

DEFECTS AND MAGNETISM IN 2D MATERIALS

Thesis by

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CERTIFICATE

This is to certify that the work incorporated in the thesis entitled “*Defects and magnetism in 2D materials*” submitted by Rohit Babar was carried out by the candidate under my supervision. To the best of my knowledge, the work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.

Dr. Mukul Kabir

Thesis Supervisor

DECLARATION

I declare that this written submission represents my ideas in my own words and where others' ideas have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

Rohit Babar

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SYNOPSIS

Two-dimensional materials are currently under vigorous investigation for their multifunctional properties. Graphene and phosphorene are at the forefront of studies that are focused on (opto)electronic and spintronic applications. In this thesis, we study the thermodynamics and kinetics of point-defects and investigate the possible ways to induce robust magnetism in these otherwise non-magnetic materials.

The kinetics of vacancy in graphene is responsible for the degradation via larger defect formation and edge reconstruction. In Chapter 3, we investigate the microscopic mechanism of vacancy defect, and the influence of the applied gate voltage is studied through carrier doping. We illustrate that the lattice relaxation perpendicular to the graphene sheet, as well as the in-plane relaxation, are remarkably important to predict the diffusion mechanism accurately. Hardening of the low-energy phonon modes, that are responsible for vacancy diffusion, explains the increase in the activation barrier under different electron and hole doping. Consequently, the substantial decrease in diffusivity under carrier doping will necessarily pin the vacancy, and any degradation that is mediated by vacancy diffusion will be severely slowed down under the applied gate voltage.

There are many ways to induce local moments in graphene, however, inducing a robust long-range magnetic order remains a challenge. In this context, in Chapter 4, we investigate the local moment formation and the concurrent long-range interaction between various defect complexes in nitrogen-doped graphene. The itinerant magnetism in the graphitic N-defects is found to be fundamentally different from the more localized moments in the vacancy containing N-complexes. The concurrent long-range interaction is complex and depends on the N-concentration, defect type, sublattice, the distance between the defects, and relative orientation.

We propose that the direct exchange mechanism between the graphitic complexes is responsible for the observed ferromagnetism and rule out any role of other possible defect complexes. In this context, we also show that boron co-doping enhances ferromagnetism, and propose an overall synthesis strategy to produce robust ferromagnetism in the N-doped graphene.

Two-dimensional phosphorene has attracted enormous attention in recent times due to its intriguing physical and electronic properties. However, it undergoes structural degradation at elevated temperatures and rapidly oxidizes in ambient condition, which severely restricts technological applications. In Chapter 5, we investigate the structural and chemical degradation of phosphorene. We identify the microscopic mechanisms for self-healing, void formation, sublimation and oxidation. These results will have significant bearing in identifying the suitable conditions for the fabrication and operation of phosphorene based devices.

Phosphorene is a two-dimensional semiconductor with a highly tunable gap along with very high carrier mobility. Thus, it will be interesting to induce magnetism and manipulate the same for spintronic applications. The very first step toward this goal, inducing local moment, is discussed in Chapter 6. We show that very high diffusivity of transition-metals on the pristine phosphorene would hinder the possibility of controlled magnetism. In contrast, the thermodynamically stable point-defects can anchor the transition-metals, while the semiconducting property of the phosphorene is retained. We conclude that V/Mn/Fe absorbed at the divacancy defect to be excellent candidates for spintronic applications with high exchange-splitting and spin-flip energies. It would be interesting to further investigate the long-range interaction between the transition-metals. Among all the $3d$ transition-metals, Cr is very different and interesting, as it induces Lifshitz transition in the semiconducting band structure, which precedes Kondo screening. In Chapter 7, we show that, in sharp contrast to the conventional Kondo systems,

the Cr absorbed at a divacancy induces a multi-channel and high-temperature Kondo screening. The Kondo screening is further showed to be robust against the substrate, strain in the lattice, and layer-thickness, which simplify its experimental realization.

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CHAPTER 1

INTRODUCTION

1.1 Rise of two dimensional materials

The search for materials with novel properties has driven the discovery of two-dimensional (2D) materials in recent years. (1–7) While the quantum confinement in reduced dimensions lead to remarkable but anticipated changes, many of the surprises have emerged from the different crystal symmetries and chemical environment of these 2D materials. Extensive experimental efforts have resulted in fabrication of electronic, optical, spintronic, valleytronic, topological devices based on single or multiple layers of 2D materials. Among the plethora of 2D materials that have been synthesized, four materials stand out on account of their distinct features: graphene, molybdenum disulfide (MoS_2), hexagonal boron nitride (h-BN), phosphorene. These materials have been investigated by physicists and chemists in equal measure, and are representative of the diversity found across 2D materials.

