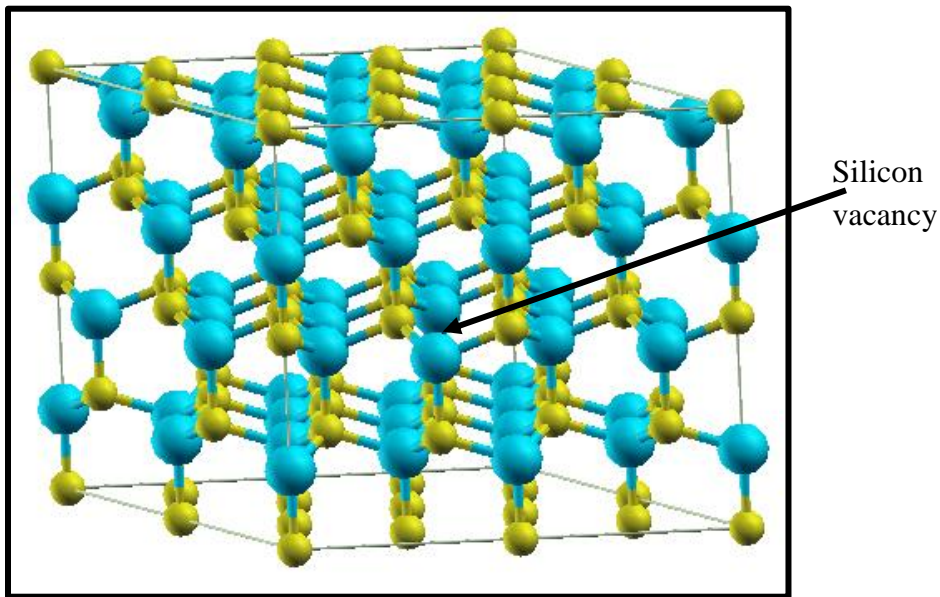


Fig 3.1.4: Silicon vacancy in 4H-SiC structure

We insert lithium atoms in such vacancies and run the calculations to get converged energies. Using DFT self-consistent simulation, total energy of lithiated structure can be calculated directly. Total energy thus obtained can be used to calculate formation energy. To calculate formation energy, we used the expression given below (Chen, Xiao et al. 2008):

$$E(\text{formation}) = E(\text{structure}) - E(\text{SiC} - \text{bulk}) + p \times \mu_c + q \times \mu_{si} - r\mu_{li} \dots \dots \dots (3.1.1)$$

Where, E (structure) = Energy of structure obtained after lithiation. Its value is the converged energy (output of PWscf code of quantum espresso) of corresponding structure.

E (SiC-bulk) = Energy of bulk SiC with 96 atoms. Its value is the converged energy (output of PWscf code of quantum espresso) of SiC with 96 atoms.

$p \times \mu_c$ = Number of Carbon vacancy (p) \times chemical potential of Carbon.

$q \times \mu_{si}$ = Number of Silicon vacancy (q) \times chemical potential of Silicon.

$r\mu_{li}$ = Number of lithium inserted (r) \times chemical potential of Lithium.

3.2 Input files description

Some of the important parts of our PWscf input file is written below. It has various different blocks. We discuss the meaning of different lines. *Italic letters shown by arrow represents the meaning of corresponding line and bold words represent the part of input file. Reference for this section is from quantum espresso official website (https://www.quantum-espresso.org/Doc/INPUT_PW.html#idm739)*

&control \rightarrow *the first block “& control” represent the control block. It controls the calculation.*

calculation = 'relax' \rightarrow *it will relax the atomic positions.*

restart_mode = '**from_scratch**' \rightarrow *It means new structure will be generated.*

prefix = '**4Hsic**' \rightarrow file name used.

tstress = **.false.** \rightarrow *This is used to calculate the stress.*

tpnfor = **.true.** \rightarrow *This is used to calculate the force.*

pseudo_dir = './' → location to store the pseudopotential.

outdir = './scratch/' → location for temporary file.

/ → it represents end of block.

&system → It specify the required system to be studied.

ibrav = 0 → it represents crystal systems. *ibrav = 0* is used for free structure.

nat = 96 → total number of unique atom.

ntyp = 2 → it means two different types of atoms are used.

ecutwfc = 50.0 → cut-off energy for pseudopotential.

/

&electrons → the variables in this block control the algorithms for self-consistent solution of Kohn Sham equation for electron.

diagonalization = 'david' → diagonalization by Davidson iterative with overlap matrix.

/

&ions → this block is needed if the atoms move. It controls motion of ions during structural relaxation.

/

ATOMIC_SPECIES → In this block, name, pseudopotential and mass of atomic species used in the system are specified.

ATOMIC_POSITIONS → type of atom in the unit cell and their coordinate are included in this block.

K_POINTS → this block include weights and coordinates of *k* – points used for Brillion zone integration.

Chapter - 4

4. Result and Discussion

4.1 Calculation of chemical potential

4.1.1. Calculation of chemical potential of lithium:

Lithium is the lightest alkali metal. The body-centered cubic (*bcc*) structure of lithium is the most stable form for lithium metal at room temperature (around 25⁰C). This form is also known as β -Li. Lattice parameter of most stable lithium with bcc structure is 3.5091 Å

(periodictable.com) [i.e celldm (1) = $\frac{3.5091}{0.529177249} = 6.6312$ bohr]. We made an Input structure

in Quantum Espresso pw.x. with that celldm (1) value. We run the calculation for different value of K points; the table below shows the converged total energy at different K points.

k points	total energy
6*6*6	-14.2099
8*8*8	-14.2100
10*10*10	-14.2101
12*12*12	-14.2108
14*14*14	-14.2105
16*16*16	-14.2103
18*18*18	-14.2104
20*20*20	-14.2106
22*22*22	-14.2106
24*24*24	-14.2105
26*26*26	-14.2105
30*30*30	-14.2105

40*40*40	-14.2106
50*50*50	-14.2105
60*60*60	-14.2106

Table 4.1.1.1: K points vs total energy for lithium

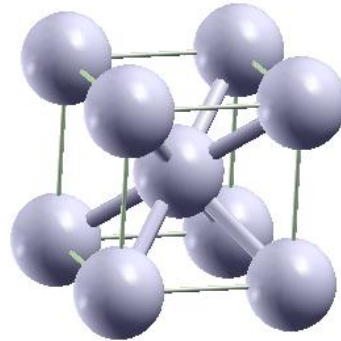


Fig 4.1.1.1: bcc structure of lithium

If we plot the graph between total energy and K points, we get the following curve.

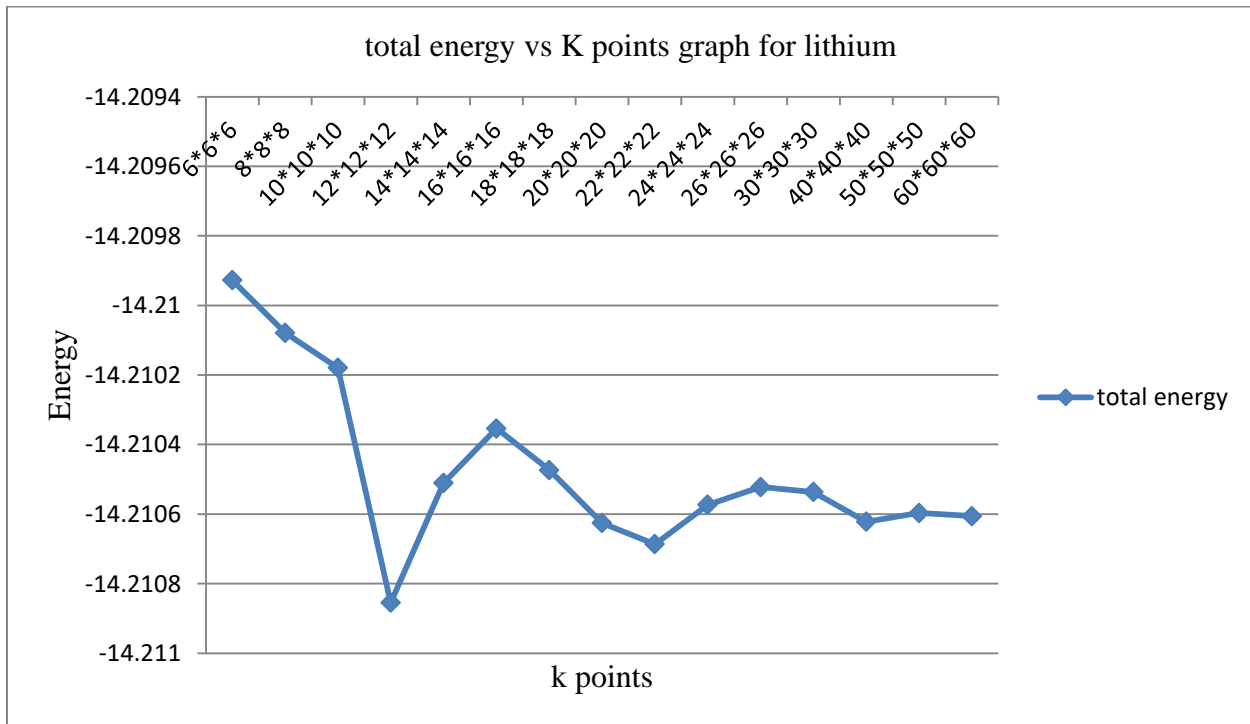


Fig 4.1.1.2: graph between k points and converged total energy

The energy did not converge for small k points but for large k points, the energy is conserved. If we take a look at selected k points, we come to the conclusion that energy starts to converge from the energy -14.2106 corresponding to 20*20*20 k points.

To see the convergence, table for selected k points has been shown in the table below.

K points	Total energy
10*10*10	-14.2101
20*20*20	-14.2106
30*30*30	-14.2105
40*40*40	-14.2106
50*50*50	-14.2105
60*60*60	-14.2106

Table 4.1.1.2: selected K points vs total energy for lithium

The corresponding graph is as shown below.

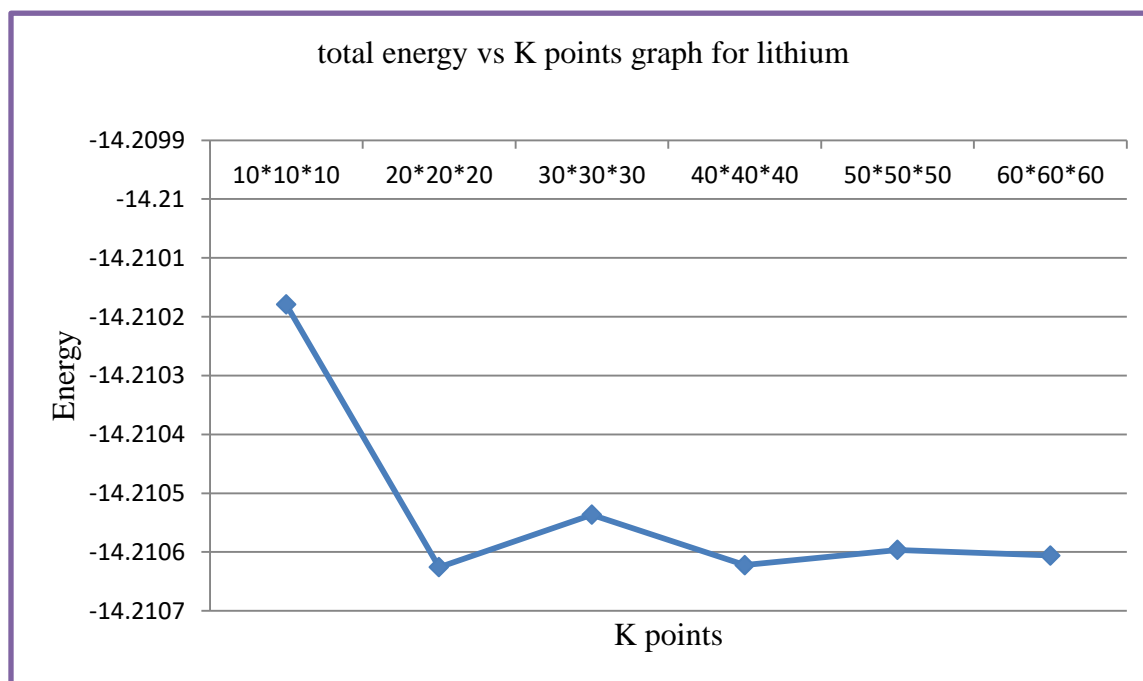


Fig 4.1.1.3: graph between k points and converged total energy for selected k points.

From this graph, we can easily choose the K point 20*20*20.

To prove that the lattice constant we choose is correct, we run the simulation with different possible lattice constants to get converged energy. The table for the value of lattice constant and corresponding energy is shown below.

lattice constant	energy
2.5	-14.1093
3	-14.1944
3.5091	-14.2106
4	-14.2015
4.5	-14.1840

Table 4.1.1.3: Lattice constant and converged energy at k-points 20*20*20

The graph of above table is plotted below.

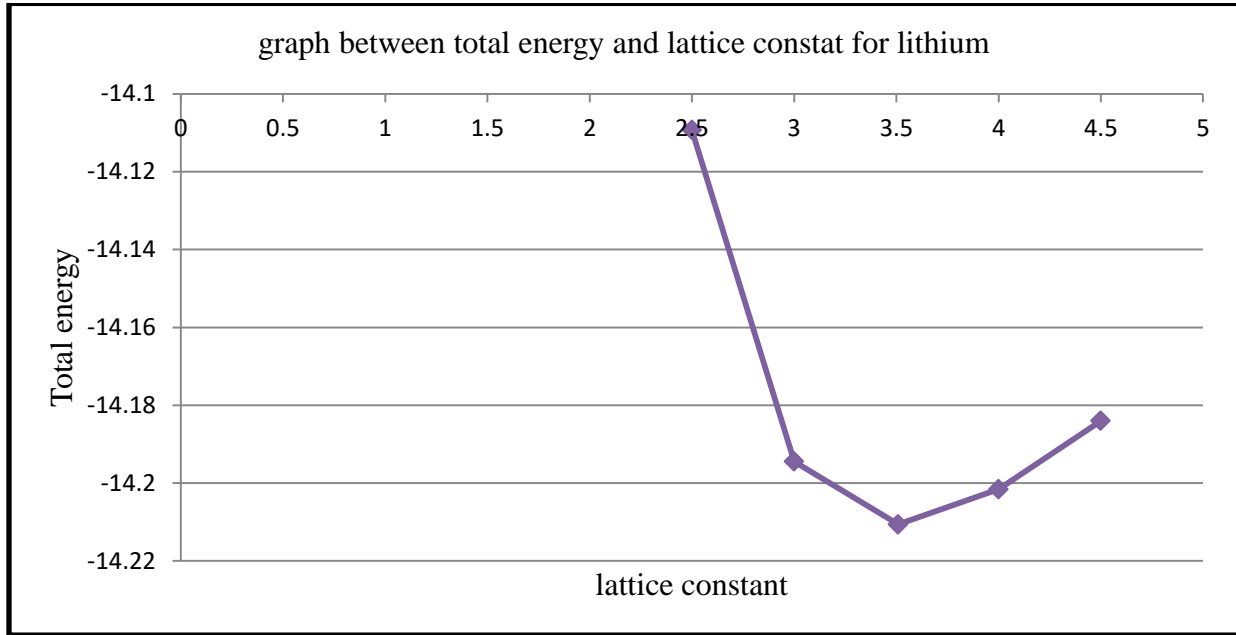


Fig 4.1.1.4: graph between lattice constant and converged total energy for lithium.

From graph, it is clear that energy is the least when lattice constant is 3.5091 Å. So our choice to calculate chemical potential at k points 20*20*20 with lattice parameter 3.5091 Å is suitable.

Total energy at this K point = -14.2106 Ry

So, the chemical potential of lithium μ (Li) = -14.2106 Ry

4.1.2 Calculation of chemical potential of Carbon

In the nano scale, diamonds are found to be more stable than graphite (Badziag, Verwoerd et al. 1990). In the carbon clusters, number of atoms is nearly equal to 104 at temperature of 1200 K and at a pressure of 2700 Pa, this is the reason why diamond is more stable than graphite (Hwang, Hahn et al. 1996). So to find chemical potential of carbon, we have used Diamond structure in this thesis. It has the face-centered cubic (*fcc*) structure. The lattice parameter of Diamond with *fcc* structure is 3.567 Å (Argon National Labs (Advanced Photon Source) Retrieved 19 October 2014). [i.e $\text{celldm}(1) = \frac{3.567}{0.529177249} = 6.7406$ bohr]. We made an Input structure in Quantum Espresso pw.x. with that $\text{celldm}(1)$ value. We run the calculation to get converged final energy.

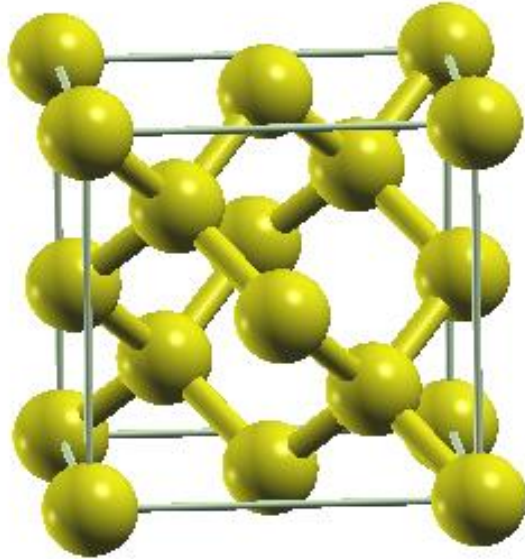


Fig 4.1.2.1: *fcc* structure of Diamond

To find suitable k – points at which total energy starts to converge, from self-consistent simulation, with different values of k points, we get different total energies. The table given below shows obtained energies with corresponding k points.

K points	Total Energy
6*6*6	-22.7642 Ry
8*8*8	-22.7647 Ry
10*10*10	-22.7648 Ry
12*12*12	-22.7648 Ry
14*14*14	-22.7648 Ry

Table 4.1.2.1: K points vs total energy for carbon

If we plot the graph between total energy and K points, we get the following curve.

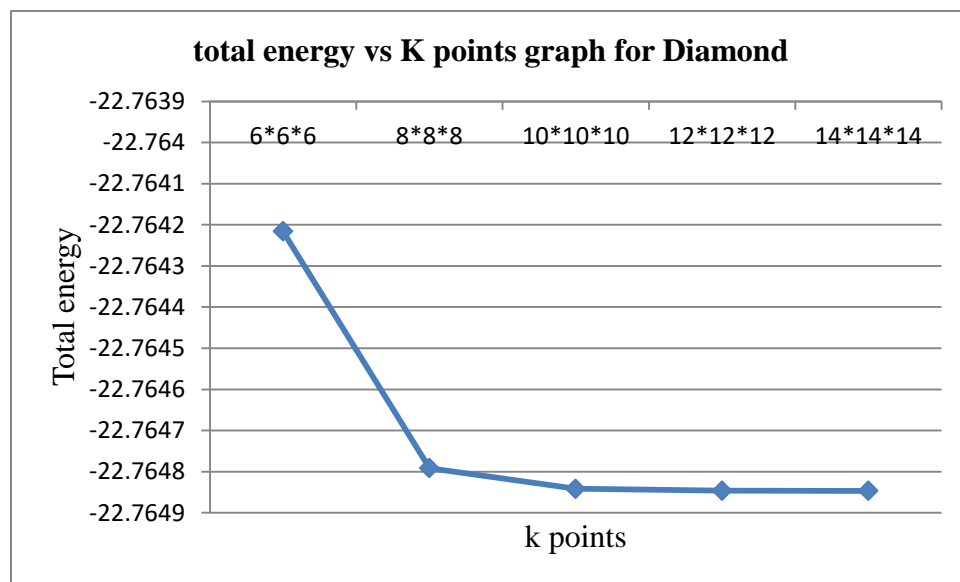


Fig 4.1.2.2 graph between total energy and k points for diamond

From this graph, it is clear that energy is almost constant after k points 10*10*10, so we can easily choose the K point 10*10*10 for our calculation.

Total energy at this K point = -22.7648 Ry

So, the chemical potential of Carbon μ (C) = $\frac{-22.7648}{2} = -11.3824$ Ry

4.1.3 Calculation of the chemical potential of Silicon

Silicon has the face-centered cubic (*fcc*) structure. The lattice parameter of Silicon with *fcc* structure is 5.431Å. [i.e $\text{celldm}(1) = \frac{5.431}{0.529177249} = 10.2631$ bohr]. We made an Input structure in Quantum Espresso pw.x. with that $\text{celldm}(1)$ value. We run the calculation to get converged final energy.

