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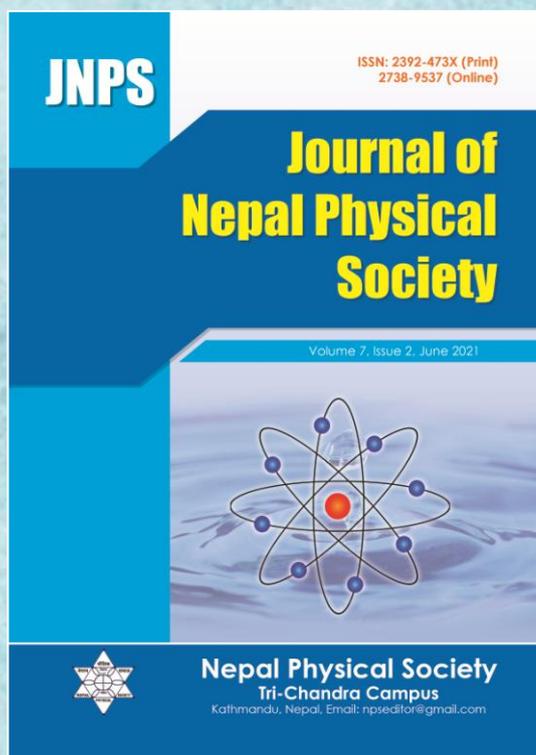
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Substitutional Lithium Doping on Germanene: A First-principles Study

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ABSTRACT

The density functional theory (DFT) based first-principles calculations have been adopted for the study of structural, electronic and magnetic properties of pure and single Lithium (Li) atom doped germanene monolayer. Due to the higher intrinsic carrier mobilities and large spin orbit gap, germanene has great possibility of being integrated into the silicon based semiconductor industry. Different studies have been done to change the band gap value from its' pristine zero band gap state. We have doped the single Li atom into the germanene system with the intention of tuning the band gap and other electronic and magnetic properties. Band structure calculations show pristine germanene is semi-metallic in nature whereas the Li doped system is fully metallic with the overlapping of the conduction and valance bands in the Fermi level. Under density of states (DOS) calculations, it is evident that both pristine and doped system are non-magnetic in nature with symmetric DOS plot.

Keywords: Electronic structures, First-principles calculations, Germanene, Lithium atom doping.

1. INTRODUCTION

Two dimensional (2D) materials are 2D allotropes of elements or compounds. The elemental 2D allotropes carry -ene suffix in general. Almost 700 2D materials have been predicted to be stable, very few of them being synthesized till date [1]. They are of wide use in the fields of semiconductors, opto-electronics, sensors, photovoltaics, composite material markets, engineering and medicine.

The breakthrough in the field of 2D materials was the discovery of graphene way back in 2004. Since then, this field has drawn interest of the scientists and researchers till date. Graphene consists of carbon atoms arranged in hexagonal honeycomb structure with sp^2 hybridization. With the huge popularity and wide applications of graphene being explored, the scientists are curious to extract more of these 2D materials. Silicene and germanene were obvious choices to look at, both of which are in same IV group of periodic table and having similar electronic configurations [2].

Due to the large buckled distance and small effective mass, intrinsic carrier mobilities of

germanene are 2-3 times higher than that of silicene [3]. Germanene has large spin-orbit gap of 23.9 meV (much more than ~ 0.05 meV of graphene and 1.55 meV of silicene) [4]. The robust 2D topological insulator character is predicted nearly up to the room temperature due to this large effective spin-orbit coupling as a result of large atomic number. This opens way for germanene sheets to be ideal for quantum spin hall effect (QSHE) [2, 5]. The spin-orbit coupling leads to an internal magnetic field that couples to the spin of the electrons. This asymmetry will result into two spin-polarized conduction channels at the edges of the 2D material that propagate in opposite directions [2]. This phenomenon is called QSHE. These special characteristics of germanene provoked us to choose germanene over its' another two cousins graphene and silicene.