Graphene is a semi-metal with a record high carrier mobility of $10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. (8–10) Although the lack of band gap has limited its application in semiconductor electronics, the high mechanical strength and inert nature has practical merits. The presence of a moderate and direct band gap of 1.8 eV in MoS_2 [Figure 1.1] has resulted in fabrication of ultrathin semiconducting devices. (2; 11) A consequence of the lack of inversion symmetry and strong spin-orbit coupling in MoS_2 and other transition-metal dichalcogenides results in presence of multiple valleys at the band edge. (12) The spin-valley coupling at the band edge has given way to

valley-based optoelectronic devices where the orientation of incoming circularly polarized light determines the valley edge excitation. (13; 14) Though graphene and MoS₂ have distinct electronic structures, both materials are isotropic in the layered direction. Phosphorene is unique from other 2D materials due to its in-plane anisotropy. (3; 4) This aspect is reflected in virtually all properties of phosphorene and has led to devices that demonstrate highly directional behavior. (3; 4; 15; 16) Further, phosphorene is a better semiconducting candidate than MoS₂ or other 2D materials because of its direct, tunable band gap and higher carrier mobility. Unlike above materials, h-BN represents the insulating spectrum of electronic structure. (17) The wide band gap, high dielectric constant and inert nature make it an excellent encapsulation and substrate material. (18) Thus, these four materials provide a glimpse into the possibilities that exist within the 2D materials.

For example, we present the range of electromagnetic spectrum that are covered by above four materials in [Figure 1.1]. Graphene occupies the microwave and lower frequency range and can be utilized in satellite and radio communication. Both 2D and few-layer phosphorene offer a relatively wide range in the infra-red and visible end of the electromagnetic spectrum with demonstrated applications in infra-red imaging and light emitting devices. The visible window of the electromagnetic spectrum is covered by transition-metal dichalcogenides and other 2D materials where energy conversion applications such as water splitting and solar cells have been realized. The ~ 6 eV band gap of h-BN has limited its application to the ultra-violet region although defects can turn h-BN into single photon emitter with the brightest emission at 1.99 eV, that is desirable for quantum information processing. (20) Similarly, these materials show unique mechanical, thermal and chemical strengths. (21–25)

However, a major shortcoming of these materials has been the absence of intrinsic magnetism that can be exploited for building ultrathin magnetic and spintronic