K points	Total Energy
6*6*6	- 15.7660Ry
8*8*8	- 15.7674Ry
10*10*10	- 15.7677Ry
12*12*12	- 15.7677Ry
14*14*14	- 15.7677Ry

Table 4.1.3.1: K points vs total energy for silicon

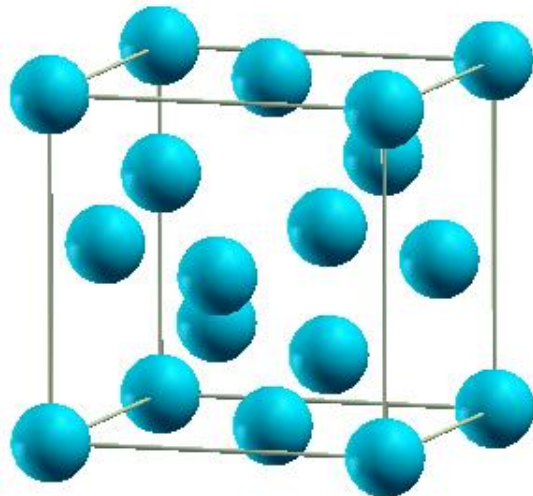


Fig 4.1.3.1: *fcc* structure of Silicon

If we plot the graph between total energy and K points, we get the following curve.

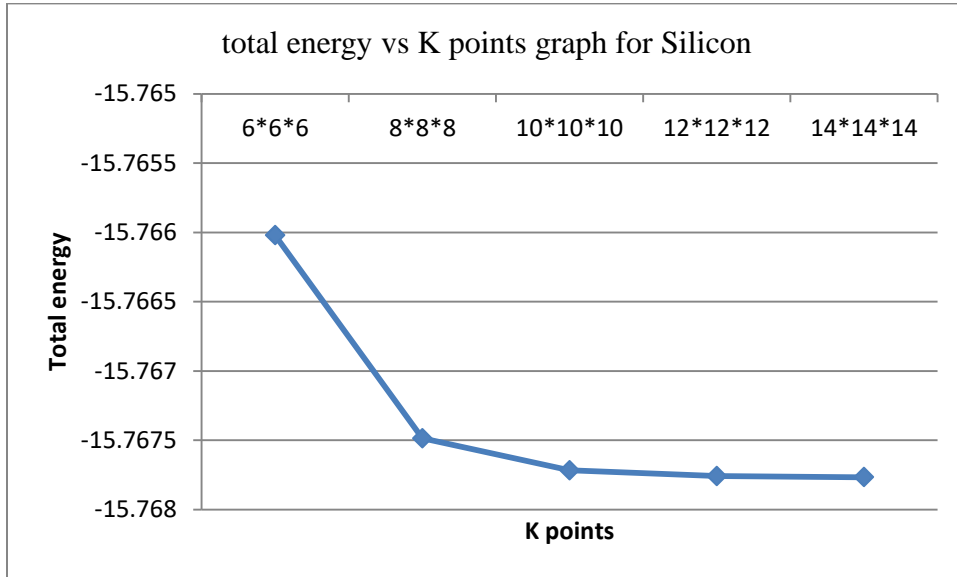


Fig 4.1.3.2: Total energy vs K points graph for silicon

From this graph, it is clear that energy is almost constant after k points 10*10*10, so we can easily choose the K point 10*10*10 for our calculation.

$$\text{Total energy at this K point} = -15.7677 \text{ Ry}$$

$$\text{So, chemical potential of Silicon } \mu (\text{Si}) = \frac{-15.76771685}{2} = -7.8838 \text{ Ry}$$

4.2. Calculation of formation energies

The difference in energy of crystal before and after the creation of defect is called formation energy of defect. With the help of formation energy we can find the stability of structure.

There are so many ways to create “n” vacancy in “N” atoms of 4H - SiC. We can use Binomial distribution to calculate all the possibilities. We don't go through all the possibilities in this short period of time. We make different structures of 4H-SiC with different silicon and carbon vacancies. We insert different concentration of lithium atoms in such vacancies. We run the PWscf code for all structures to get converged energy by using quantum espresso software. In this chapter all the input and output structures are presented. Although, Axes of orientation for all the individual structures are not shown along with the structure; orientation of coordinate axes x, y, Z is same for all structures. The common coordinate system for all the structures is as shown below.

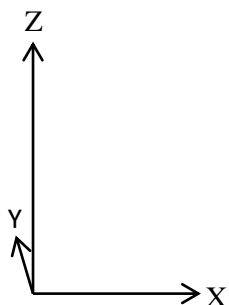


Fig 4.2.1: coordinate system used for all the structures.

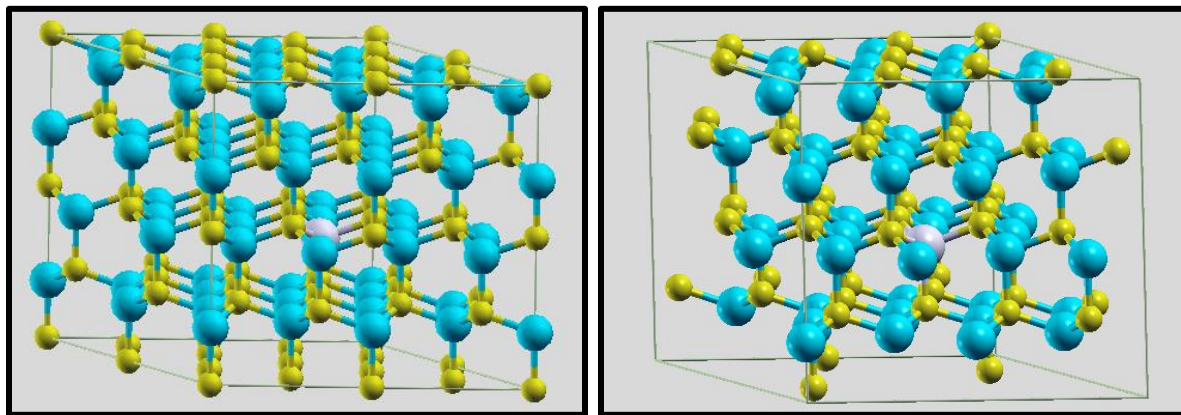
In the first part of this chapter, we have discussed formation energy of lithium in Silicon vacancies. In the second part, formation energy of lithium atoms in the Carbon vacancies and finally the insertion of lithium atoms in both silicon and carbon vacancies at the same structure is explained. We have presented the result obtained into tabular form and into graphical form as well.

4.2.1. Calculation of formation energy when distance between lithium atoms is large

In this section, we have created vacancies on SiC. Distance between vacancies is made larger than the average distance between two atoms in the structure. First, we start with lithium atoms in silicon vacancy. After that, we make similar structure for lithium atoms in carbon vacancy and we compare the result.

4.2.1.1. One lithium atom in one silicon vacancy

Both input and output structures for given conditions are shown in the figure below. We have created a vacancy on silicon side almost at the middle of the structure. One lithium atom is inserted on that vacancy. Here we put only a single lithium atom, so it didn't interact with other lithium atoms; as a result, it remains in the same position in output structure.



“Lithium atom in Silicon vacancy”
input structure

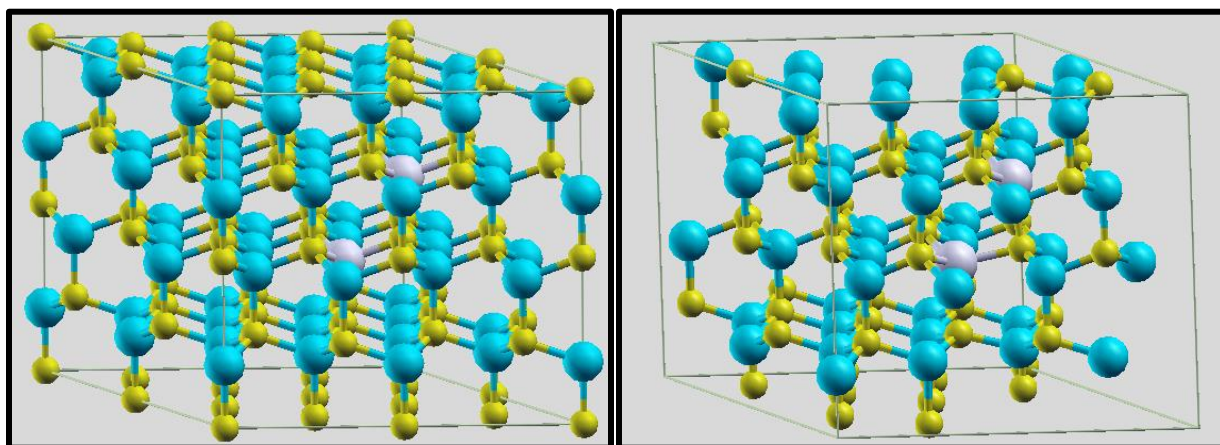
“Lithium atom in Silicon vacancy” output
structure

Fig 4.2.1.1: input and output of one lithium atom in one silicon vacancy

From the calculation by using formula of formation energy presented in third chapter, formation energy is found to be 5.7173 eV.

4.2.1.2. Two lithium atoms in two silicon vacancies

The following two picture represents the input and output structure of two lithium atoms into two silicon vacancies. One lithium atom is at distance 3.0960\AA far from another atom in input structure. As the distance between lithium atoms is large, there is not much interaction between two lithium atoms, as a result distance between them slightly decreased to 2.9769\AA in output structure.



“Two lithium atoms in two silicon vacancies” input structure

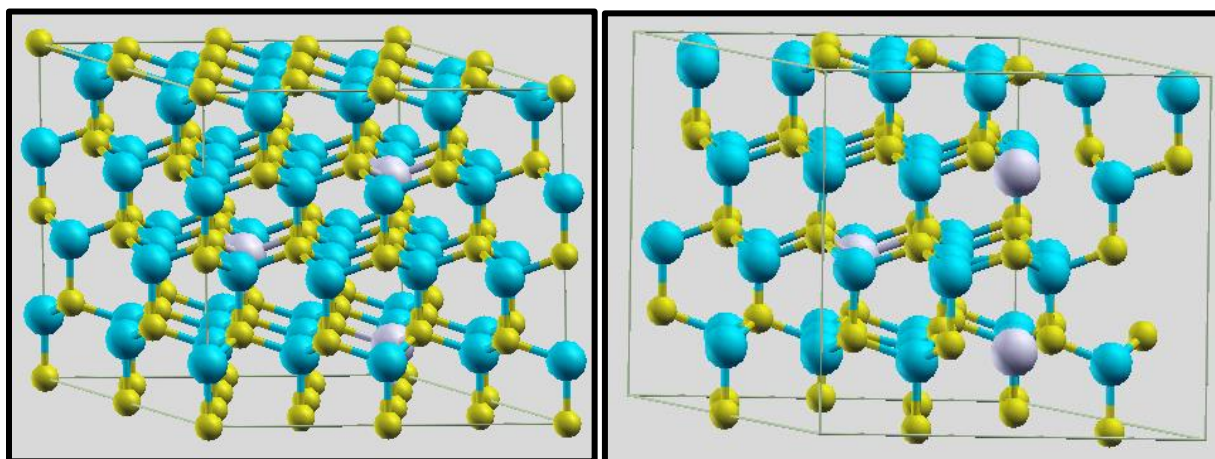
“Two lithium atoms in two silicon vacancies” output structure

Fig 4.2.1.2: input and output of two lithium atom in two silicon vacancy

From the calculation, we found the formation of energy to be 9.6648 eV .

4.2.1.3. Three lithium atoms in three silicon vacancies

Here, in the input structure, three lithium atoms are placed in three silicon vacancies in a triangular form, the distance between the left and the top atom is 5.3561Å. The distance between the left and the bottom atom is 5.3555Å and the distance between the top and the bottom atom is 5.0590Å.



“Three lithium atoms in three silicon vacancy” input structure

“Three lithium atoms in three silicon vacancy” output structure

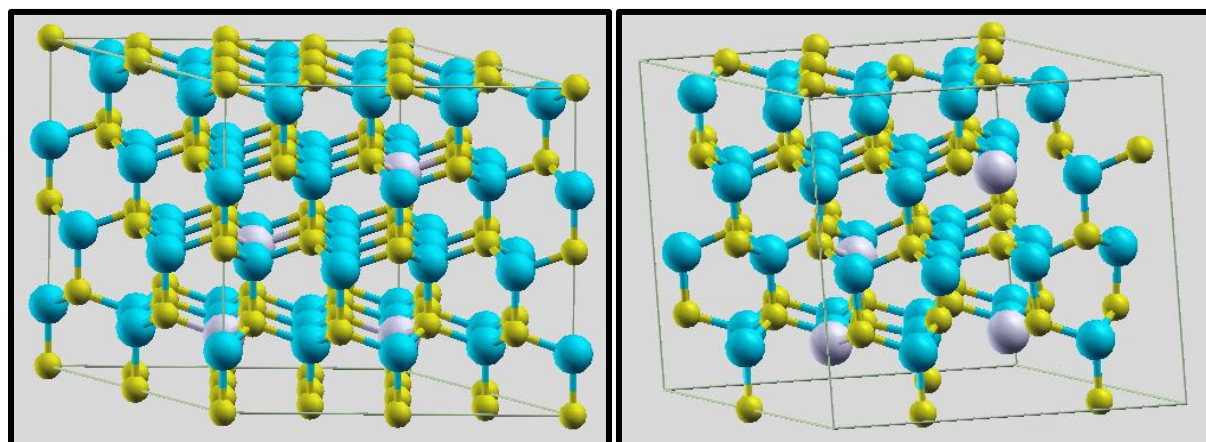
Fig 4.2.1.3: input and output of three lithium atom in three silicon vacancy

In the output structure, the distance between the left and the top atom is 5.3669Å. The distance between the left and the bottom atom is 5.2742Å and the distance between the top and the bottom atom is 4.9998Å. All the distances slightly changed but not significantly. This is because they couldn't interact with each other because of their large distance.

From the calculation, Formation energy is found to be 14.0323 eV.

4.2.1.4. Four lithium atoms in four silicon vacancies

Both the inputs and outputs structures are as shown in figure.



“Four lithium atoms in four silicon vacancies” input structure

“Four lithium atoms in four silicon vacancies” output structure

Fig 4.2.1.4: input and output of four lithium atom in four silicon vacancy

(Lithium atoms are named as first, second and fourth from the left to the right respectively and the topmost atom is considered as the third atom)

Here, four lithium atoms have been inserted into four silicon vacancies. The distance between them is listed in the table below:

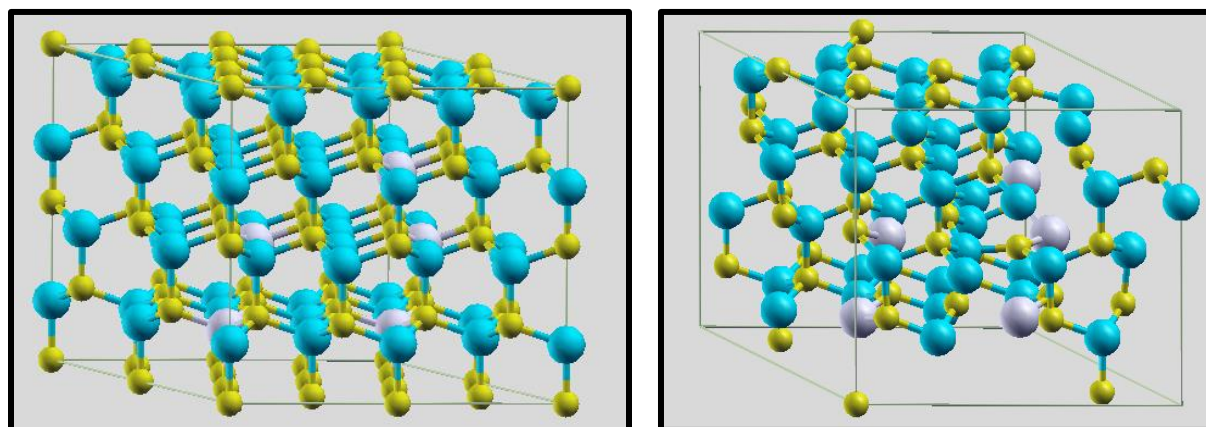
Atoms	Distance in input	Distance in output
First and second	3.0950Å	2.8848Å
Second and third	5.3561Å	5.3594Å
Third and fourth	5.0590Å	4.9088Å
First and fourth	5.3530Å	5.3808Å

Table 4.2.1.4: distance between lithium atoms in input and output for four lithium atom structure.

Formation energy in this case is found to be 18.9598 eV.

4.2.1.5. Five lithium atoms in five silicon vacancies

Both the input and output structures are depicted below.



“Five lithium atoms in five silicon vacancies” input structure

“Five lithium atoms in five silicon vacancies” output structure

Fig 4.2.1.5: input and output of five lithium atom in five silicon vacancy

(Lithium atoms are named as first, second, fourth and fifth from the left to the right respectively and the topmost atom is considered as the third atom)

Here, five lithium atoms have been inserted into five silicon vacancies. The distance between them is listed in the table below:

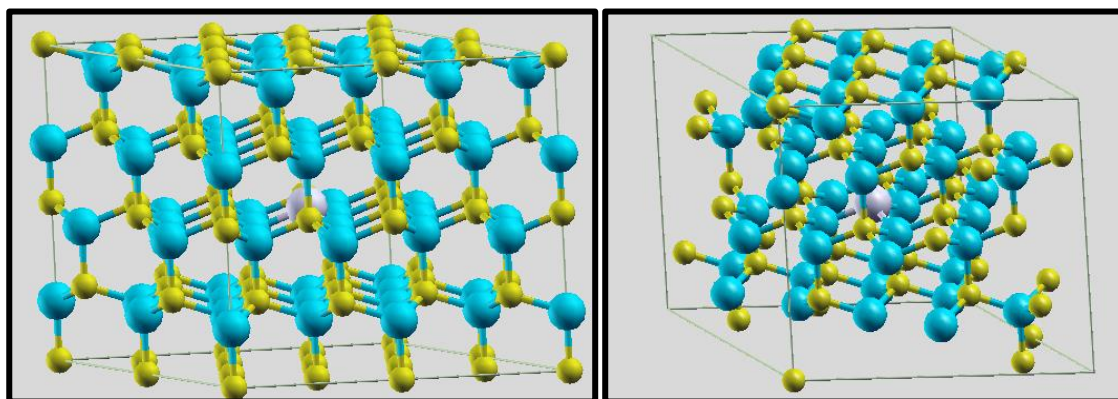
Atoms	Distance in input	Distance in output
First and second	3.0950Å	2.8850Å
Second and third	5.3561Å	5.2836Å
Third and fifth	3.0960Å	2.9130Å
First and four	5.3530Å	5.2921Å
Fourth and fifth	3.0950Å	2.9995Å

Table 4.2.1.5: distance between lithium atoms in input and output for five lithium atom structure
Formation energy in this structure is 24.2377 eV.

Now we insert lithium atoms in carbon vacancy.

4.2.1.6. One lithium atom in one carbon vacancy

Both input and output structures for given conditions are shown in figure below. We have created a vacancy on carbon side almost at the middle of the structure. One lithium atom is inserted on that vacancy. Here we put one lithium atom so it didn't interact with other lithium atoms; as a result it remains in the same position in output structure.



“Lithium atom in carbon vacancy” input structure

“Lithium atom in carbon vacancy output” structure

Fig 4.2.1.6: input and output of one lithium atom in one carbon vacancy

Formation energy is found to be 7.2747 eV.

4.2.1.7. Two lithium atoms in two carbon vacancy

Here, we have used two lithium atoms in two carbon vacancies. Both input and output structures as shown below.