Germanium (Ge) is the 32th element of periodic table with symbol Ge and electronic configuration [Ar] $3d^{10} 4s^2 4p^2$. It is a semiconductor material akin to silicon. The first decade of semiconductor electronics was fully based on germanium which is

now over-ridden by silicon. The development of germanium semiconductor in 1948 is considered as the huge invention and path breaker for the solid state electronics [6]. Here we study germanene as a member of two dimensional materials formed of germanium atoms.

Germanene is a material having the structure similar to graphene with corners of the hexagon being filled with germanium atoms. The hexagons of single layer are bound together by strong covalent bonds whereas one layer is held to another such layer with weak van der Waals forces. This weak inter-layer bond allows us to take out a single 2D layer and study various properties as a 2D material. Germanene is extracted by depositing germanium atoms on a substrate with application of high temperature and ultra-vacuum. It was first proposed in 2009 and extracted in 2014 [5, 7]. While graphene exhibits fully planar honeycomb structure, germanene has a buckled honeycomb geometry which is composed of two triangular sub-lattices.

Similar to graphene, pristine germanene has zero band gap showing semi-metallic property. This property restricts germanene to apply in the semiconductor industry. However, germanene offers to open a controllable band gap via externally applied electric field, adsorption and substitutional doping of foreign atoms [2]. This controllable band gap widens the applications of germanene to be used as electronic materials, gas sensors and photocatalyst supports [8]. Its higher carrier mobility and good compatibility with Silicon are positive signs for the integration of germanene in silicon based electronic devices. This makes germanene the frontier topic of scientific interest and promising application for various fields [3, 4].

Lithium is the 3rd element in the periodic table with electronic configuration [He] 2s¹ and symbol Li. It is the lightest metal and the lightest solid element known to us. Thus, lithium metal atom is expected to fit easily into the germanene sheet by means of substitutional doping. These special characteristics of Lithium has drawn our interest to use this specific alkali metal (AM) atom among others as a dopant in our work.

Pamungkas *et al.* (2018) [9] studied the effects of adsorption of Na and Cl on germanene sheet. They were only able to conclude that all three (pristine, Na-adsorbed and Cl-adsorbed germanene) exhibit zero band gap though there is a slight change in shape of band structures in each case. Many such

works have been done in the area of adsorption of alkali, alkali earth, group III and 3d transition metal (TM) on germanene [10]. However, very few works can be found in the field of substitutional doping of metals on germanene. Among those few works, Minglei Sun *et al.* (2016) [11] investigated electronic and magnetic properties of 3d series transition metals (TM) (Sc-Ni) doped germanene. The result showed the strong bond strength between TM impurities to germanene. Moreover, few of those TM doping (V, Cr, Mn, Fe and Co) showed the magnetic behavior. This result has added more evidence to the statement that the electronic and magnetic properties can be controlled/tuned with metal impurities doping into the pristine germanene sheet. The substitutional doping effects of alkali metal in germanene still remains as an open question. In the present work, we study the effects and changes in the electronic and magnetic behaviors of AM (Li) doped germanene nanosheet in comparison to pristine germanene. After this introduction part, we describe the computational methods, results and discussion, and conclusions in the respective order.

2. METHOD AND COMPUTATIONAL DETAILS

We have performed the first principles calculations to investigate the structural stability, the electronic and magnetic properties of pure germanene and Lithium doped germanene within the framework of density functional theory with van der Waals (vdW) interactions in DFT approach using Quantum ESPRESSO code [12-14]. To incorporate the electronic exchange and correlation effect in our system, the generalized gradient approximation (GGA) developed by three scientists Perdew, Burke and Ernzerhof (PBE) [15] has been used. We have used Kresse-Joubert (KJ) projector augmented wave (PAW) pseudopotential from the official website of Quantum ESPRESSO in order to replace the complicated effects of the motion of the core (*i.e.*, non-valence) electrons of an atom and its nucleus with an effective potential for all species (Ge, Li), so that, only the chemically active valence electrons are included explicitly in our entire calculation.