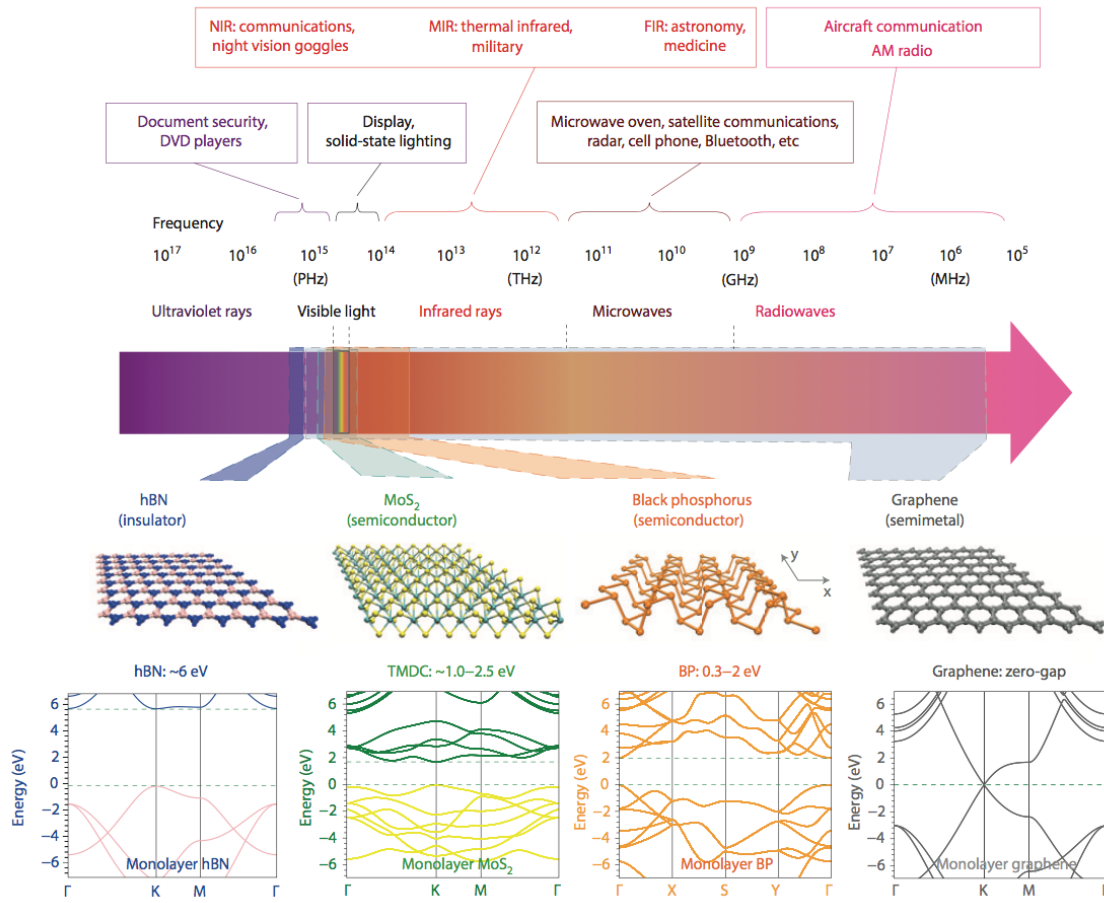


Figure 1.1: A wide range of applications for 2D materials: h-BN, MoS₂, phosphorene and graphene cover a broad region in the electromagnetic spectrum. Few of the existing as well as potential applications are shown in the top-most panel. The anisotropic structure of phosphorene along the two axes sets it apart from other 2D materials. The electronic structure shown in the lower panel highlights the diversity within these four materials. Figure reprinted from (19) by permission of Springer Nature.

devices. (26) Such devices offer dual advantage of energy and storage efficiency as the spin degree of freedom requires low energy to manipulate than electron charge and the non-binary nature of multiple spin system and phase convey additional information. What makes 2D materials potent candidates for spintronic devices is their large spin diffusion lengths, high carrier mobility, easy gating, absence of lattice mismatch issues. (27–29) We turn our attention to graphene and phosphorene, two of the above four remarkable materials that are deemed to be

promising spintronic candidates. In the following section, we introduce the reader to the structural, electronic and magnetic properties of graphene and phosphorene.

1.2 Graphene

Graphene has naturally attracted extraordinary attention by virtue of being the first 2D material to be synthesized via the exfoliation technique. (1) What has sustained the attention of scientific community in graphene for close to two decades is discussed in this section. Graphene is a single atom thick arrangement of carbon atoms in a hexagonal lattice. The carbon atoms are separated by 1.42 Å and the thickness of graphene is 3.5 Å. Each carbon atom has three nearest neighbors that are bonded by sp^2 hybridization. In the absence of curvature, the strength of in-plane bonds of graphene result in the strongest known 2D material. (30)

The hexagonal cell of graphene is made from two triangular sub-lattices A and B, each sub-lattice contributing with one delocalized p_z electron [Figure. 1.2(a)]. The lattice vectors are given by $\vec{a}_1$ and $\vec{a}_2$ and the two interpenetrating lattices are connected by $\vec{\delta}_i$. The reciprocal space has three distinct k-points - Γ , K and M. Of which the K point is significant since the low-energy states reside at K point [Figure. 1.2(b)]. The tight-binding model for nearest neighbor jump of the delocalized electron is sufficient to obtain the electronic structure of graphene near the Fermi level. A linear, symmetric and gapless electronic dispersion is obtained at K and K' points in the first Brillouin zone [Figure. 1.2(c)]. These gapless points are known as Dirac points and the resultant Fermi velocity close to K (K') is $\sim 10^6 \text{ ms}^{-1}$. However, these two k-points belong to different sub-lattice and give rise to an extra degree of freedom, namely the valley pseudospin. The p_z states in graphene are half-filled since each carbon atom contributes one delocalized p_z electron. The emergence of magnetism can be understood through a mean-field Hubbard model