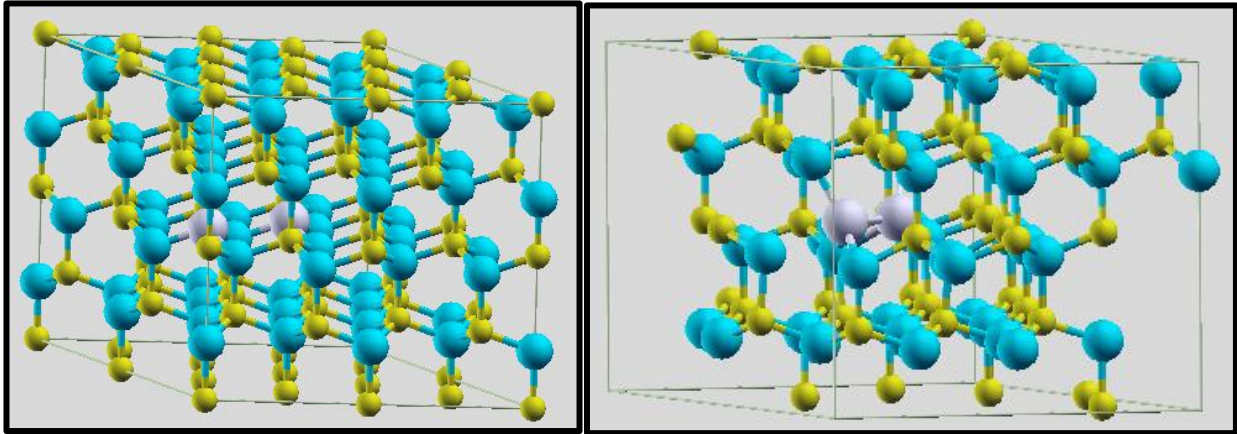


Fig4.2.1.7: Two lithium atoms in two carbon vacancy

Distance between two atoms in input structure is 3.0905 Å and distance between them in output structure is 1.9367Å.

Formation energy in this case is found to be 12.0142 eV

4.2.1.8. Three lithium atoms in three carbon vacancy

Here three lithium atoms are placed in three carbon vacancies. To avoid the mutual interaction between lithium atoms, they are kept at distance about 5Å. This is shown in pictures below.

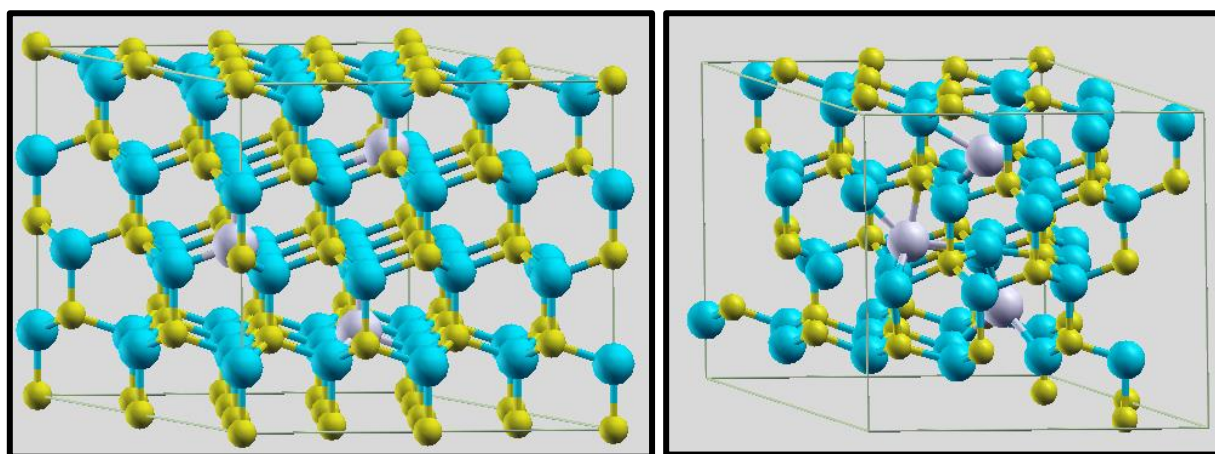


Fig: 4.2.1.8. Three lithium atoms in three carbon vacancy

(Here, the lithium atom on the left is named as first, topmost atom is second and last one is third atom.)

Distance between Li atoms is written in the table below.

Atoms	Distance in input	Distance in output
First and second	5.3528Å	3.6390Å
Second and third	5.3644Å	5.0270Å
Third and fifth	4.3738Å	3.8536Å

Table: 4.2.1.8. Distance between three lithium atoms in three carbon vacancy

Formation energy in this case is calculated to be 18.2864 eV.

4.2.1.9. Four lithium atoms in four carbon vacancy

Four lithium atoms have been inserted in four carbon vacancies as in structures below.

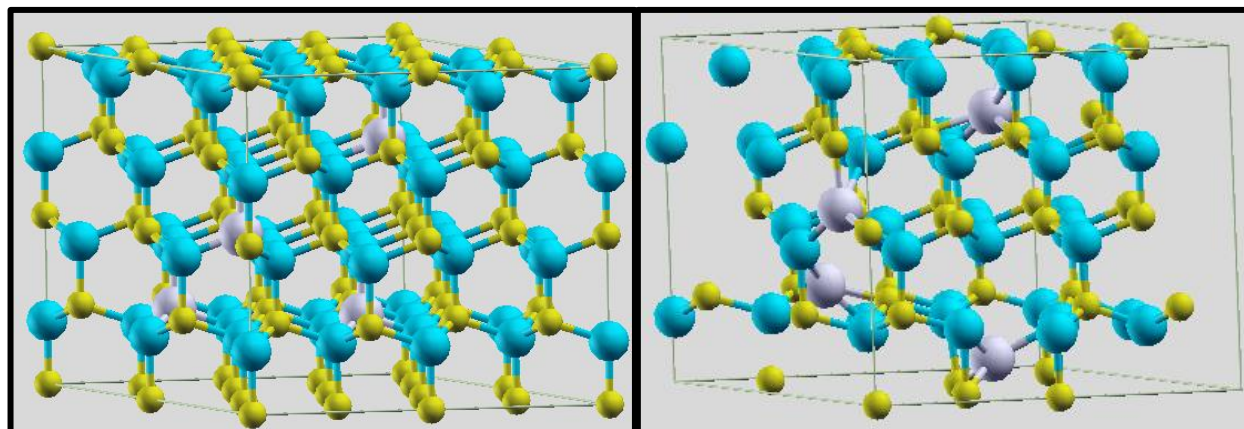


Fig: 4.2.1.9. Four lithium atoms in four carbon vacancy

(Lithium atoms are named as first, second and fourth from the left to the right respectively and the topmost atom is considered as the third atom)

Distance between the above atoms are measured and written below.

Atoms	Distance in input	Distance in output
First and second	4.3778Å	4.1277Å
Second and third	5.3528Å	5.4556Å
Third and fifth	5.3644Å	7.2239Å
First and fourth	6.1811Å	5.5471Å

Table: 4.2.1.9. Distance between four lithium atoms in four carbon vacancy

Formation energy is 23.1735 eV for this structure.

4.2.1.10. Five lithium atoms in five carbon vacancy

Five lithium atoms in five carbon vacancies are kept to find the formation energy. the respective pictures are shown below.

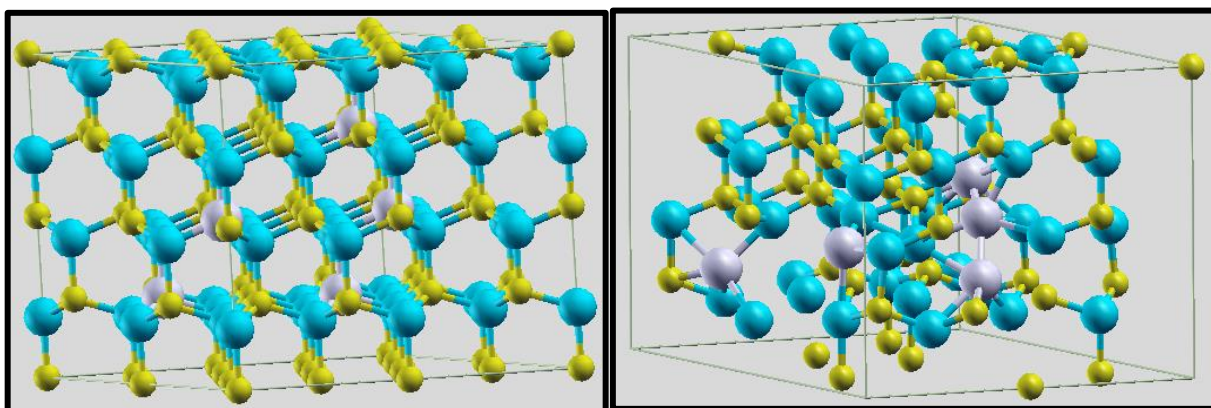


Fig: 4.2.1.10. Five lithium atoms in five carbon vacancy

(Lithium atoms are named as first, second, fourth and fifth from the left to the right respectively and the topmost atom is considered as the third atom)

Measured distances are listed below.

Atoms	Distance in input	Distance in output
First and second	4.3778Å	4.5670Å
Second and third	5.3528Å	8.3953Å
Third and fifth	3.0903Å	1.9661Å
Fourth and fifth	3.1007 Å	2.0949 Å
Fourth and first	6.1811Å	4.4425Å

Table: 4.2.1.10. Distance between five lithium atoms in five carbon vacancy

Formation energy calculated to be 27.1418 eV

Now, we have accumulated all the results obtained above in to the tabular form. The table below shows formation energy with a different number of lithium atoms in silicon vacancies.

Number of lithium atoms	Formation energy (in eV) in silicon side	Formation energy (in eV) in carbon side
1	5.7173	7.2747
2	9.6648	12.0142
3	14.0323	18.2864
4	18.9598	23.1735
5	24.2377	27.1418

Table 4.2.1.10 (A): Table showing variation of formation energy with number of lithium atom inserted in carbon vacancies.

The graph below describes the relation between formation energy and number of lithium atoms into silicon and carbon vacancy.

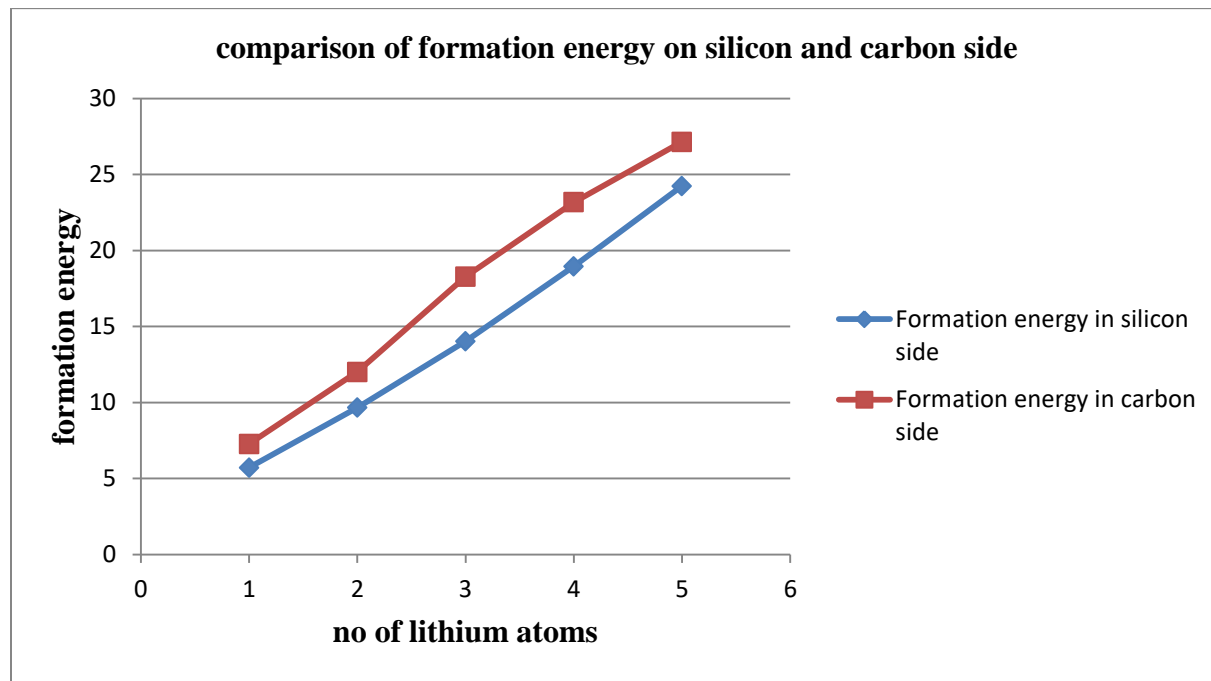


Fig 4.2.1.10(A): formation energy vs no. of li atoms in silicon and carbon vacancy graph

The graph plotted above shows the variation of the formation energy with a number of lithium atoms inserted in silicon and carbon vacancies. We found that, formation energy increases slowly with the increase of number of lithium atoms in both the sides. Furthermore, we found that formation energy in carbon side is more than that on silicon side.

To study the stability of structures we have calculate the formation energy per atom in the table below.

Number of lithium atoms	formation energy per atom in silicon side (eV/atom)	Formation energy per atom in carbon side (eV/atom)
1	5.7173	7.2747
2	4.8324	6.0071
3	4.6774	6.0954
4	4.7399	5.7933
5	4.8475	5.42836

Table 4.2.1.10 (B): Table showing variation of formation energy per li atom with number of lithium atom inserted in carbon and silicon vacancies.

The graph is plotted from this tabulated data. This is shown in next page.

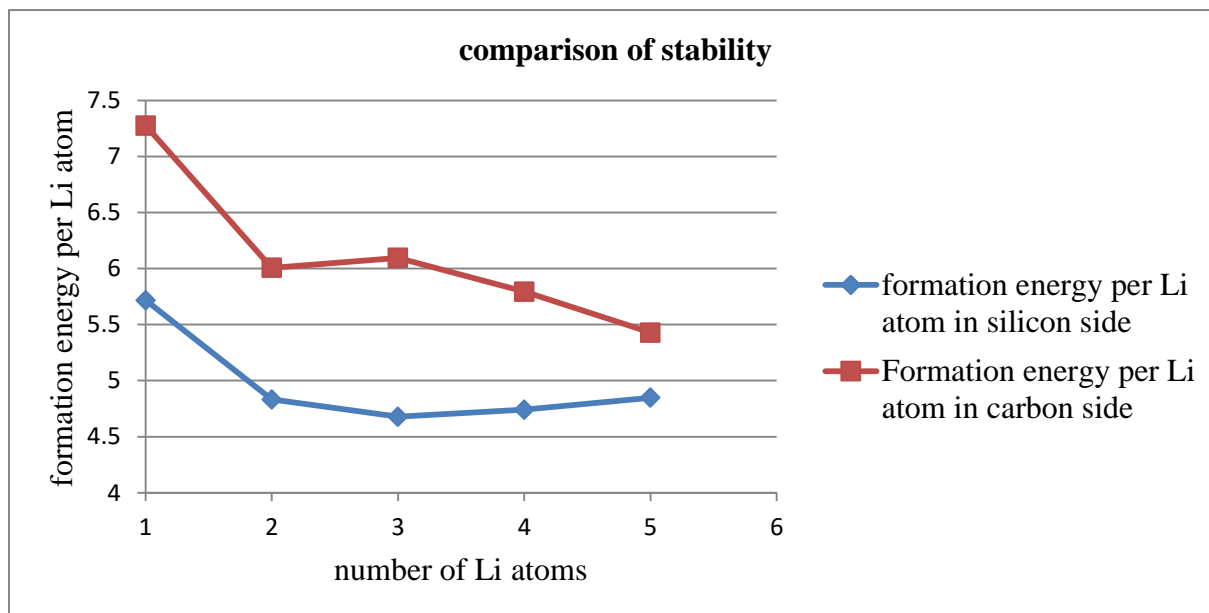


Fig 4.2.1.10(B): formation energy per atom versus no. of li atoms in silicon and carbon vacancy graph.

From this graph, we can conclude that lithiation of silicon side is more stable than lithiation of carbon side in bulk SiC. And stability increases with the lithiation density.

4.2.2. Calculation of formation energy when distance between lithium atoms is small

In this part of chapter, vacancies have been created on SiC. Distance between vacancies is made smaller than in previous section. First, lithium atoms in silicon vacancy will be studied and after that, we will study similar structure for lithium atoms in carbon vacancy. Finally we will compare the result.

4.2.2.1. Two lithium atoms in two silicon vacancy

Two pictures below represent input and output structures of two lithium atoms inserted in two vacancies created on silicon side.

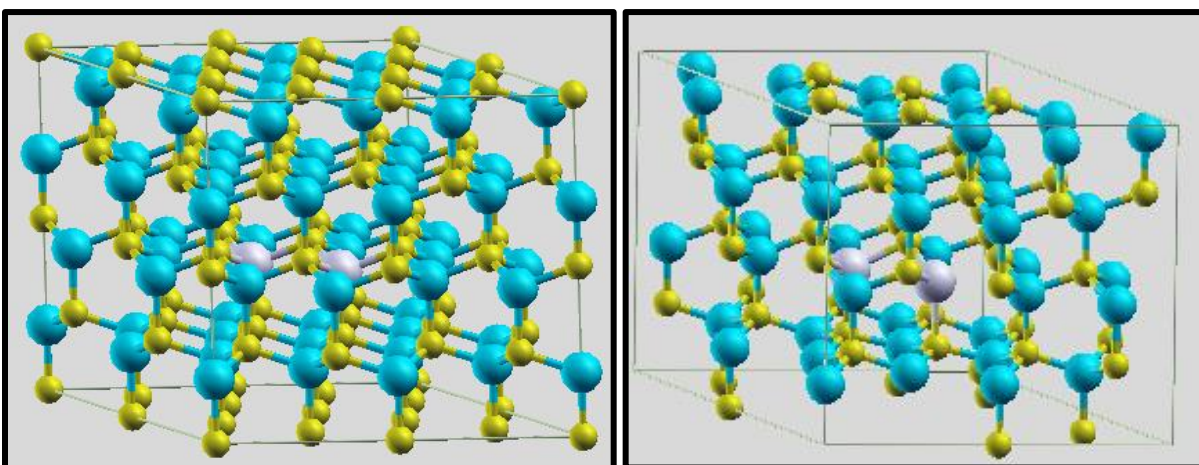


Fig: 4.2.2.1. Two lithium atoms in two silicon vacancy

Two lithium atoms in input are 3.0905\AA apart and their distance decreased to 2.9358\AA in the output structure.

9.6861 eV is the calculate formation energy for this structure.

4.2.2.2. Three lithium atoms in three silicon vacancy

We have shown input and output structure for given combination of lithium atoms in silicon vacancies.

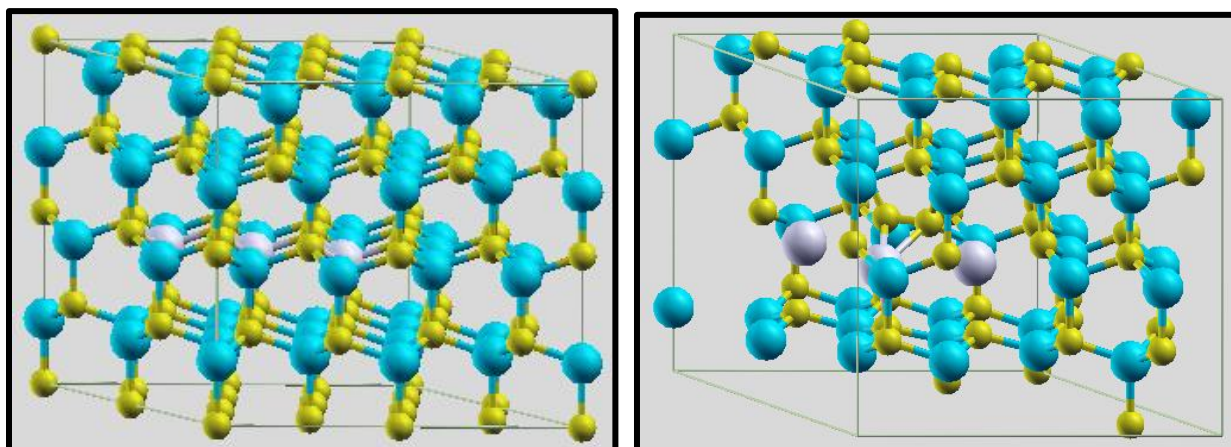


Figure 4.2.2.2: Three lithium atoms in three silicon vacancy

(Atoms are named as first, second and third from left to right respectively)

Respective distances between atoms are tabulated below.

Atoms	Distance in input	Distance in output
First and second	3.0950Å	2.9221Å
Second and third	3.0905Å	2.9221Å

Table: 4.2.2.2. Distance between three lithium atoms in three silicon vacancy

Formation energy is 12.8663 eV in this case.

4.2.2.3. Four lithium atoms in four silicon vacancy

Four lithium atoms are used in the 4H – Sic structure after removing four silicon atoms from the structure. Input and output are shown below.