The vacuum of 20 Å was taken in the direction perpendicular to the plane of germanene monolayer (z-direction) for the purpose of removing any possibility of the interaction from neighboring layers of germanene. For this, we simply put the value of lattice parameter (c) as 20 Å. During the

calculation, the structure was allowed to relax under Broyden-Fletcher-Goldfarb-Shanno (BFGS) [16] scheme until the total energy change was less than 10^{-4} Ry between two consecutive self-consistent field (scf) steps and each component of force acting is less than 10^{-3} Ry/Bohrs to get geometrically optimized structure. After the relaxation calculations, we have done self consistent total energy calculations. The Brillouin zone of germanene was sampled in K-space using Monkhorst-Pack scheme [17] with appropriate number of mesh of K-points which was determined from the convergence test. For relaxation calculations, we have used k-points mesh of $10 \times 10 \times 1$ and for all other calculations, k-points mesh of $16 \times 16 \times 1$ were used. Using convergence test, we have chosen the wave function cutoff energy value (ecutwfc) of 40 Ry and charge density cutoff energy value (ecutrho) of 400 Ry. With the relaxations, the lattice parameter was found to be 7.65 Bohr. Also, we have used 'Marzari-Vanderbilt (m-v)' [18] method of smearing or cold smearing with a small smearing width of 0.01 Ry.

In addition, we have chosen 'david' diagonalization method with 'plain' mixing mode and mixing factor of 0.7 for self consistency. All the figures were extracted using the software XCrySDen [19].

3. RESULTS AND DISCUSSION

Here we discuss the ground state energy and equilibrium configurations of 3×3 supercells of pristine and Li doped germanene. To analyze the electronic and magnetic properties of both pristine and Li doped germanene, band structure, density of states (DOS) and projected density of states (PDOS) were calculated. Hence, we have compared our results with available experimental and theoretical values of already reported results.

Geometrical structure and formation energy

Figure (1) shows the primitive unit cell in side view and top-view structures. The space of 20 \AA (seen in side-view) was for the purpose of removing any possibility of the interaction from neighboring layers of Germanene.

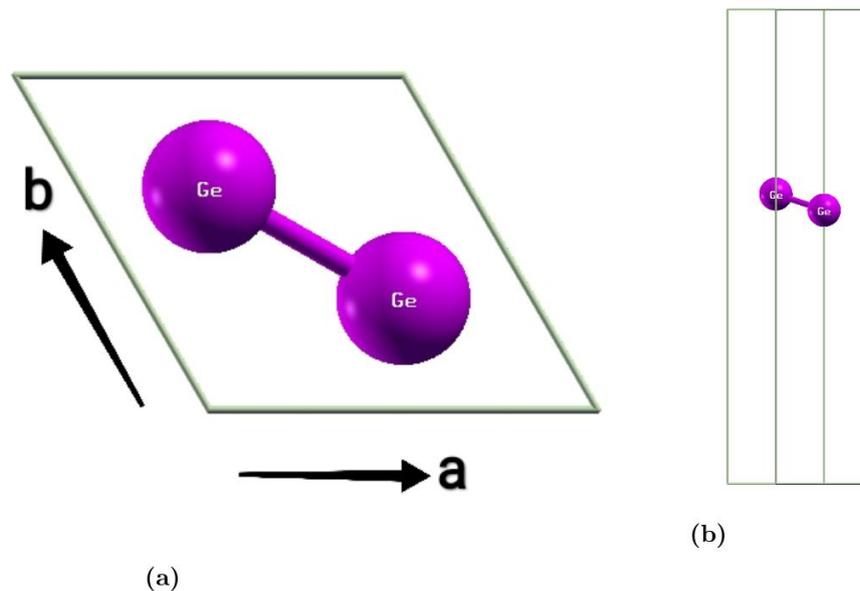


Fig. 1: (a) Top view and (b) side view of optimized primitive cell of germanene monolayer (arrows indicate the directions of lattice parameters a and b)

Table (I) shows various parameters of unit cell after relaxation. The table also includes the results from three of the previous studies (based in computation and experiment) on germanene. The work of Cahangirov *et al.* [7] used the DFT-LDA approach whereas Garcia *et al.* [20] used the DFT-GGA approach to study the different properties of

germanene. The work of P. Bampoulis *et al.* [21], however, is an experimental one. They have studied the growth of Pt on a Ge(1 1 0) substrate and found a buckled honeycomb structure in top of the 3D nanocrystals formed. They have analyzed and then interpreted that this honeycomb structure including two buckled sub-lattices must be germanene.