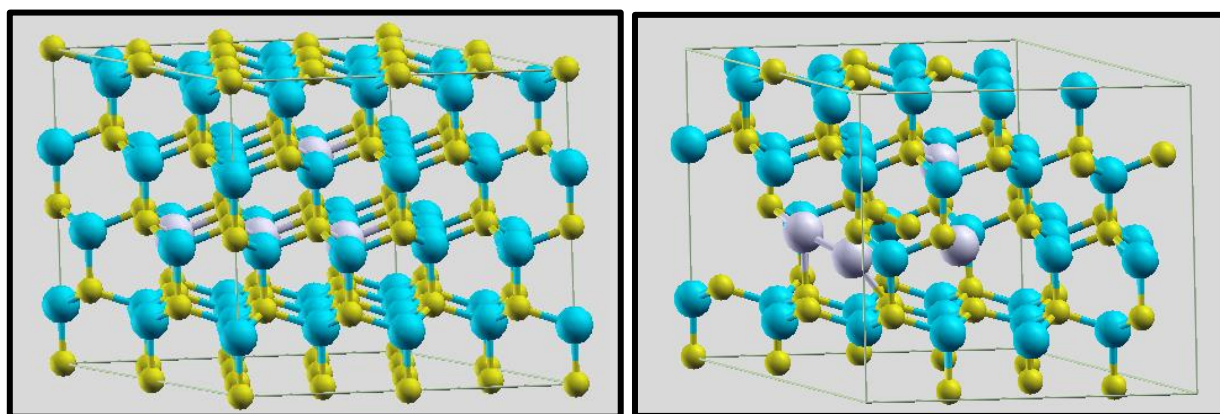


Figure 4.2.2.3. Four lithium atoms in four silicon vacancy

(Atoms are considered first, second, third and fourth from left to right respectively.)

Table shows the separation between lithium atoms.

Atoms	Distance in input	Distance in output
First and second	3.0950Å	2.2982Å
Second and third	3.0960Å	4.1660Å
First and third	5.3561Å	5.2850Å
Second and fourth	3.0905Å	3.7077Å

Table: 4.2.2.3. Distance between four lithium atoms in four silicon vacancy

Formation energy is 16.6410 eV for this structure.

4.2.2.4. Five lithium atoms in five silicon vacancy

Input and output structures for five lithium atoms in five silicon vacancies as are shown below.

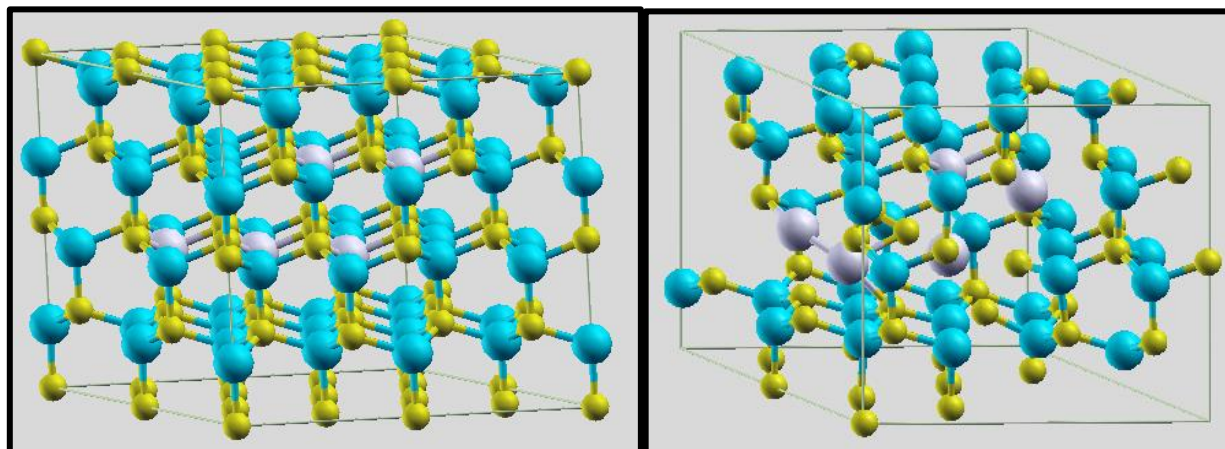


Figure: 4.2.2.4. Five lithium atoms in five silicon vacancy

Atoms in the input are regarded as first to fifth from left to right respectively. In the output corresponding atoms are also named as first to fifth.

Atoms	Distance in input	Distance in output
First and second	3.0950Å	2.2380Å
Second and third	3.0960Å	4.2538Å
First and third	5.3561Å	5.3588Å
Second and fourth	3.0905Å	3.3587Å
Fourth and fifth	3.0960 Å	3.2482Å
Third and fourth	3.0905Å	2.8999Å

Table: 4.2.2.4. Distance between five lithium atoms in five silicon vacancy

Formation energy is 21.5187 eV for structure with five li atoms.

Now, we start with lithium atoms in carbon vacancy. We already did for one lithium atom, so we are starting from two lithium atoms.

4.2.2.5 Two lithium atoms in carbon vacancy

Input and output structure for two lithium atoms in carbon vacancy are presented below. We have tried to use two lithium atoms almost at the centre of our structure.

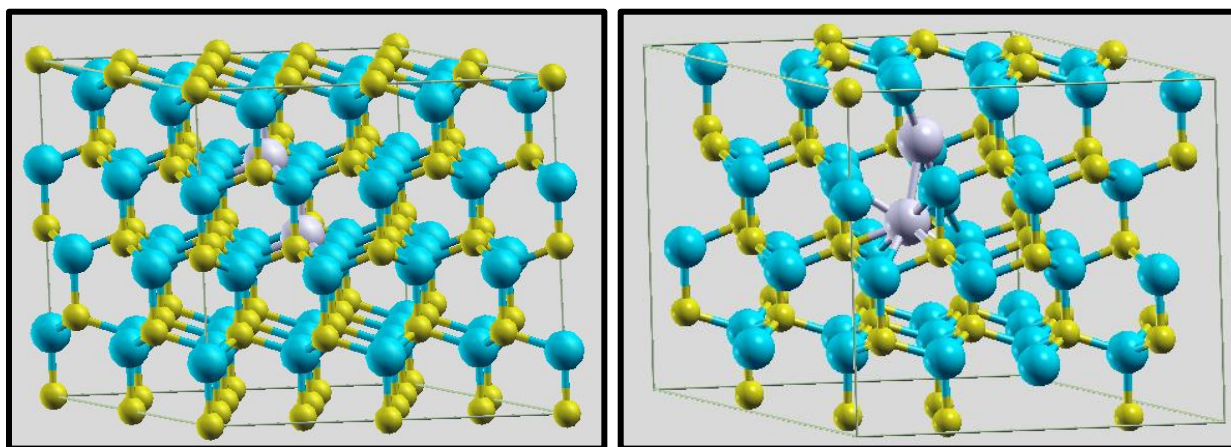


Fig: “Two lithium atoms in carbon vacancies” input structures.

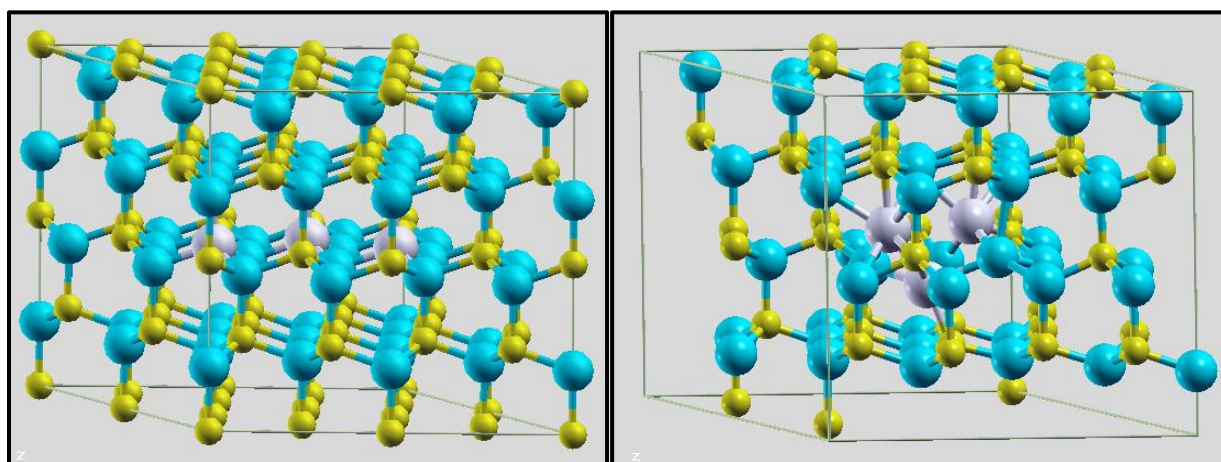
Fig: “Two lithium atoms in carbon vacancies” output structures.

Fig 4.2.2.5: input and output of two lithium atom in two carbon vacancy

In the input structure the distance between two lithium atoms is 3.0903\AA and in the output structure, the distance between two lithium atoms is 2.4475\AA . One lithium atom tries to interact with another lithium atom; as a result, they are closer in output structure.

Formation energy is 9.5898714 eV .

4.2.2.6 Three lithium atoms in three carbon vacancies



“Three lithium atoms in three carbon vacancy” input structure

“Three lithium atoms in three carbon vacancy” output structure

Fig 4.2.2.6: input and output of three lithium atom in three carbon vacancy

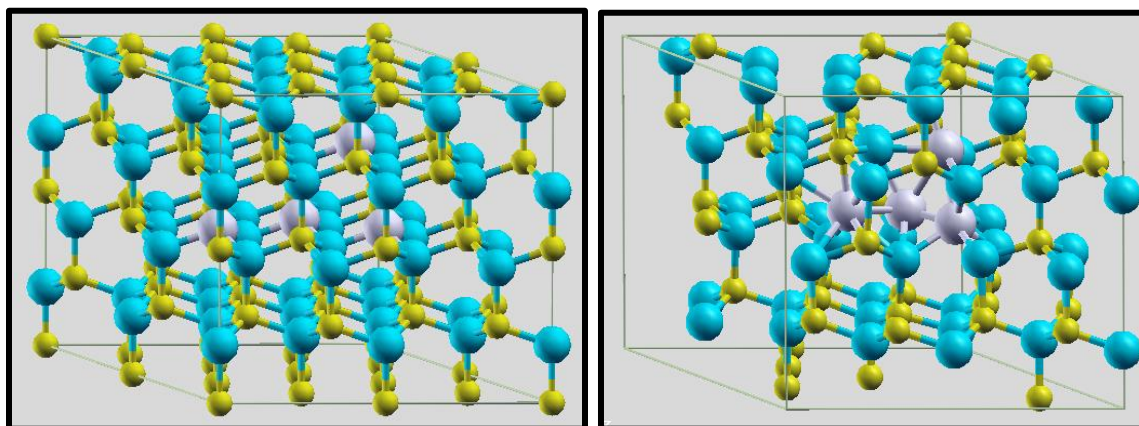
(Lithium atoms are named first, second and third from the left to right respectively)

In the input file, the distance between first and second lithium atom is equal to the distance between second and third lithium atom which is 3.0905\AA . In the output file distance between first and second 1.9787\AA and the distance between second and third is 2.5975\AA .

Here also lithium atoms try to form a cluster, so they shifted towards each other as a result distance between them decreases.

Formation energy is equal to 13.5525 eV

4.2.2.7 Four lithium atoms in four carbon vacancies



“Four lithium atoms in four carbon vacancy” input structure

“Four lithium atoms in four carbon vacancy” output structure

Fig 4.2.2.7: input and output of four lithium atom in four carbon vacancy

(Lithium atoms are named first, second, third and fourth from the left to right respectively)

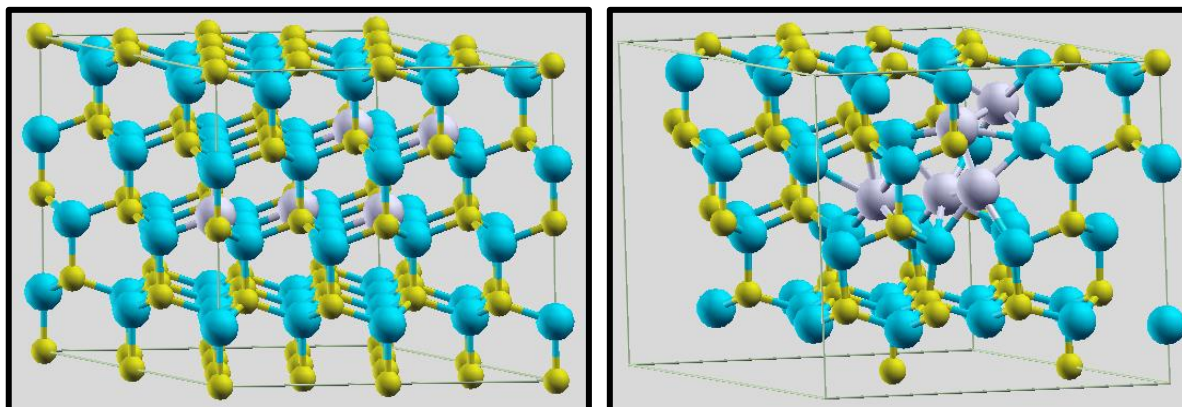
Four lithium atoms have been inserted in four carbon vacancies. The distance between them is listed in the table below:

Atoms	Distance in input	Distance in output
First and second	3.0905Å	2.4066Å
Second and third	3.0903Å	2.4316Å
Third and four	3.0903Å	2.3491Å
Second and four	3.0905Å	1.9802Å

Table 4.2.2.7: distance between lithium atoms in input and output for four lithium structure

Formation energy is equal to 20.5265 eV

4.2.2.8. Five lithium atoms in five carbon vacancies



“Five lithium atoms in five carbon vacancies” input structure

“Five lithium atoms in five carbon vacancies” output structure

Fig 4.2.2.8: input and output of five lithium atom in five carbon vacancy

(Lithium atoms are named as one, two, three, four and five from left to right respectively)

Here, five lithium atoms have been inserted into five carbon vacancies. The distance between them is listed in the table below:

Atoms	Distance in input	Distance in output
First and second	3.0905Å	2.5904Å
Second and third	3.0903Å	2.6454Å
Third and four	3.0903Å	2.0436Å
Second and four	3.0905Å	2.3024Å
Four and five	3.0903Å	2.1331Å

Table 4.2.2.8: distance between lithium atoms in input and output for five lithium structure

Formation energy is 20.1442 eV.

Now we collect result obtained above in tabulated form and we will plot the graph to compare the formation energy of carbon side and silicon side.

In the first column of the table, number of lithium atoms inserted has been kept and in the second and third column, corresponding formation energies are kept.

Number lithium atoms	Formation energy in silicon side (eV)	formation energy in carbon side (eV)
1	5.7173	7.2747
2	9.6861	9.5898
3	12.8663	13.5525
4	16.6410	20.5265
5	21.5187	20.1442

Table 4.2.2.8(A): Table showing variation of formation energy with number of lithium atom inserted in carbon and silicon vacancies.

The graph below shows the variation of formation energy with number of Lithium atoms inserted in the carbon and silicon vacancies. With the increase of number of lithium atoms, formation energy increases slowly. In this graph also we found silicon side is more stable than carbon side.

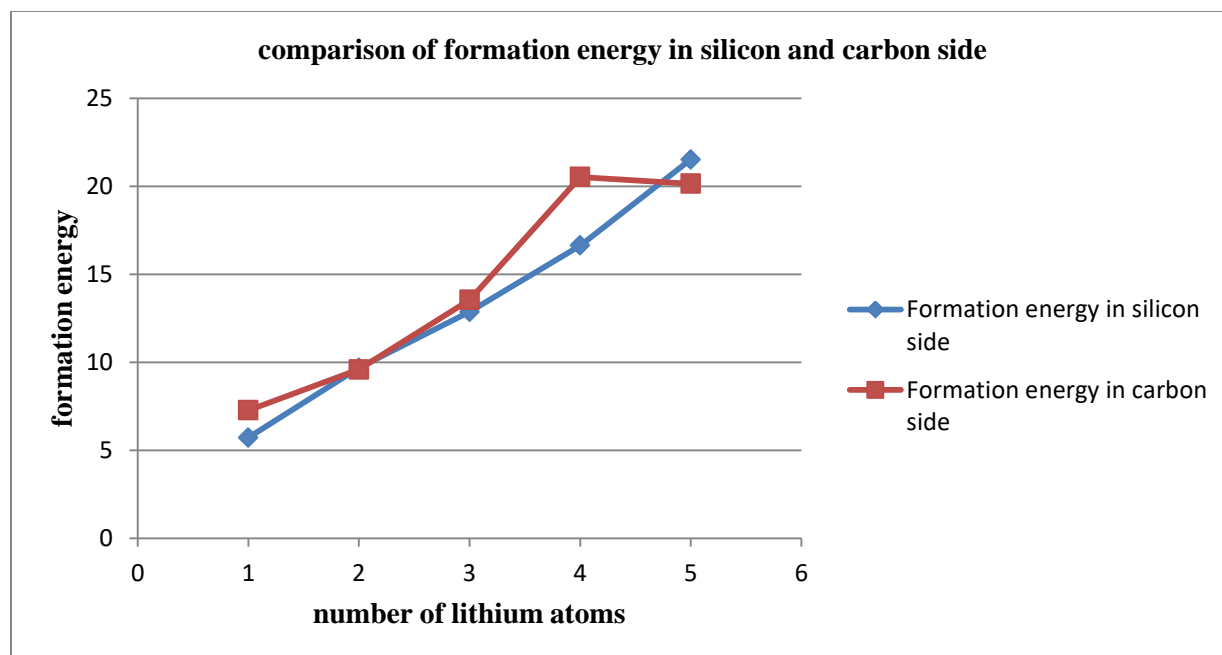


Fig 4.2.2.8 (A): graph between formation energy and number of lithium in carbon and silicon vacancy

To study stability process, we have made one table for formation energy per li atom.

Number lithium atoms	Formation energy per Li atom in silicon side (eV/atom)	formation energy per Li atom in carbon side (eV/atom)
1	5.7173	7.2747
2	4.8430	4.7949
3	4.2887	4.5175
4	4.1602	5.1316
5	4.3037	4.0288

Table 4.2.2.8 (B): table between formation energy and number of lithium in carbon and silicon vacancy

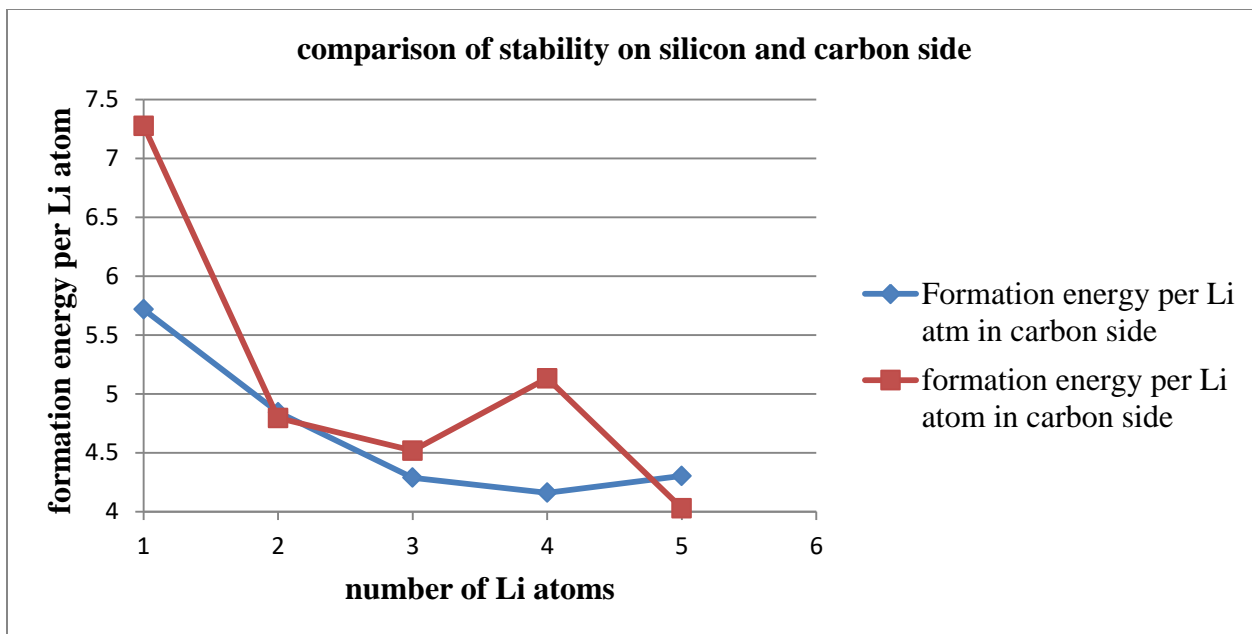


Fig 4.2.2.8 (B): graph between formation energy per li atom and number of lithium in carbon and vacancy

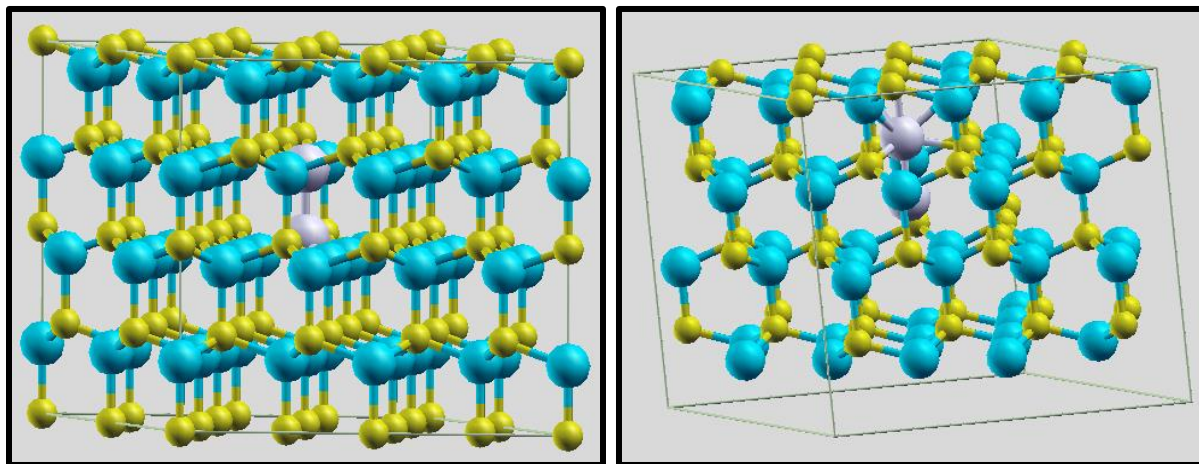
This graph also shows that, silicon side is more stable than carbon side for lithiation process.

The graph for carbon side is not smooth when number of li atom is four.

4.2.3. Lithium atoms in some random structures

4.2.3.1. Two lithium atoms in silicon and carbon vacancies

Both input and output structure for two lithium atoms in silicon and carbon vacancies are presented below. Here two lithium atoms are inserted almost at the center of our input structure. Here two lithium atoms in input are at distance 1.8968\AA apart and in output at distance 1.8425\AA apart. The distance in output is slowly decreased because of interaction between two lithium atoms.



“Lithium atom in Silicon and Carbon vacancy” input structure

“Lithium atom in Silicon and carbon vacancy” output structure

Fig 4.2.3.1: input and output of two lithium atom in silicon and carbon vacancy

Formation energy is equal to 5.2373 eV

4.2.3.2. Three Lithium atoms (Two in silicon vacancy and one Interstitial)

The input structure for the three lithium atoms in 4HSIC is presented below.

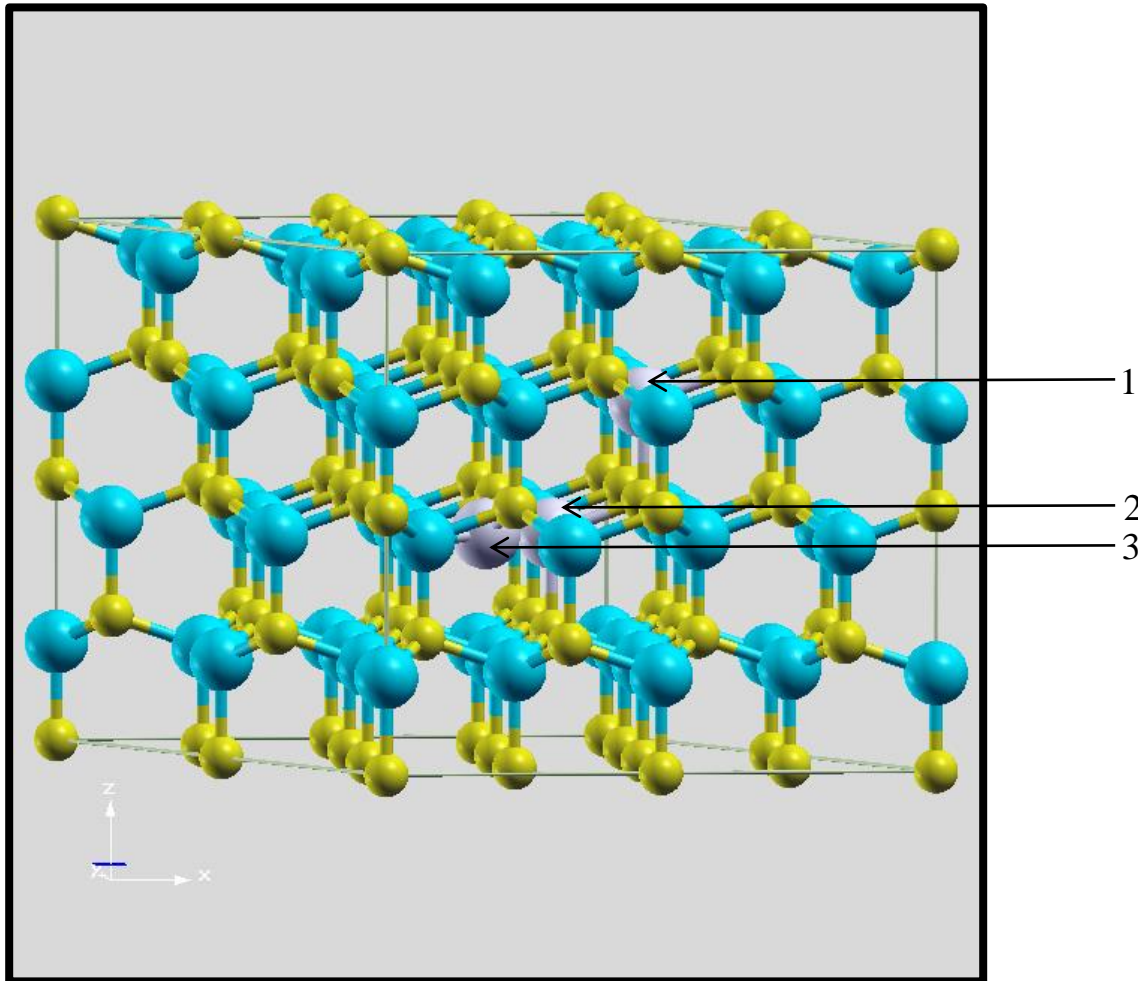


Fig 4.2.3.2: 4H - SiC input structure with three lithium atom (two in silicon and one in interstitial position)

Here we have inserted three lithium atoms in the 4H SiC structure. Atom number one and two are inserted in place of two silicon atoms and atom number three is inserted at distance 1.2847\AA from second lithium atom. Third atom is placed in interstitial position. It doesn't have any

regular pattern and it hasn't replaced any silicon or carbon atom. All together we have 97 atoms in this structure.

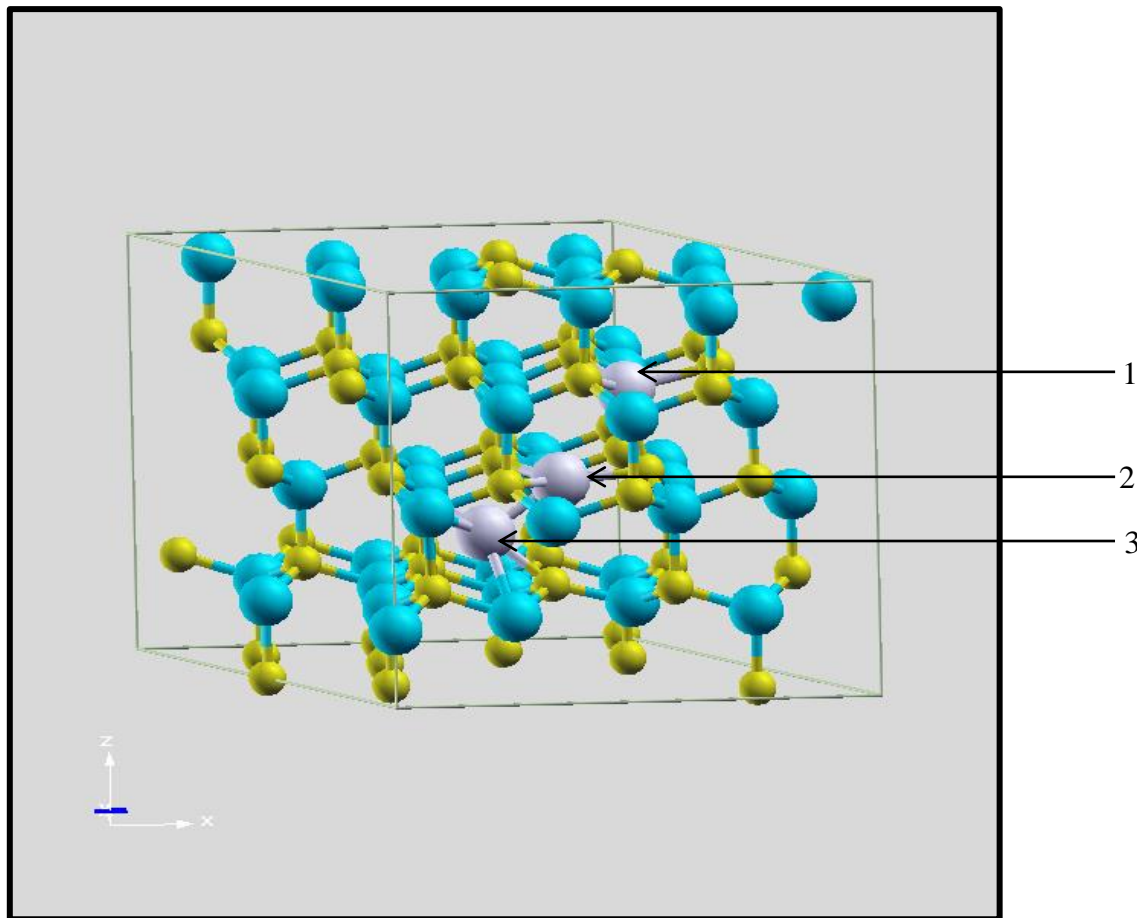


Fig 4.2.3.2 (A): 4H - SIC output structure with three lithium atom (two in silicon and one in interstitial position)

The output structure is as shown in picture above. All the atoms are shifted slightly upward. And distance between them also increases to 2.0791\AA . In the input file all three atoms were connected with three other atoms but in the output structure, second and third atoms are connected with four and six other atoms respectively. Third atom started interaction with one more silicon and carbon atom.

Formation energy is 9.3823 eV

4.2.3.3. Three lithium atoms (two in silicon vacancy and one in carbon vacancy)

Input structure is shown below.

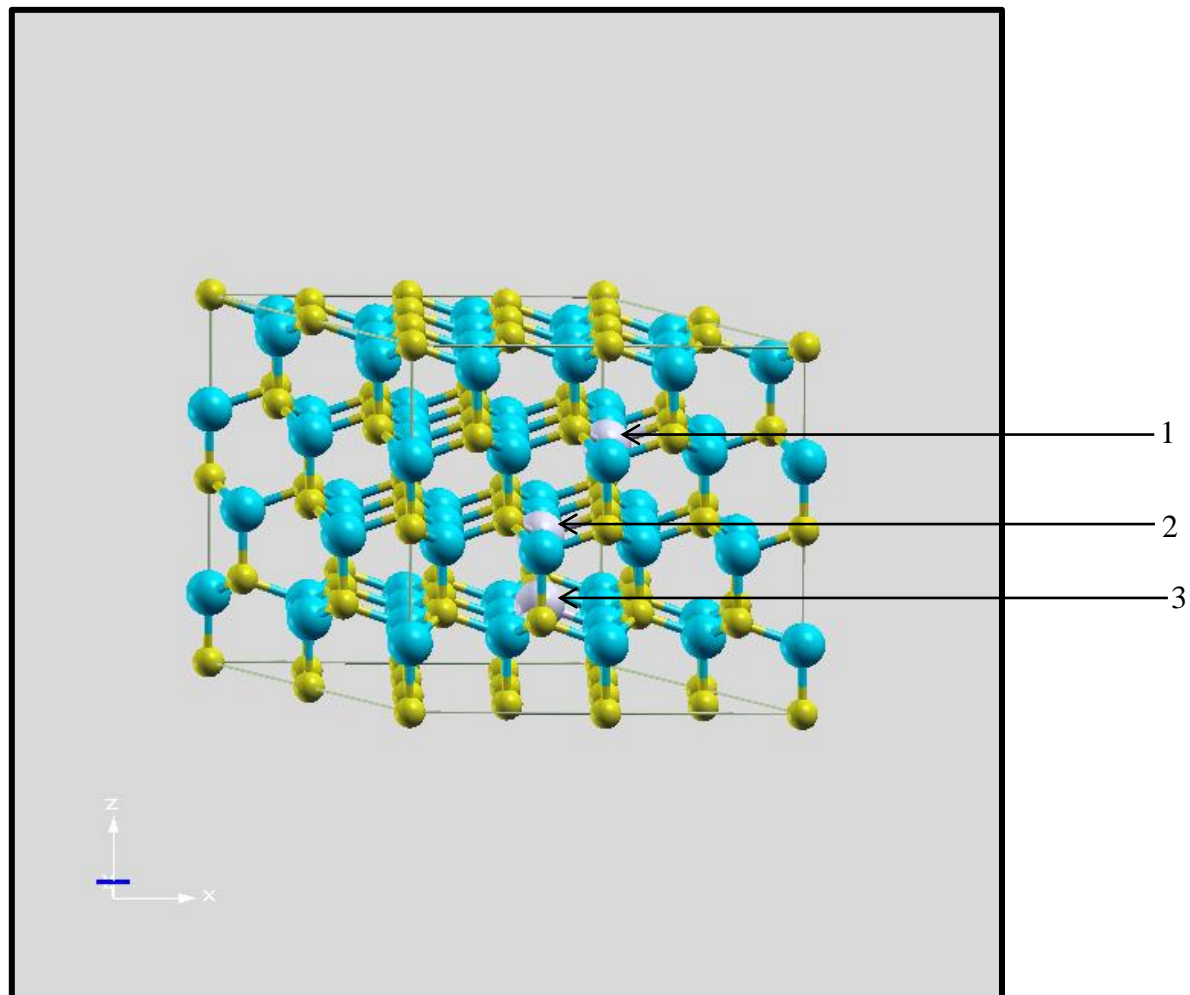


Fig 4.2.3.3: Three lithium atoms input (two in silicon vacancy and one in carbon vacancy)

Here, first and second lithium are not connected directly, but second and third atoms are connected directly. Distance between second and third atom is 1.9025\AA . The distance between first and second atom is 4.7782\AA and the distance between first and third atom is 3.0690\AA .

Output structure is as shown below.

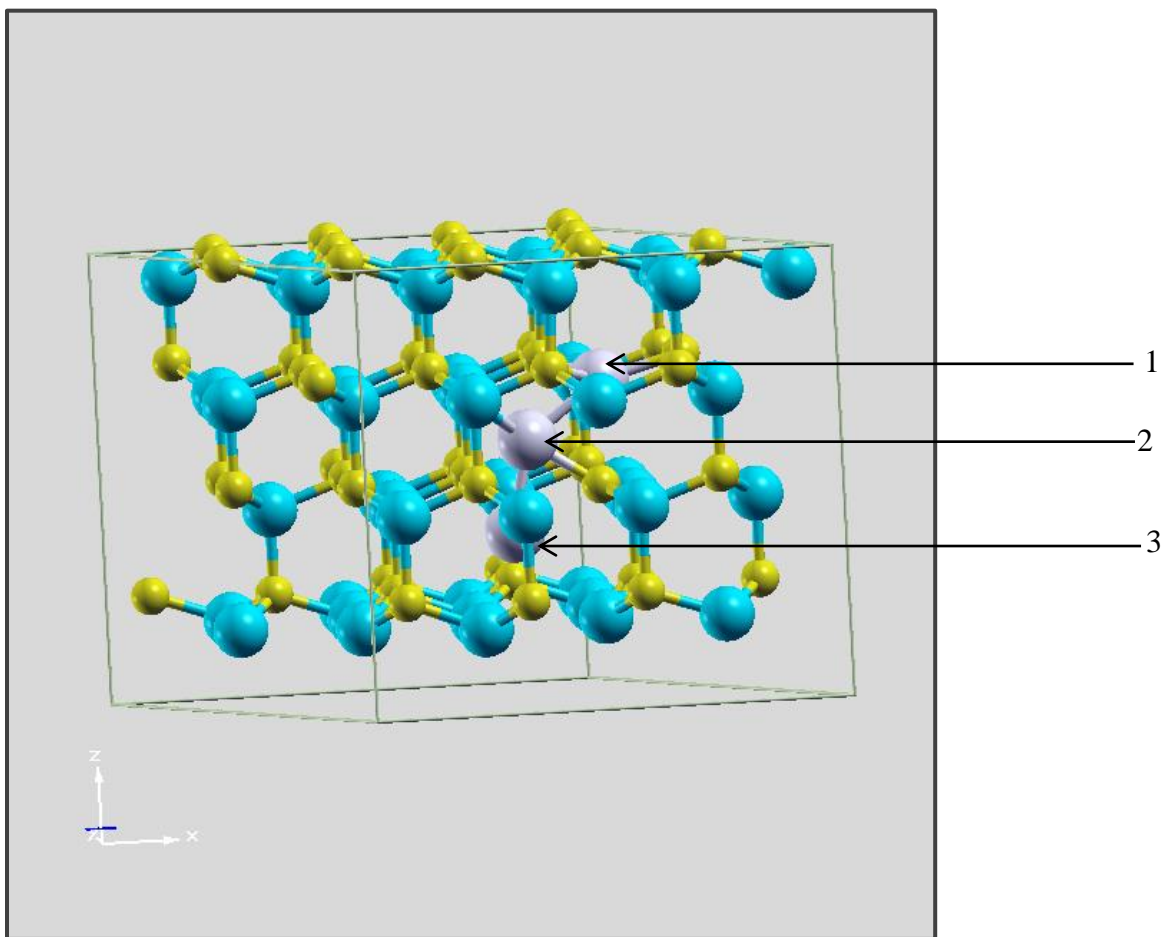


Fig 4.2.3.3 (A): Three lithium atoms output (two in silicon vacancy and one in carbon vacancy)

The output structure obtained is as shown in figure above. The distance between first and second lithium atom is 2.0929\AA and distance between second and third atom is 2.0782\AA . The distance between first and third is 3.8867\AA .

Formation energy = 9.5037 eV

4.2.3.4. Four lithium atoms (Two in silicon vacancy and two in carbon vacancy)

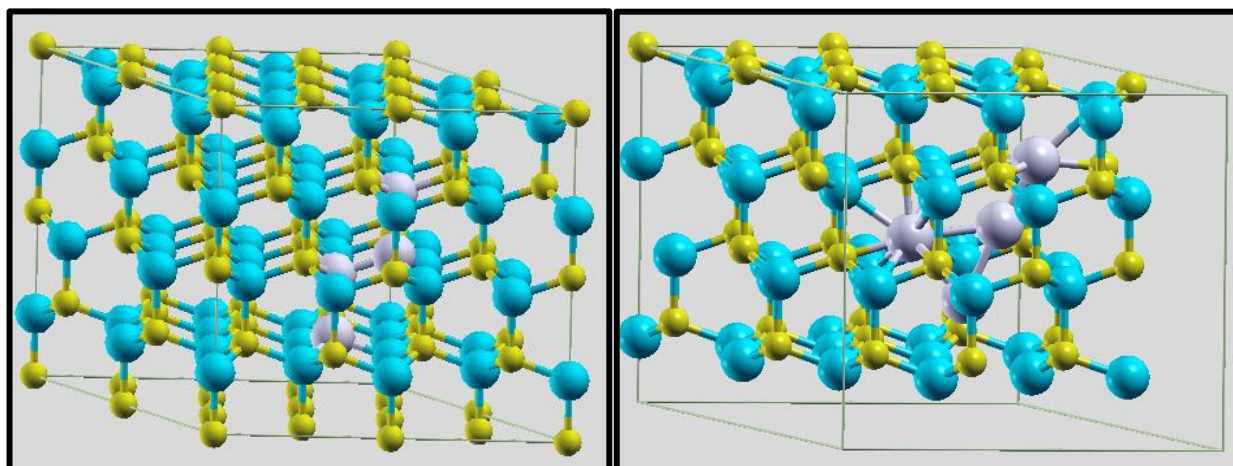


Fig 4.2.3.4: Input and output structure for four lithium atoms (Two in silicon vacancy and two in carbon vacancy)

Here four lithium atoms have been inserted in two carbon and two silicon vacancies. Atoms are numbered first to fourth from top to bottom respectively. The distance between them is listed in the table below:

Atoms	Distance in input	Distance in output
First and second	1.8968Å	2.1012Å
Second and third	1.8934Å	2.5512Å
Third and four	1.9025Å	2.3617Å

Table 4.2.3.4: distance of li atoms in input and output structure for four lithium atoms (Two in silicon vacancy and two in carbon vacancy)

Formation energy = 8.5196 eV

4.2.3.5. Five lithium atoms (three in silicon vacancy and one two in carbon vacancy)

Input structure for given condition is as shown below.