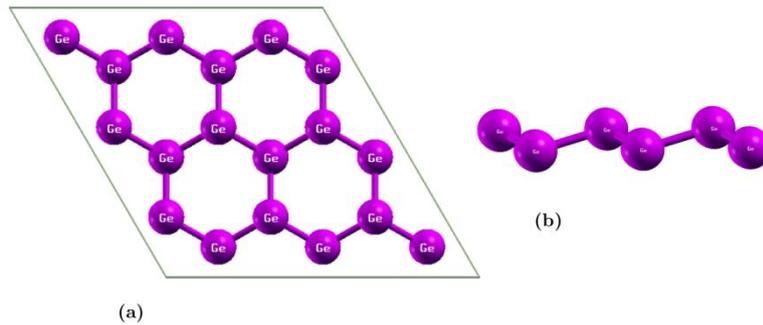
Table 1: Optimized structural parameters of the relaxed primitive germanene. $a=b$, d and Δ refer to lattice parameter, Ge-Ge bond length and buckling height of sub-lattices respectively

Parameters in study	Our study results	Previous DFT-LDA [7]	Previous DFT-GGA [20]	Experimental values [21]
$(a=b)\text{\AA}$	4.048	3.970	4.061	-
$(d)\text{\AA}$	2.434	2.380	2.444	2.500 ± 0.100
$(\Delta)\text{\AA}$	0.681	0.640	0.690	0.200

From table (1), it is evident that the parameters of our study are in excellent agreement with those of Garcia *et al.* whereas our parameters are slightly greater than those of Cahangirov *et al.*'s values. This must be due to the fact that we have also used the DFT-GGA approximation in our calculations. LDA undermines the underlying exchange correlation between the atoms and thus the lowered values of parameters. The experimental value of bond length ($2.5\pm 0.1\text{\AA}$) is in vicinity of all computational works and that was the reason how Bampoulis *et al.* estimated that this must be

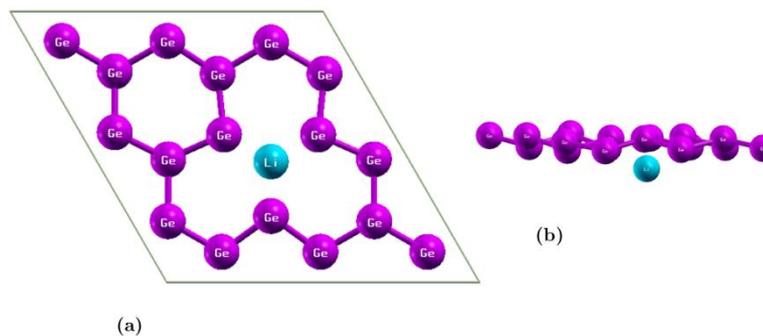
germanene. However, the experimental buckling height between two sub-lattices (0.2\AA) is very lower than what simulations have predicted it to be. Further analysis and examination is to be done before this formed structure is confirmed as germanene as suggested by them.

The 3×3 supercell of germanene (obtained by the translation of primitive unit cell along x and y directions) monolayer contains 18 atoms. It works as a unit cell with the basis of 18 atoms and cell size three times of primitive cell size. The outlook of 3×3 supercell can be seen in the figure (2).


Fig. 2: (a) Top view and (b) side view of optimized 3×3 supercell of monolayer germanene

After obtaining the desired structure and geometry of pure germanene, we substituted a Ge atom with Li atom. This is substitutional doping and number of atoms in a unit cell remains preserved. As we doped Li on the pure germanene, several distortions

have been observed. Nearest Ge atoms are pulled away from the plane. Accordingly, the nearest neighbor Ge-Ge bond lengths and bond angles are also altered. The distorted structure of the system after Li doping can be visualized from figure (3).


Fig. 3: (a) Top view and (b) side view of Li substituted germanene after relaxation

The features of structural distortion can be appreciated with the help of table (2).