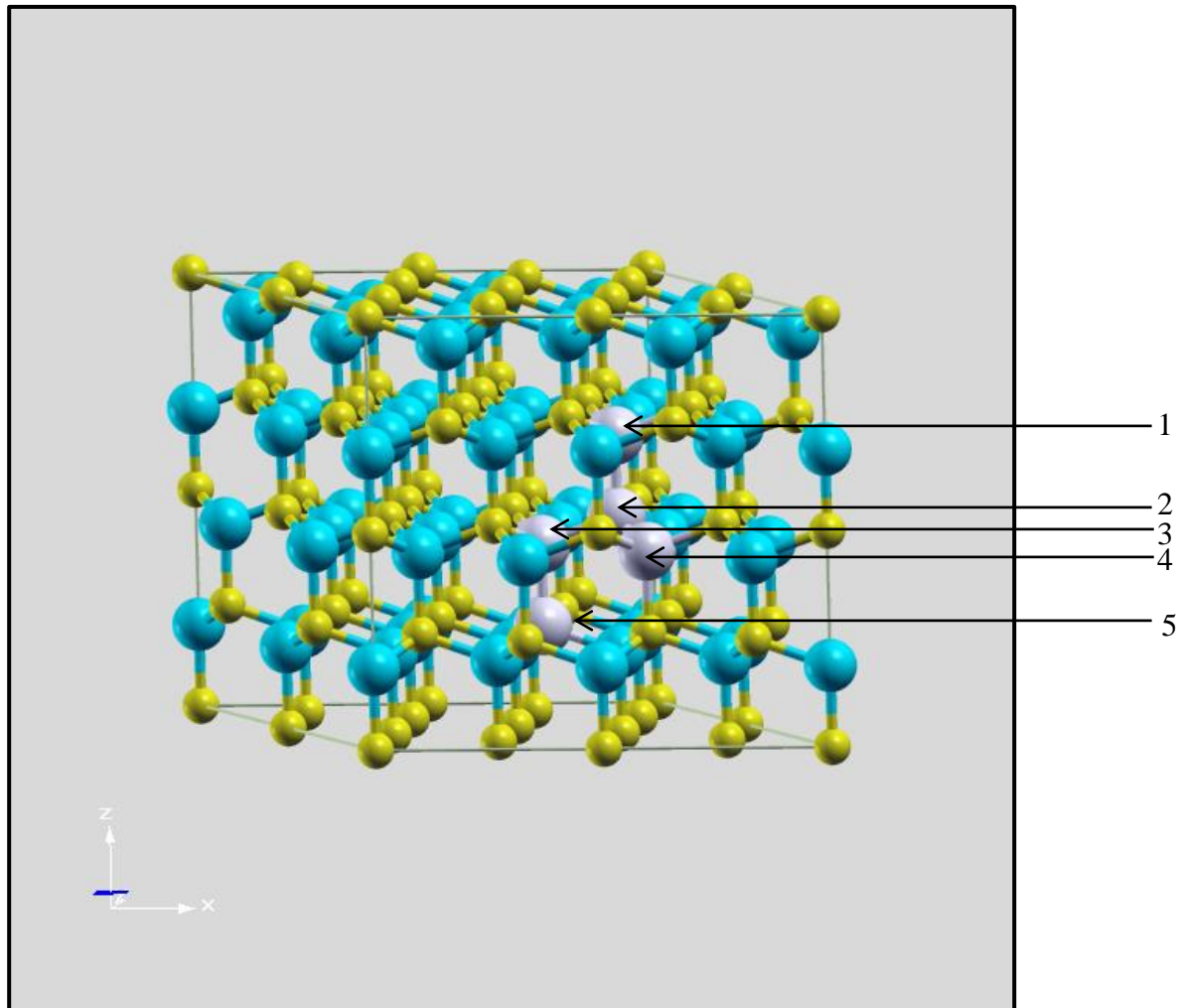


Fig 4.2.3.5: Input structure five lithium atoms (three in silicon vacancy and one two in carbon vacancy)

Here, three lithium atoms are placed in silicon vacancy and two lithium atoms are placed in carbon vacancy. The distance between first and second lithium atom is 1.8968\AA . The distance

between second & third and second and fourth is same which is 1.8934Å. The distance between third and fifth lithium atom is 1.9024Å.

Output structure is presented below.

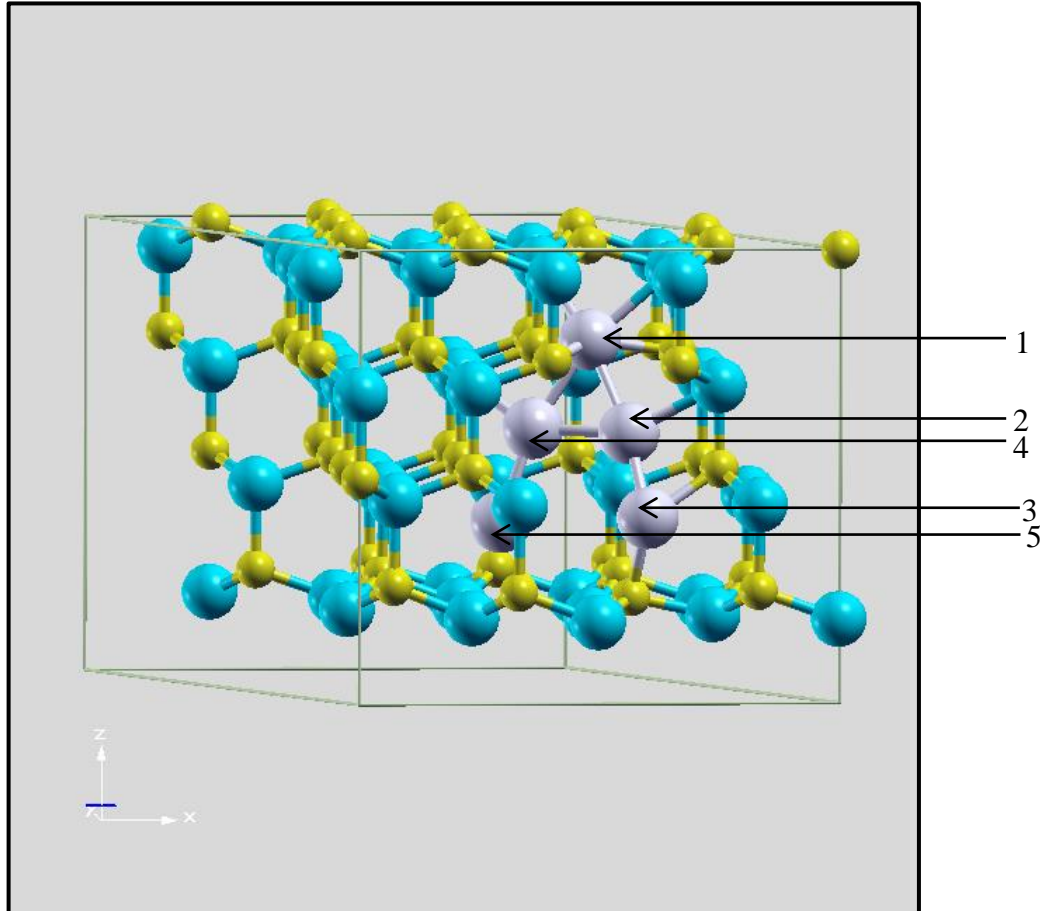


Fig 4.2.3.5 (A): Output structure five lithium atoms (three in silicon vacancy and one two in carbon vacancy)

All the atoms are shifted upward.

atoms	input	output
1 & 2	1.8968Å	2.3491Å
2 & 3	1.8934Å	2.1754Å
2 & 4	1.8934Å	2.3087Å
3 & 5	1.9024Å	3.7204Å

Table 4.2.3.5: distance between lithium atoms in input and output for five lithium structure
Formation energy 10.7912 eV

Number of lithium in carbon & Silicon vacancies	Formation energy (eV)
2 lithium (1 Si & 1 C)	5.2373
3 lithium (2@Si & 1 interstitial)	9.3823
4 lithium (2@Si & 2@C)	8.5196
5 lithium (3@Si & 2@C)	10.7917

Table 4.2.3.5(A): Formation energy versus number of lithium atoms in SiC

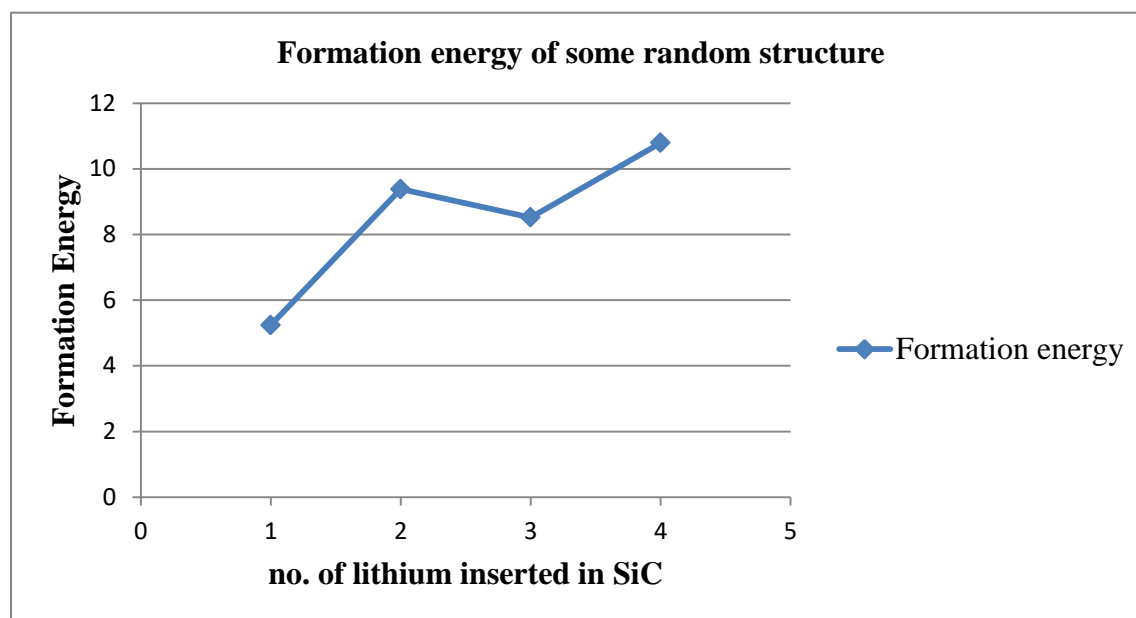


Fig 4.2.3.6 (A): Graph between formation energy and no of lithium inserted in SiC

The graph between number of lithium atoms and formation energy doesn't have smooth shape because in some structures, number of lithium atoms in silicon side are more and in some structures, number of lithium atoms in carbon sides are more. Formation energy is less if number of lithium atoms in silicon side is more and formation energy is more if number of lithium atoms in carbon side is more.

The table below shows formation energy per lithium atom.

Number of lithium in carbon & Silicon vacancies	Formation energy per Li atom (ev/atom)
2 lithium (1 Si & 1 C)	2.6186
3 lithium (2@Si & 1 interstitial)	3.1274
4 lithium (2@Si & 2@C)	2.1299
5 lithium (3@Si & 2@C)	2.1582

Table 4.2.3.5(B): Formation energy per Li atom versus number of lithium atoms in SiC

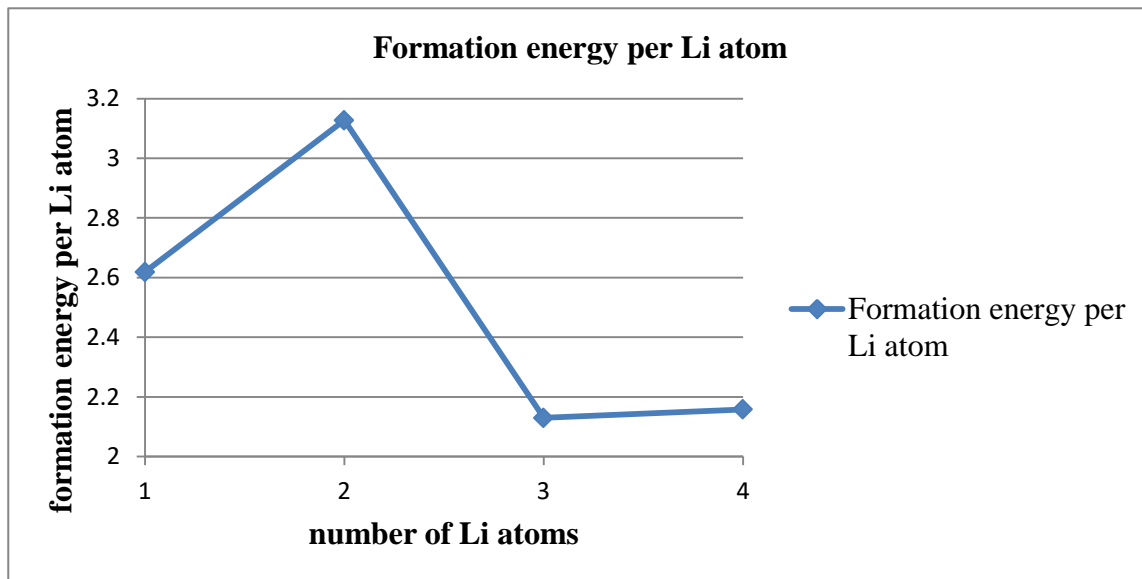


Fig 4.2.3.5(B): Graph between formation energy and no of lithium inserted in SiC

From this graph we can say that, structures with interstitial atoms are not much stable in comparison to other structures with symmetric atomic positions.

4.2.4. Lithium atoms in some symmetrical structures

4.2.4.1. Two lithium atoms in two silicon vacancy.

We have already explained this in previous chapters.

Formation energy = 9.686133489 eV

4.2.4.2. Two lithium atoms in two carbon vacancy.

We have already explained this previously.

Formation energy = 12.01421878 eV

4.2.4.3. Three lithium atoms in two silicon vacancy and one carbon vacancy

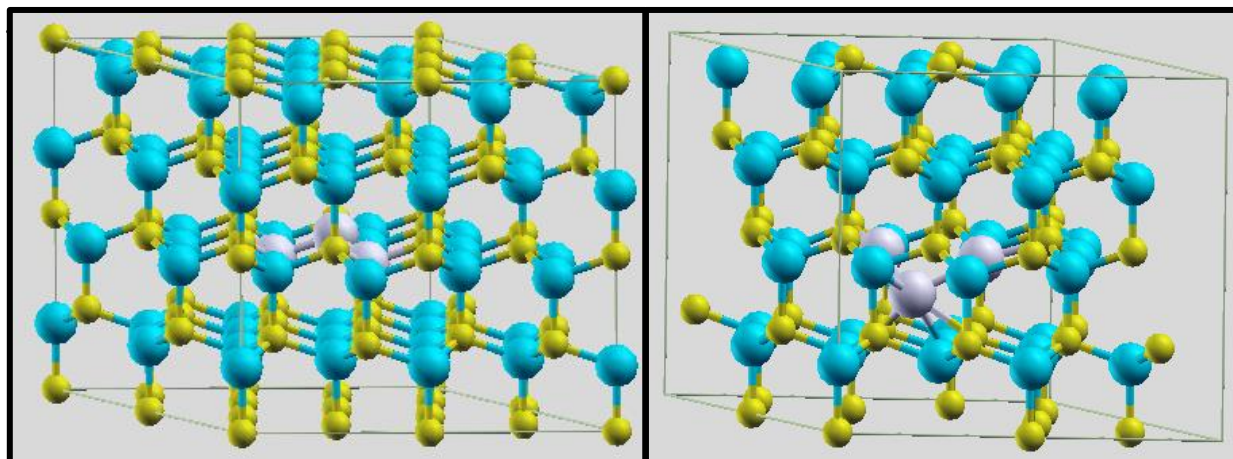


Fig 4.2.4.3: Three lithium atoms in two silicon vacancy and one carbon vacancy

The distance between the lithium atom to the left and the lithium atom to the top is 1.8934Å in the input structure and this distance increase to 2.1521Å in the output structure. Similarly the gap is 1.8934Å between the lithium atoms at top and atom at right, this distance increase to 2.1521 Å in the output structure. The lithium atom initially at the top goes to bottom in the output structure due to their interaction. Also, the separation increases by 0.3Å between lithium atom at left and the atom at right.

From the calculation, we found formation energy = 7.7742 eV

4.2.4.4. Three lithium atoms in two carbon vacancies and one silicon vacancy

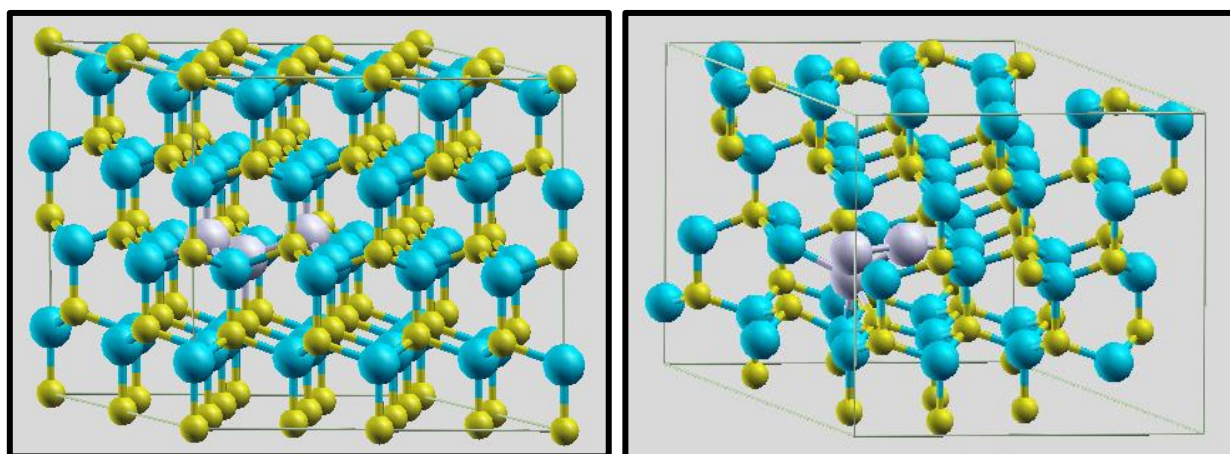


Fig 4.2.4.4: Three lithium atoms in two carbon vacancies and one silicon vacancy.

Three lithium atoms are arranged in the silicon vacancies as in figure above. The left most lithium atom and right most lithium atoms are placed at distance 1.8934 Å from central lithium atom in input structure. This distance of left most lithium atom from central atom increase to 2.1885Å and distance of right most atom from central atom increase to 2.0033Å in output structure. Orientation of lithium atoms change in the output structure due to interaction as a result their separation increases in output structure.

From calculation we get formation energy 10.2508 eV.