Table 2: Structural parameters of the germanene sheet doped with Li atom. The bond length are taken in between the nearest neighbors.

Structural details of single Li atom doped 3×3 germanene	
Ge-Li bond length	2.615 Å
Ge-Li buckling height	1.543 Å
Ge-Ge bond length	2.431 Å
Ge-Ge Buckling height	0.535 Å

From the table (2), it is seen that Li atom has been pushed away from the buckled plane by some extent with the significant increase of Ge-Li bond length (2.615 Å) as compared to Ge-Ge bond length (2.434 Å) in pristine structure. The nearest neighbor bond lengths around the site of doping have been constrained by some amount as evident in above tables (1) and (2). Along with this, we have found the structural modification in overall sheet. The amount of distortion continuously reduces as we go farther from the doped atom.

The defect formation energy gives an idea of tendency of forming a new compound from its constituents/reactants. We use equation (1) to calculate such a parameter for Li (single atom) doping into the germanene sheet [22].

$$E_F = E_{Li} - E_p - (E_1 - E_2). \dots\dots\dots(1)$$

Where, E_{Li} is the total energy of Li doped germanene sheet, E_p is total energy of pristine germanene sheet, E_1 is energy of single Li atom and E_2 is energy of single Ge atom. The energy of isolated Li and Ge atoms were calculated by considering an isolated system of single atom.

Table 3: Different energy values required to calculate the formation energy (in Rydbergs; 1 Rydberg = 13.6 eV)

Formation energy of single Li atom doped germanene	
System	Energy (Ry)
Li doped germanene (E_{Li})	-5378.486
Pristine 3×3 germanene (E_p)	-5679.075
Energy of isolated Li atom (E_1)	-14.909
Energy of isolated Ge atom (E_2)	-315.266
Formation Energy (E_F)	0.232

It is clearly seen that formation energy is 0.232 Ry (3.155 eV). All the energies of the systems in the study are in negative values, indicating their stable nature. However, the formation energy of doped system is obtained as positive. This indicates that the external energy of that value should be supplied to form the doped system.

Electronic and Magnetic properties of pristine germanene

The first Brillouin zone represents the Wigner-Seitz cell of reciprocal space (K-space). However, it can be reduced in size by using the symmetries that are applicable to the structure. The part of first Brillouin zone of hexagonal lattice with Γ --M--K-- Γ high symmetric points (shown in figure (4)) was chosen to select 100 k-points along this path for the band structure calculations of our sample.

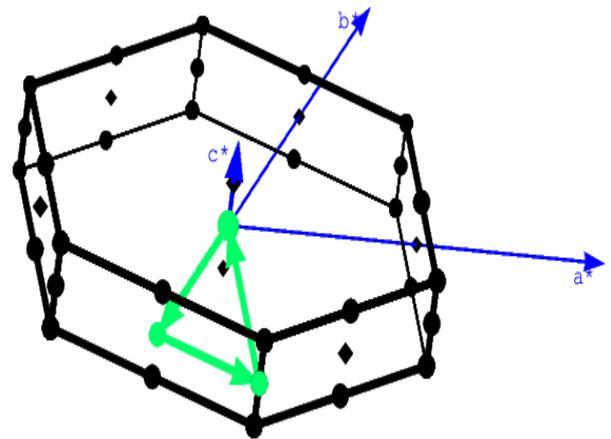


Fig. 4: First Brillouin zone of hexagonal lattice with high symmetric points. We have chosen Γ --M--K-- Γ path.

Electronic band structure of pristine germanene

Each Germanium atom in the honeycomb lattice structure of germanene, containing four valence electrons, interacts with its three nearest Germanium atoms through strong σ -bonds. The strong σ -bonds occurs due to sp^2 hybridization of s, p_x and p_y orbitals of three valence electrons. The remaining fourth electron of each atom fills the p_z orbital which overlaps with nearest p_z orbital of p_z electrons and form weak π -bond perpendicular to the germanene layer. These electrons forming π -bonds have higher energy than those electrons that form σ -bonds and are loosely bound so that they get delocalized over the lattice. These delocalized electrons are responsible for determining the most of the electronic properties of germanene [23].

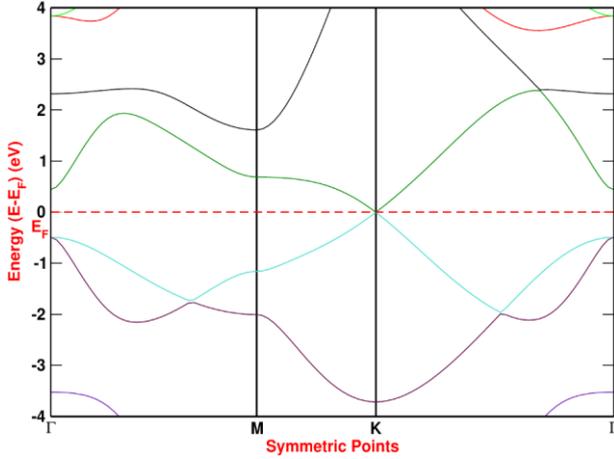


Fig. 5: Band structure of pristine germanene primitive cell, energies have been measured relative to Fermi energy ($E_F = -2.4281$ eV)

The band structure of unit cell of pure germanene is shown in figure (5), where X-axis represents high symmetric points in the first Brillouin zone and Y-axis represents the corresponding energy values. Conduction band above the Fermi level is represented by π^* and the valence band below the Fermi level is represented by π . The valence band and conduction band intersect linearly at some points in a Fermi level called Dirac points. The charge carriers act as massless Dirac fermions in a small energy range near the Fermi level [7]. This shows that there is a zero band gap between the valence band and conduction band, which signifies that the germanene is a zero band gap semi-metal.

Density of States (DOS) of pristine germanene

The band structure calculation is followed by the density of states calculations. The DOS plot not only corroborates the band gap explanation given by the band structure plot, but also gives the idea about the magnetization of the system. The pictorial representation of the DOS plot of pristine germanene is shown in the figure (6) below.

The unavailability of any spin states in the Fermi level can be seen in figure (6). It supports the conclusion of the band structure plot that this system is a zero band gap semi-metallic system. More importantly, the non-magnetic nature of pristine germanene can be visualized from this plot. Distribution of available states for both up and down spin can be described as symmetric in nature, barring a few glitches here and there. These small discrepancies can be due to the imperfection of the pseudopotential and other parameters we take.

Moreover, even if we tried to optimize and relax the system to the fullest, we have to be limited to some value. In conclusion, pristine germanene is a non-magnetic system. The output of the relaxed structure gives no magnetization, and the symmetric DOS plot also verifies the same.

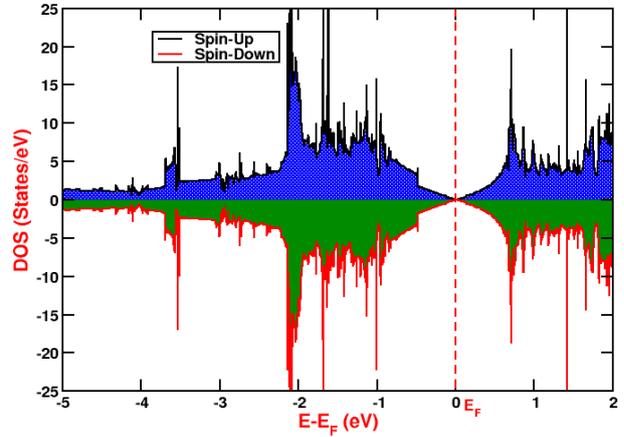


Fig. 6: Density of States of pristine germanene showing zero band gap. The vertical dotted line represents the Fermi-level.

Further, we calculated the projected density of states (PDOS) for different orbitals of Germanium. The sum of all these orbital contributions gives the total DOS of the system. The PDOS plot gives an idea of which particular orbital contributes more near the Fermi level for the total states of the system. Figure (7) shows the PDOS plot of pristine germanene.