4.2.4.5. Four lithium atoms in three silicon vacancy and one carbon vacancy

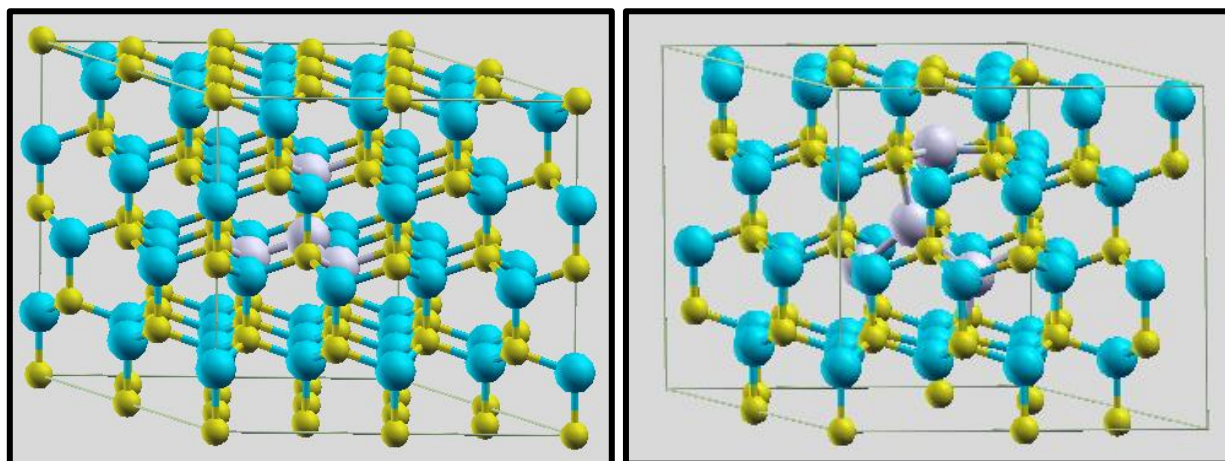


Fig 4.2.4.5: Four lithium atoms in three silicon vacancy and one carbon vacancy

(Topmost lithium atom is named as third and other atoms are named as first, second and third from left to right respectively)

In this case, we have inserted four lithium atoms in three silicon vacancy and one carbon vacancy as shown in figure. The structure is symmetrical about z - axis. The distances between atoms are listed in the table below.

Atoms	Distance in input	Distance in output
First and second	1.8934Å	2.3751Å
Second and third	1.8968Å	2.4710Å
Third and fourth	3.0960Å	4.0894Å
Second and fourth	1.8934Å	2.3751Å

Table: 4.2.4.5. Distance between four lithium atoms in three silicon vacancy and one carbon vacancy

After calculation formation energy is found to be 10.7020 eV.

4.2.4.6. Four lithium atoms in three carbon vacancies and one silicon vacancy

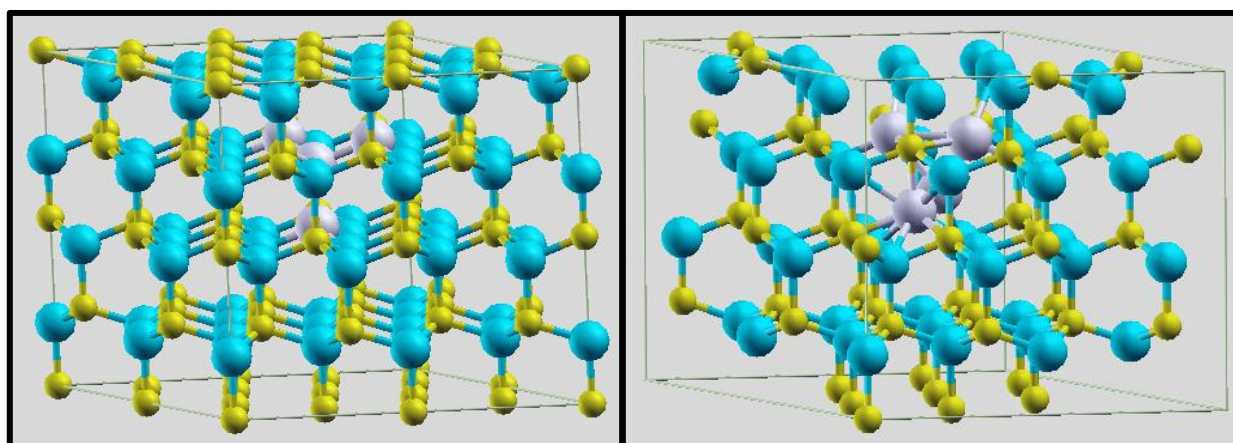


Fig 4.2.4.6: Four lithium atoms in three carbon vacancies and one silicon vacancy

(Bottom most lithium atom is named as third and other atoms are named as first, second and third from left to right respectively)

Four lithium atoms are placed symmetrically about z axis as in figure above. Three of them are in carbon vacancies and one of them is in silicon vacancy. The distance between them are shown in the table below.

Atoms	Distance in input	Distance in output
First and second	1.8911Å	2.2261Å
Second and third	1.8968Å	2.0552Å
Third and four	3.0903Å	2.7506Å
Second and four	1.8911Å	2.2261Å

Table: 4.2.4.6. Distance between five lithium atoms in three carbon vacancies and one silicon vacancy

Formation energy is calculated to be 12.9919 eV.

4.2.4.7. Five lithium atoms as a tetrahedral structure in four silicon and one carbon vacancies

Both the input and output structures for given condition is shown below. Here we have inserted five lithium atoms in to four silicon vacancies and on carbon vacancy. They have formed a tetrahedral structure.

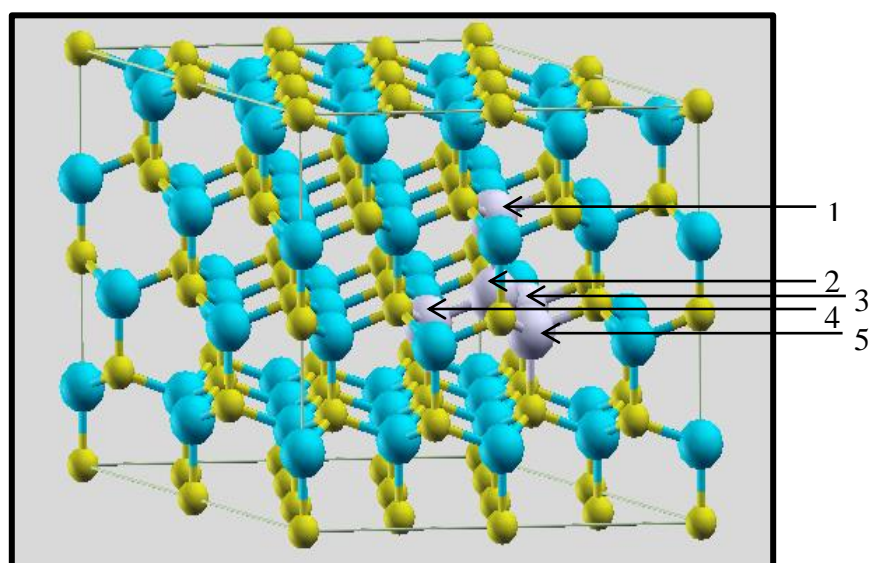


Fig 4.2.4.7: Input structure five lithium atoms as a tetrahedral structure in four silicon and one carbon vacancies:

The table below shows the distance between lithium atoms in input and output structure.

Atoms	Distance in input	Distance in output
First and second	1.8968Å	1.9734Å
Second and third	1.8934Å	2.7239Å
Second and fourth	1.8934Å	2.7239Å
Second and fifth	1.8934Å	2.7239Å

Table 4.2.4.7: distance between lithium atoms in input and output structure

First and second atoms shifted up as a result distance of these atoms from other atoms has increased by nearly 0.8 \AA .

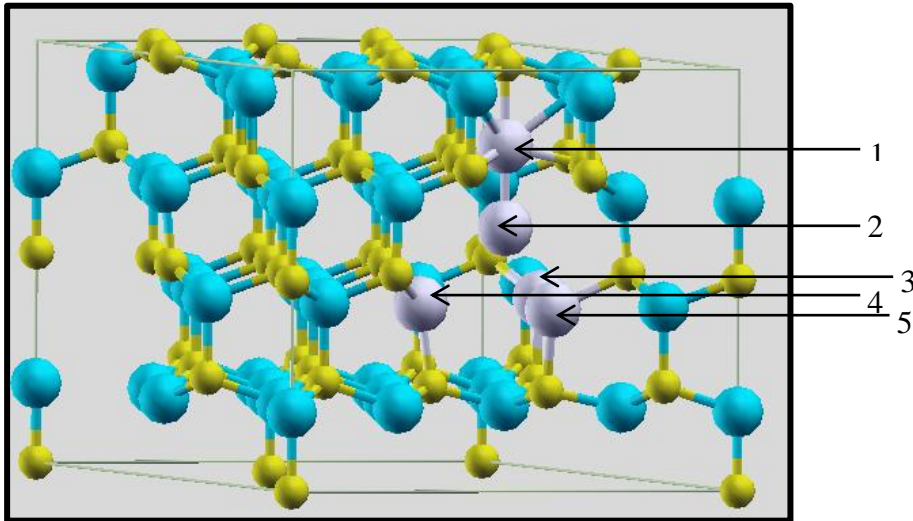


Fig 4.2.4.7(A): output structure five lithium atoms as a tetrahedral structure in four silicon and one carbon vacancies:

From the calculation, formation energy is found to be 13.7469 eV .

4.2.4.8. Five lithium atoms as a tetrahedral structure in four carbon vacancies and one silicon vacancy and one silicon vacancy

We have shown both input and output structure of five lithium atoms in silicon carbide structure. In the tetrahedral structure, we have inserted four carbon atoms and one silicon atom at the middle.

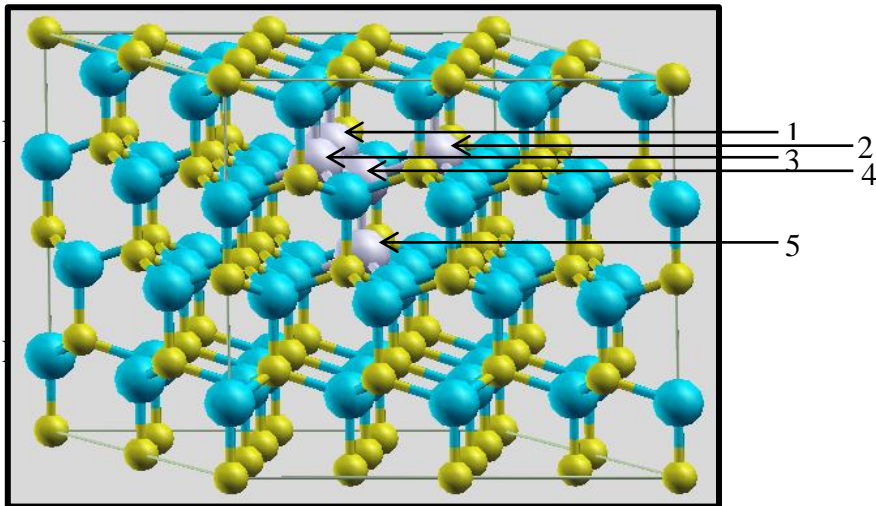


Fig 4.2.4.8.: input structure for five lithium atoms as a tetrahedral structure in four carbon vacancies and one silicon vacancy

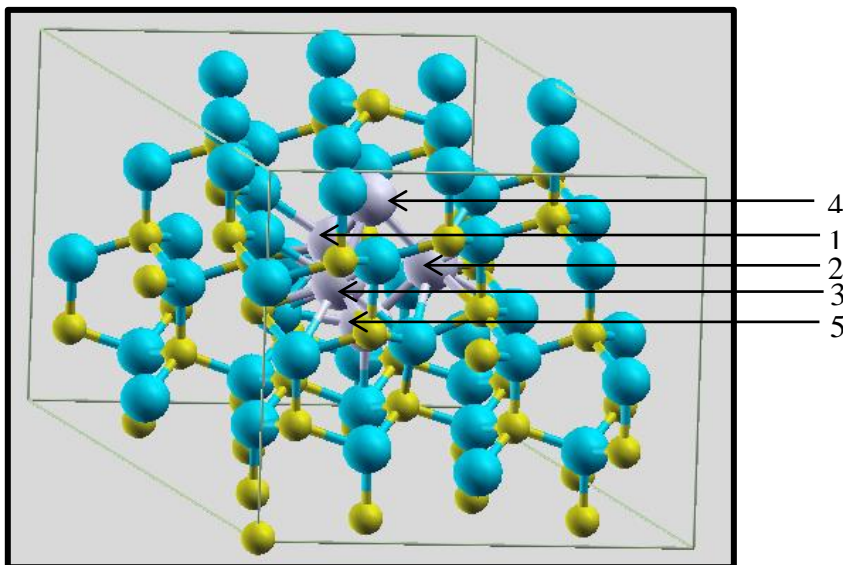


Fig 4.2.4.8(A): output structure for five lithium atoms as a tetrahedral structure in four carbon vacancies and one silicon vacancy

Formation energy is found to be 17.8928 eV

Now, all the formation energies found above are listed in table below. The number 1,2,3,4 represents number of lithium atoms inserted in vacancies. Si and C represent silicon and carbon vacancies.

Structures	Formation energy(eV)	Similar structures	Formation energy(eV)
1Si1C	5.2373	1Si1C	5.2373
2C	12.0142	2Si	9.6861
2C1Si	10.2508	2Si1C	7.7742
3C1Si	12.9919	3Si1C	10.7020
4C1Si	17.8928	4Si1C	13.7469

Table 4.2.4.8: formation energy for different structures

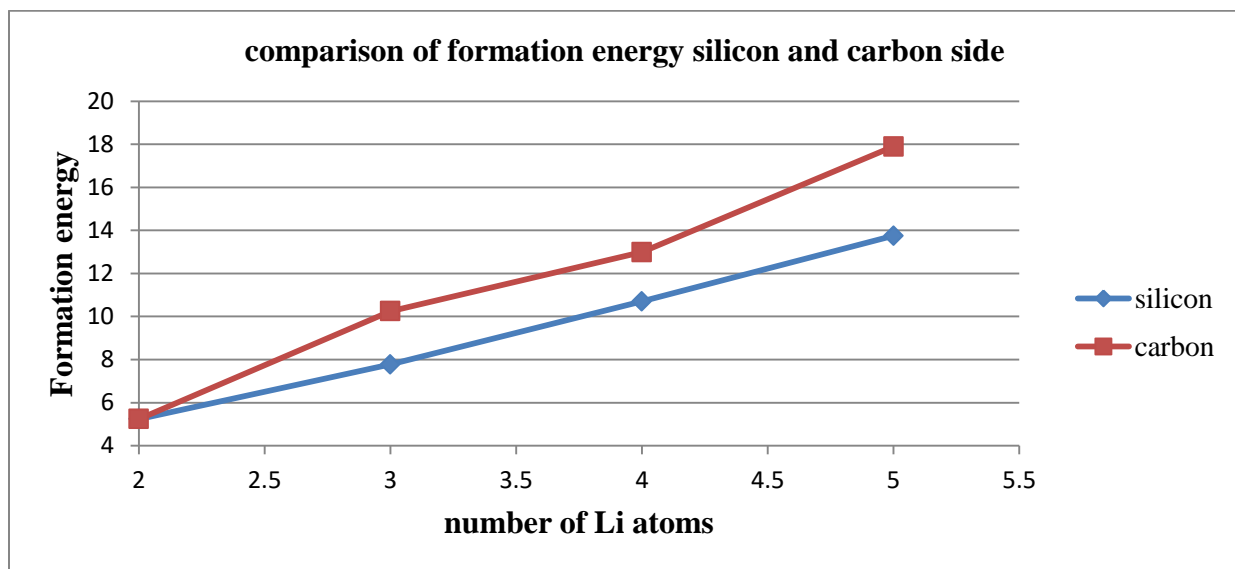


Fig 4.2.4.8 (B): comparison of formation energy in silicon and carbon side

(Note: 2Si and 2C is not plotted in the graph, only the mixed structures are plotted)

Both the lines in this graph start from the same energy. We put two lithium atoms on two silicon and two carbon sides respectively and the energy suddenly rises. We then add lithium in other side (other in the sense that, adding one more lithium atom in silicon side on the structure previously with two lithium atoms in carbon side), and then energy goes down for both of the cases. With increase in one more lithium atom on the same side energy starts to rise slowly.

Structures	Formation energy per li atom (eV/atom)	Similar structures	Formation energy per li atom (eV/atom)
1Si1C	2.6186	1Si1C	2.6186
2C	6.0071	2Si	4.8430
2C1Si	2.5914	2Si1C	3.4169
3C1Si	2.6755	3Si1C	3.2479
4C1Si	2.7493	4Si1C	3.5785

Table 4.2.4.8 (A): formation energy per li atom for different structures

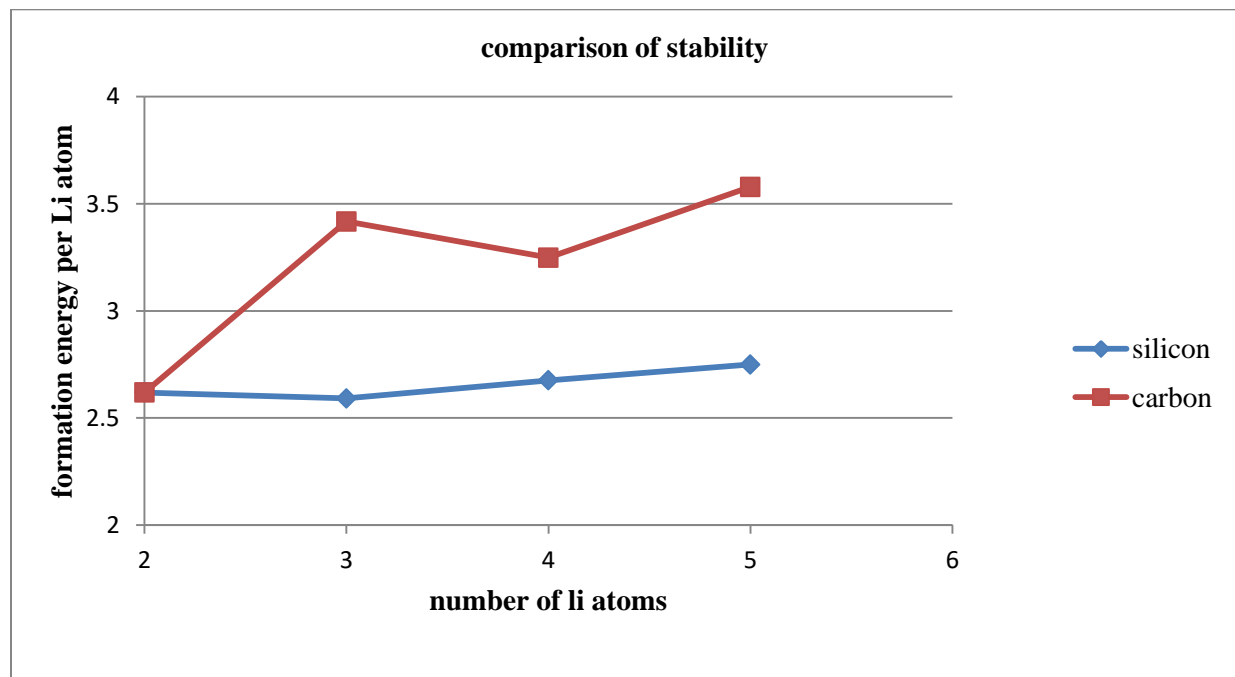


Fig 4.2.4.8 (C): comparison of formation energy per li atom in silicon and carbon side

Chapter – 5

Conclusion

There are 96 atoms in our bulk 4H – SiC input structure. There are so many possibilities to remove some atoms from the input structures. It is not possible to study all the possible structures due to time constraint. However, we have made only a few structures with minimum formation energy to study lithiation process. Some of the selected results of chapter four are rewritten below;

One lithium atom in one silicon vacancy, formation energy is 5.7173 eV.

One lithium atom in one carbon vacancy, formation energy is 7.2747 eV

Two lithium atoms (one in silicon and one in carbon vacancy), formation energy is 5.2373 eV and formation energy per li atom is 2.6186 eV/atom.

Four lithium atoms (two in silicon and two in carbon vacancies), formation energy is 8.5196 eV

And formation energy per lithium atom is 2.1299 eV/atom.

The following are the conclusions from our work.

1. Silicon side has less formation energy and therefore is more stable than carbon side.
2. Combined structures are more stable than individual structures with lithium in silicon vacancy and lithium in carbon vacancies.
3. Structures with less distance between lithium atoms (neighboring pair) are more stable.
And
4. Stability increases with more lithium atoms.

Hence, Si component of SiC can be used in collecting and releasing the li-ion so as to increase the capacity where as carbon component can behave as active electrode. So, SiC can be one of the good electrodes for Li-ion batteries.

Future work

Due to time constraint, we couldn't go through all the possible studies related formation energy. This result will be helpful to find the region where lithium atoms are to be inserted to obtain stable structure. From the formation energy, voltage curve during lithiation process can also be found according to method described by Aydinol et al.1997. Elastic properties of material can be found and diffusion process also can be studied.