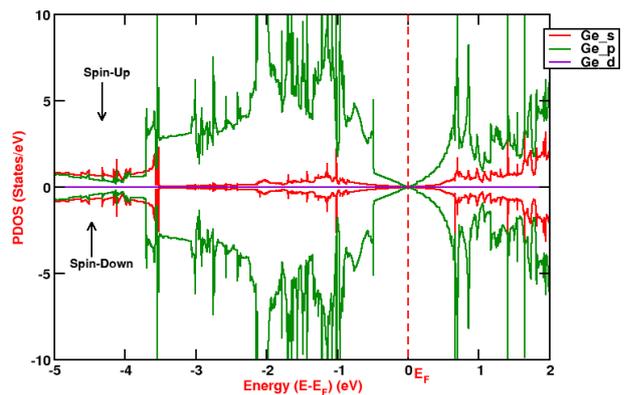


Fig. 7: PDOS for different orbitals of Ge in 3x3 supercell of pristine germanene. The vertical dotted line represents the Fermi-level set to zero.

From the PDOS plot (figure (7)), we observed that the valence 4p orbitals of Ge contribute the most

near the Fermi level for total spin states. 4s orbitals also can be seen with smaller peaks. The contribution of 3d orbitals are negligible. Also, the DOS for s, p and d orbitals in up and down spin state are exactly symmetrical. This further illustrates that germanene is a non-magnetic material and doping it with impurity atom/s element like Li will be discussed in subsequent sections.

Electronic and Magnetic properties of Li doped germanene

Due to presence of impurity atom Li in germanene structure, severely distorted system is observed and thus affecting the ionic potential around defected sites. We also observed significant changes in band structure induced due to doping. We studied spin polarized scf, band structure, DOS and Projected DOS calculations on our doped system.

Electronic band structure of Li doped germanene

The band structure of the single Li atom doped germanene monolayer is given in figure (8).

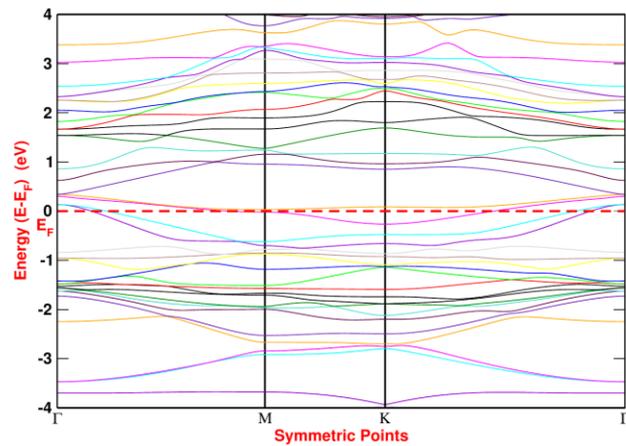


Fig. 8: Band structure of Li doped germanene along Γ -M-K- Γ path of Brillouin zone. Energies have been measured relative to Fermi energy ($E_F = -2.5224$ eV).

From figure (8), the bands around the Fermi level are significantly different to those in the pristine system. Also, it can be analyzed that, when Li is doped in the germanene sheet, the system gains metallic behavior. Now the bands from the conduction band are crossing the Fermi level and reaching down to the valence band, thus giving overlapped bands and hence a metallic system. The occurrence of this difference in the patterns of the bands can be best explained by two reasons. First, the interaction of the Li-atom with π^* and π states of Germanium atoms are responsible for breaking the initial symmetry of

germanene. Second, the band folding phenomenon occurs while going from the unit cell to the supercell due to the hidden translational symmetry inside the supercell. This has caused the vanishing of the Dirac cones of the pristine structure.

Density of States (DOS) of Li doped germanene

Following the band structure calculations, we see the density of states of Li doped germanene (shown in figure (9)).