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Appendix

Calculation of formation energies

Calculation of formation energy when distance between lithium atoms is large

1. One lithium atom in one silicon vacancy

Here the value of μ (Li) and μ (Si) has been taken from the calculation above. And E (structure) and E (SiC ideal) are converged energy calculated from quantum espresso.

$$E(\text{structure}) = E(\text{lithium in silicon vacancy}) = -933.17730455 \text{ Ry}$$

$$E(\text{SiC ideal}) = -927.27075579 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu(\text{Si}) = -7.883858425 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu(\text{Li}) = -14.21062572 \text{ Ry}$$

$$E(\text{formation}) = E(\text{structure}) - E(\text{sic ideal}) + \mu(\text{Si}) - \mu(\text{Li})$$

$$= -933.17730455 + 927.27075579 - 7.883858425 + 14.21062572$$

$$= 0.420218535 \text{ Ry}$$

$$= 0.420218535 \times 13.6056981 \text{ eV}$$

$$= 5.7173665 \text{ eV}$$

Hence formation energy is 5.7173665 eV.

2. Two lithium atoms in two silicon vacancies

$$E(\text{Structure}) = -939.21393787 \text{ Ry}$$

$$E(\text{Sic ideal}) = -927.27075579 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu(\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu(\text{Si}) = -7.883858425 \text{ Ry}$$

$$E(\text{formation}) = E(\text{structure}) - E(\text{sic-ideal}) + 2\mu(\text{Si}) - 2\mu(\text{Li})$$

$$= -939.21393787 + 927.27075579 - 15.76771685 + 28.42125144$$

$$= 0.71035251$$

$$= 9.664841796 \text{ eV}$$

Hence formation energy is 9.664841796 eV

3. Three lithium atoms in three silicon vacancies

$$E(\text{structure}) = E(3 \text{ lithium in silicon}) = -945.21969794 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry}$$

$$\begin{aligned} E(\text{formation}) &= E(\text{structure}) - E(\text{Si ideal}) + 3\mu(\text{Si}) - 3\mu(\text{Li}) \\ &= -945.21969794 + 927.27075579 - 23.65157528 + 42.63187716 \\ &= 1.031359735 \text{ Ry} \\ &= 14.03236919 \text{ eV} \end{aligned}$$

Hence formation energy is = 14.03236919 eV

4. Four lithium atoms in four silicon vacancies

$$E(\text{structure}) = E(\text{four lithium in silicon}) = -951.18430323 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry}$$

$$\begin{aligned} E(\text{formation}) &= E(\text{structure}) - E(\text{Si ideal}) + 4\mu(\text{Si}) - 4\mu(\text{Li}) \\ &= -951.18430323 + 927.27075579 - 31.5354337 + 56.84250288 \\ &= 1.39352174 \text{ Ry} \\ &= 18.95983609 \text{ eV} \end{aligned}$$

Hence formation energy = 18.95983609 eV

5. Five lithium atoms in five silicon vacancies

$$E(\text{structure}) = 5 \text{ lithium in silicon} = -957.12315124 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry}$$

$$\begin{aligned} E(\text{formation}) &= E(\text{structure}) - E(\text{Si ideal}) + 5\mu(\text{Si}) - 5\mu(\text{Li}) \\ &= -957.12315124 + 927.27075579 - 39.41929213 + 71.0531286 \\ &= 1.781441025 \text{ Ry} \\ &= 24.23774877 \text{ eV} \end{aligned}$$

Hence formation energy = 24.23774877 eV

Similar structures but in carbon vacancy

6. One lithium atom in one Carbon vacancy

Here the value of μ (Li) and μ (Si) has been taken from the calculation above.

$$E(\text{structure}) = E(\text{lithium in Carbon vacancy}) = -929.56427315 \text{ Ry}$$

$$E(\text{Sic ideal}) = -927.27075579 \text{ Ry}$$

$$\text{So, chemical potential of Carbon } \mu(\text{C}) = -11.3824209 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu(\text{Li}) = -14.21062572 \text{ Ry}$$

$$E(\text{formation}) = E(\text{structure}) - E(\text{Sic ideal}) + \mu(\text{C}) - \mu(\text{Li})$$

$$= -929.56427315 + 927.27075579 - 11.3824209 + 14.21062572$$

$$= 0.53468746 \text{ Ry}$$

$$= 0.53468746 \times 13.6056981 \text{ eV}$$

$$= 7.274796158 \text{ eV}$$

Hence formation energy = 7.274796158 eV

7. Two lithium atoms in carbon vacancy

$$E(\text{Structure}) = E(\text{two lithium atoms in carbon vacancies}) = -932.22232314 \text{ Ry}$$

$$E(\text{Sic ideal}) = -927.27075579 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu(\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Carbon } \mu(\text{C}) = -11.3824209 \text{ Ry}$$

$$E(\text{formation}) = E(\text{structure}) - E(\text{sic-ideal}) + 2\mu(\text{C}) - 2\mu(\text{Li})$$

$$= -932.22232314 + 927.27075579 - 22.7648418 + 28.42125144$$

$$= 0.70484229 \text{ Ry}$$

$$= 9.5898714 \text{ eV}$$

Hence formation energy = 9.5898714 eV

8. Three lithium atoms in three carbon vacancies

$$E(\text{structure}) = E(3 \text{ lithium in carbon}) = -934.75927714 \text{ Ry}$$

$$\text{Chemical potential of Carbon } \mu(\text{C}) = -11.3824209 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu(\text{Li}) = -14.21062572 \text{ Ry}$$

$$E(\text{formation}) = E(\text{structure}) - E(\text{Sic ideal}) + 3\mu(\text{C}) - 3\mu(\text{Li})$$

$$\begin{aligned}
&= -934.75927714 + 927.27075579 - 34.1472627 + 42.63187716 \\
&= 0.99609311\text{Ry} \\
&= 13.55254213 \text{ eV}
\end{aligned}$$

Hence formation energy = 13.55254213 eV

9. Four lithium atoms in four carbon vacancies

$$\begin{aligned}
4 \text{ lithium in carbon} &= -937.07490464 \text{ Ry} \\
\text{Chemical potential of Carbon } \mu (\text{C}) &= -11.3824209 \text{ Ry} \\
\text{Chemical potential of lithium } \mu (\text{Li}) &= -14.21062572 \text{ Ry} \\
E (\text{formation}) &= E (\text{structure}) - E (\text{Sic ideal}) + 4\mu (\text{C}) - 4\mu (\text{Li}) \\
&= -937.0749046 + 927.27075579 - 45.5296836 + 56.84250288 \\
&= 1.50867043\text{Ry} \\
&= 20.5265144 \text{ eV}
\end{aligned}$$

Hence formation energy = 20.5265144 eV

10. Five lithium atoms in five carbon vacancies

$$\begin{aligned}
E (\text{Structure}) &= E (5 \text{ lithium in carbon}) = -939.93120288 \text{ Ry} \\
\text{Chemical potential of Carbon } \mu (\text{C}) &= -11.3824209 \text{ Ry} \\
\text{Chemical potential of lithium } \mu (\text{Li}) &= -14.21062572 \text{ Ry} \\
E (\text{formation}) &= E (\text{structure}) - E (\text{Sic ideal}) + 5\mu (\text{C}) - 5\mu (\text{Li}) \\
&= -939.93120288 + 927.27075579 - 56.9121045 + 71.0531286 \\
&= 1.48057701\text{Ry} \\
&= 20.14428381\text{eV}
\end{aligned}$$

Hence energy = 20.14428381eV

Calculation of formation energy when distance between atoms is small

11. Two lithium atoms in two silicon vacancies

$$\begin{aligned}
E (\text{Structure}) &= -939.212373 \text{ Ry} \\
E (\text{Sic ideal}) &= -927.27075579 \text{ Ry} \\
\text{Chemical potential of lithium } \mu (\text{Li}) &= -14.21062572 \text{ Ry}
\end{aligned}$$

$$\begin{aligned}
&\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry} \\
&E (\text{formation}) = E (\text{structure}) - E (\text{sic- ideal}) + 2\mu (\text{Si}) - 2 \mu (\text{Li}) \\
&= -939.212373 + 927.27075579 - 15.76771685 + 28.42125144 \\
&= 0.71191742 \\
&= 9.686133489\text{eV}
\end{aligned}$$

Hence formation energy is 9.686133489eV

12. Three lithium atoms in three silicon vacancies

$$\begin{aligned}
&E(\text{structure}) = E(3 \text{ lithium in silicon}) = -945.30540032 \text{ Ry} \\
&\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry} \\
&\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry} \\
&E (\text{formation}) = E (\text{structure}) - E (\text{Sic ideal}) + 3\mu (\text{Si}) - 3\mu (\text{Li}) \\
&= -945.30540032 + 927.27075579 - 23.65157528 + 42.63187716 \\
&= 0.945657355 \text{ Ry} \\
&= 12.86632848 \text{ eV}
\end{aligned}$$

Hence formation energy is = 12.86632848eV

13. Four lithium atoms in four silicon vacancies

$$\begin{aligned}
&E(\text{structure}) = E(\text{four lithium in silicon}) = -951.35473081\text{Ry} \\
&\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry} \\
&\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry} \\
&E (\text{formation}) = E (\text{structure}) - E (\text{Sic ideal}) + 4\mu (\text{Si}) - 4\mu (\text{Li}) \\
&= -951.35473081 + 927.27075579 - 31.5354337 + 56.84250288 \\
&= 1.22309416 \text{ Ry} \\
&= 16.64104989 \text{ eV}
\end{aligned}$$

Hence formation energy = 16.64104989 eV

14. Five lithium atoms in five silicon vacancies

$$\begin{aligned}
&E (\text{structure}) = 5 \text{ lithium in silicon} = -957.32299507\text{Ry} \\
&\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry} \\
&\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry}
\end{aligned}$$

$$\begin{aligned}
E(\text{formation}) &= E(\text{structure}) - E(\text{Sic ideal}) + 5\mu(\text{Si}) - 5\mu(\text{Li}) \\
&= -957.32299507 + 927.27075579 - 39.41929213 + 71.0531286 \\
&= 1.581597195 \text{ Ry} \\
&= 21.51873395 \text{ eV}
\end{aligned}$$

Hence formation energy = 21.51873395 eV

Similar structures but in carbon vacancy

15. Two lithium atoms in carbon vacancy

$$\begin{aligned}
E(\text{Structure}) &= E(\text{two lithium atoms in carbon vacancies}) = -932.22232314 \text{ Ry} \\
E(\text{Sic ideal}) &= -927.27075579 \text{ Ry} \\
\text{Chemical potential of lithium } \mu(\text{Li}) &= -14.21062572 \text{ Ry} \\
\text{Chemical potential of Carbon } \mu(\text{C}) &= -11.3824209 \text{ Ry} \\
E(\text{formation}) &= E(\text{structure}) - E(\text{sic-ideal}) + 2\mu(\text{c}) - 2\mu(\text{Li}) \\
&= -932.22232314 + 927.27075579 - 22.7648418 + 28.42125144 \\
&= 0.70484229 \text{ Ry} \\
&= 9.5898714 \text{ eV}
\end{aligned}$$

Hence formation energy = 9.5898714 eV

16. Three lithium atoms in three carbon vacancies

$$\begin{aligned}
E(\text{structure}) &= E(3 \text{ lithium in carbon}) = -934.75927714 \text{ Ry} \\
\text{Chemical potential of Carbon } \mu(\text{C}) &= -11.3824209 \text{ Ry} \\
\text{Chemical potential of lithium } \mu(\text{Li}) &= -14.21062572 \text{ Ry} \\
E(\text{formation}) &= E(\text{structure}) - E(\text{Sic ideal}) + 3\mu(\text{C}) - 3\mu(\text{Li}) \\
&= -934.75927714 + 927.27075579 - 34.1472627 + 42.63187716 \\
&= 0.99609311 \text{ Ry} \\
&= 13.55254213 \text{ eV}
\end{aligned}$$

Hence formation energy = 13.55254213 eV

17. Four lithium atoms in four carbon vacancies

$$4 \text{ lithium in carbon} = -937.07490464 \text{ Ry}$$

$$\text{Chemical potential of Carbon } \mu (\text{C}) = -11.3824209 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\begin{aligned} E (\text{formation}) &= E (\text{structure}) - E (\text{Sic ideal}) + 4\mu (\text{C}) - 4\mu (\text{Li}) \\ &= -937.0749046 + 927.27075579 - 45.5296836 + 56.84250288 \\ &= 1.50867043 \text{ Ry} \\ &= 20.5265144 \text{ eV} \end{aligned}$$

Hence formation energy = 20.5265144 eV

18. Five lithium atoms in five carbon vacancies

$$E (\text{Structure}) = E (5 \text{ lithium in carbon}) = -939.93120288 \text{ Ry}$$

$$\text{Chemical potential of Carbon } \mu (\text{C}) = -11.3824209 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\begin{aligned} E (\text{formation}) &= E (\text{structure}) - E (\text{Sic ideal}) + 5\mu (\text{C}) - 5\mu (\text{Li}) \\ &= -939.93120288 + 927.27075579 - 56.9121045 + 71.0531286 \\ &= 1.48057701 \text{ Ry} \\ &= 20.14428381 \text{ eV} \end{aligned}$$

Hence energy = 20.14428381 eV

Lithium atoms in some random structures

19. two lithium atoms in silicon and carbon vacancies

$$E (\text{Structure}) = E (2 \text{ lithium atoms in Silicon \& carbon vacancies}) = -936.04078792 \text{ Ry}$$

$$E (\text{Sic ideal}) = -927.27075579 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Carbon } \mu (\text{C}) = -11.3824209 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry}$$

$$\begin{aligned} E (\text{formation}) &= E (\text{structure}) - E (\text{sic-ideal}) + \mu (\text{c}) + \mu (\text{Si}) - 2\mu (\text{Li}) \\ &= -936.04078792 + 927.27075579 - 11.3824209 - 7.883858425 + 28.42125144 \\ &= 0.384939985 \text{ Ry} \end{aligned}$$

$$= 5.237377223 \text{ eV}$$

Hence formation energy = 5.237377223 eV

20. Three Lithium atoms (Two in silicon vacancy and one Interstitial)

$$E (\text{structure}) = -953.44532942 \text{ Ry}$$

$$E (\text{Si ideal}) = -927.27075579 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry}$$

$$E (\text{formation}) = E (\text{structure}) - E (\text{sic ideal}) + 2\mu (\text{Si}) - 3\mu (\text{Li})$$

$$= -953.44532942 + 927.27075579 - 2 \times 7.883858425 + 42.63187716$$

$$= 0.68958668 \text{ Ry}$$

$$= 0.68958668 \times 13.6056981 \text{ eV}$$

$$= 9.382308182 \text{ eV}$$

Hence formation energy = 9.382308182 eV

21. Three lithium atoms (two in silicon vacancy and one in carbon vacancy)

$$E (\text{structure}) = -942.05398103 \text{ Ry}$$

$$E (\text{Si ideal}) = -927.27075579 \text{ Ry}$$

$$\text{Chemical potential of lithium } \mu (\text{Li}) = -14.21062572 \text{ Ry}$$

$$\text{Chemical potential of Silicon } \mu (\text{Si}) = -7.883858425 \text{ Ry}$$

$$\text{Chemical potential of Carbon } \mu (\text{C}) = -11.3824209 \text{ Ry}$$

$$E (\text{formation}) = E (\text{structure}) - E (\text{sic ideal}) + 2\mu (\text{Si}) + \mu (\text{C}) - 3\mu (\text{Li})$$

$$= 0.69851417 \text{ Ry}$$

$$= 9.503772916 \text{ eV}$$

Hence formation energy = 9.503772916 eV

22. Four lithium atoms (Two in silicon vacancy and two in carbon vacancy).

$$E (\text{formation}) = E (\text{structure}) - E (\text{sic-ideal}) + 2\mu (\text{c}) + 2\mu (\text{Si}) - 4\mu (\text{Li})$$

$$= -944.9545174 + 927.2707558 - 22.7648418 - 15.76771685 + 56.84250288$$

$$= 0.62618266 \text{ Ry}$$

$$= 8.519652227 \text{ eV}$$

Hence formation energy = 8.519652227 eV

23. Five lithium atoms (three in silicon vacancy and one two in carbon vacancy)

$$\begin{aligned} E(\text{formation}) &= E(\text{structure}) - E(\text{sic-ideal}) + 2\mu(\text{c}) + 3\mu(\text{Si}) - 5\mu(\text{Li}) \\ &= -951.1143247 + 927.2707558 - 22.7648418 - 23.65157528 + 71.0531286 \\ &= 0.793142595 \text{ Ry} \\ &= 10.7912587 \text{ eV} \end{aligned}$$

Hence formation energy = 10.7912587 eV

Lithium atom in some symmetrical structures

24. Three lithium atoms in two silicon vacancy and one carbon vacancy

$$\begin{aligned} E(\text{formation}) &= E(\text{structure}) - E(\text{sic-ideal}) + 1\mu(\text{c}) + 2\mu(\text{Si}) - 3\mu(\text{Li}) \\ &= -942.1810959 + 927.2707558 - 11.3824209 - 15.76771685 + 42.6318771 \\ &= 0.57139929 \text{ Ry} \\ &= 7.774286234 \text{ eV} \end{aligned}$$

Formation energy = 7.774286234 eV

25. Three lithium atoms in two carbon vacancy and one silicon vacancy.

$$\begin{aligned} E(\text{formation}) &= E(\text{structure}) - E(\text{sic-ideal}) + 2\mu(\text{c}) + 1\mu(\text{Si}) - 3\mu(\text{Li}) \\ &= -938.5005129 + 927.2707558 - 22.7648418 - 7.883858425 + 42.6318771 \\ &= 0.753419835 \text{ Ry} \\ &= 10.25080282 \text{ eV} \end{aligned}$$

Formation energy = 10.25080282 eV

26. Four lithium atoms in three silicon vacancy and one carbon vacancy.

$$\begin{aligned} E(\text{formation}) &= E(\text{structure}) - E(\text{sic-ideal}) + 1\mu(\text{c}) + 3\mu(\text{Si}) - 4\mu(\text{Li}) \\ &= -948.2926746 + 927.2707558 - 11.3824209 - 23.65157528 + 56.84250288 \\ &= 0.786587855 \text{ Ry} \\ &= 10.70207688 \text{ eV} \end{aligned}$$

Formation energy = 10.70207688 eV

27. Four lithium atoms in three carbon vacancy and one silicon vacancy.

$$\begin{aligned}
E(\text{formation}) &= E(\text{structure}) - E(\text{sic-ideal}) + 3\mu(\text{c}) + 1\mu(\text{Si}) - 4\mu(\text{Li}) \\
&= -941.1272485 + 927.2707558 - 34.1472627 - 7.883858425 + 56.84250288 \\
&= 0.954889025\text{Ry} \\
&= 12.99193179\text{ eV} \\
\text{Formation energy} &= 12.99193179\text{ eV}
\end{aligned}$$

28. Five lithium atoms as a tetrahedral structure in four silicon and one carbon vacancies:

$$\begin{aligned}
5\text{ symmetric lithium} &= -954.39564872\text{ Ry} \\
\text{Chemical potential of lithium } \mu(\text{Li}) &= -14.21062572\text{ Ry} \\
\text{Chemical potential of Carbon } \mu(\text{C}) &= -11.3824209\text{ Ry} \\
\text{Chemical potential of Silicon } \mu(\text{Si}) &= -7.883858425\text{ Ry} \\
E(\text{formation}) &= E(\text{structure}) - E(\text{Sic ideal}) + \mu(\text{C}) + 4\mu(\text{Si}) - 5\mu(\text{Li}) \\
&= -954.39564872 + 927.27075579 - 11.3824209 - 31.5354337 + 71.0531286 \\
&= 1.01038107\text{ Ry} \\
&= 1.01038107 \times 13.6056981\text{ eV} \\
&= 13.7469398\text{ eV}
\end{aligned}$$

Hence formation energy = 13.7469398 eV

29. Five lithium atoms as a tetrahedral structure in four carbon and one silicon vacancy:

$$\begin{aligned}
5\text{ symmetric lithium} &= -943.5952406\text{ Ry} \\
\text{Chemical potential of lithium } \mu(\text{Li}) &= -14.21062572\text{ Ry} \\
\text{Chemical potential of Carbon } \mu(\text{C}) &= -11.3824209\text{ Ry} \\
\text{Chemical potential of Silicon } \mu(\text{Si}) &= -7.883858425\text{ Ry} \\
E(\text{formation}) &= E(\text{structure}) - E(\text{Sic ideal}) + 4\mu(\text{C}) + 1\mu(\text{Si}) - 5\mu(\text{Li}) \\
&= -943.5952406 + 927.27075579 - 45.5296836 - 7.883858425 + 71.0531286 \\
&= 1.315101765\text{ Ry} \\
&= 1.01038107 \times 13.6056981\text{ eV} \\
&= 17.89287759\text{ eV} \\
\text{Formation energy} &= 17.89287759\text{ eV}
\end{aligned}$$