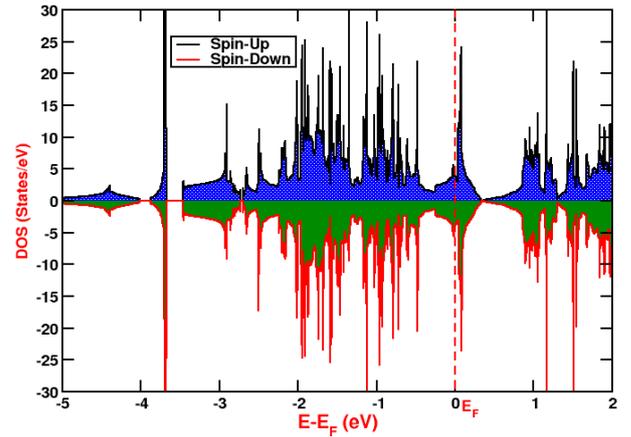


Fig. 9: Density of States of Li doped germanene showing a zero band gap. The vertical dotted line represents the Fermi-level.

From figure (9), a difference in DOS is seen significantly at the Fermi level. In the pristine system, the line of the Fermi level was void of any spin states. However, the Li-doped system has certain spin states on the Fermi level line itself, thus making it a metallic system. The symmetrical distribution of states for spin-up and spin-down shows the non-magnetic behavior of Li-doped germanene. Even if Li is a metal atom with an unpaired valence electron, Li-doped germanene still remained non-magnetic. It must be due to the transfer of charge from the Li atom to the germanene monolayer in a symmetric manner for both spin-up and spin-down states. Thus, an overall significant change of spin states could not be observed. Previously, in the work of Minglei Sun *et al.* (2016) [11], doping of transition metal atoms (Sc, Ti, and Ni) which are also magnetic ones into germanene showed non-magnetic behavior.

The projected density of states of Li-doped germanene for spin-up and spin-down is shown in figure (10). In the figure, we see that for the germanene sheet doped with a Li atom, the available states around the Fermi level are heavily and mostly due to Ge

atoms. Among Ge orbitals, 4p orbitals are dominant than s orbitals. The 2s orbital of Li atom are also available in some extent around Fermi level, thus changing the structure of whole system. In the contribution of Ge, 3d orbital is almost negligible.

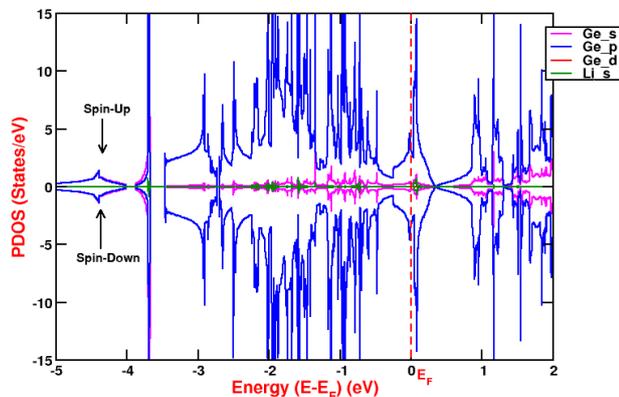


Fig. 10: PDOS for different orbitals of Ge and Li in Li doped germanene. The vertical dotted line represents Fermi-level set to zero.

4. CONCLUSIONS AND RECOMMENDATIONS

When Li atom was doped in germanene, it was repelled away from the layer and we observed structural changes in the system. Up next, we analyzed the band structure of the pristine and Li doped systems. In the band structure of unit cell, valence band and conduction band exactly meet at Dirac point on the Fermi-level. In the supercell, the valence band and conduction band meet at gamma point in the Fermi level. Thus, pristine germanene is a zero band gap semi-metallic system. However, in Li doped germanene, we observed the overlap of bands in Fermi Level which made the system metallic. This change was due to presence of Li atom resulting the breaking of initial symmetry of germanene layer. Moreover, DOS calculations clearly indicated the non-magnetic behavior of both pure and Li doped germanene with symmetrical up and down spin states. From projected DOS calculations, we found the heavy contributions of valence 4p and 4s orbitals of Ge in total spin states near Fermi level and trivial contributions of 3d orbitals of Ge and 2s orbital of Li. Thus, doping of single Li atom changed the electronic property of germanene from semi-metallic to metallic, however, no significant change in magnetic property was observed.

The present work can be extended to study the charge density profile distributions, thermal and optical properties of Lithium doped germanene

monolayer. Increasing impurity concentration and changing the doping agent to any other Alkali metal are other possible enhancements of this study.

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