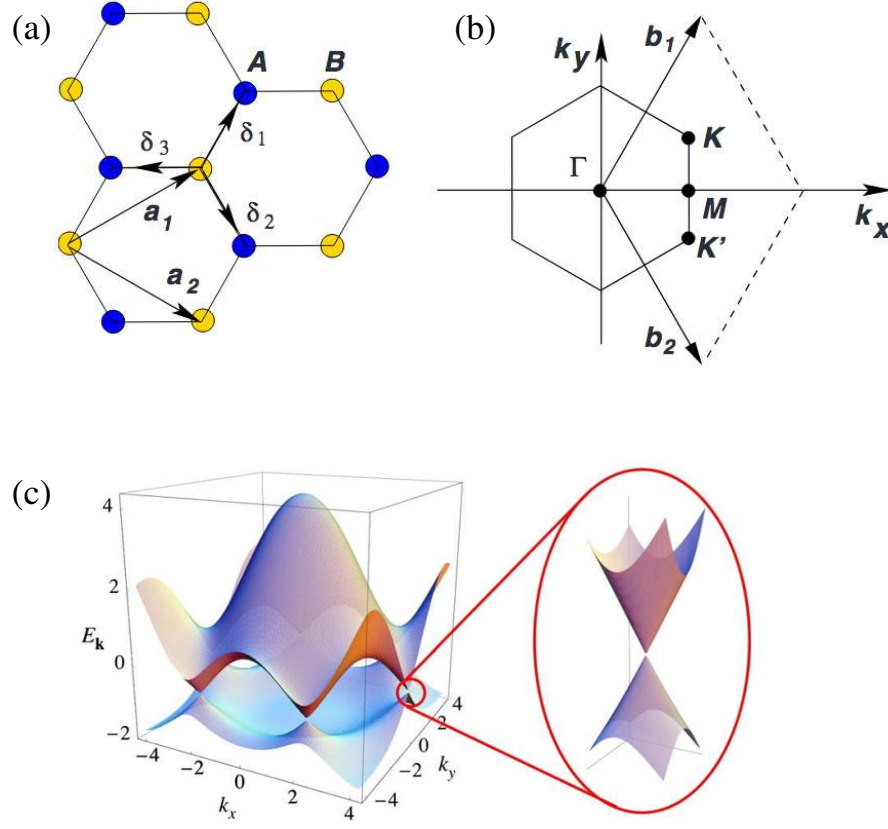


Figure 1.2: (a) The hexagonal lattice of graphene. The hexagonal lattice is made from two primitive unit cells where each primitive cell consists of two atoms (shown in blue and yellow color). The lattice vectors connecting the same primitive cell are denoted by $\mathbf{a}_1$ and $\mathbf{a}_2$. (b) The reciprocal lattice of graphene. The special symmetry points of the Brillouin zone are denoted: Γ , K and M . The valence and conduction bands meet at K and K' points. The reciprocal lattice vectors are denoted by $\mathbf{b}_1$ and $\mathbf{b}_2$. (c) The electronic structure of p_z states calculated from the nearest neighbor tight-binding model. The Fermi level is denoted by $E_{\mathbf{k}} = 0$ and the inset shows the linear dispersion near the K and K' points. Figure reprinted from (31) by permission of American Physical Society.

for p_z states, which takes into account the bipartite nature of graphene.

An ideal graphene is non-magnetic and insulating at 0 K. At finite temperature, the p_z electrons conduct electricity with a conductivity of $4e^2/h$, and exhibit weak Pauli paramagnetism below 50 K. (32) Typically, magnetism is associated with materials possessing unpaired d or f electrons. As expected, ferromagnetism in graphene is experimentally ruled out up to 2 K. (32) The tendency of graphene to

maximize bonding by occupying its valence electrons in hybridization leaves only delocalized p_z electrons. Thus, the observed diamagnetism in graphene is a result of the in-plane motion of the p_z electrons under an external magnetic field. (32) The Hubbard model offers possible means to make graphene magnetic. The Hubbard Hamiltonian is written as

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_C$$

where $\mathbf{H}_0$ is the kinetic energy term or the tight-binding term for the nearest neighbor jump of the delocalized p_z electron described before. $\mathbf{H}_0$ is given by:

$$\mathbf{H}_0 = -t \sum_{i,j,\sigma} [c_{i\sigma}^\dagger c_{j\sigma} + h.c.]$$

where $c_{i\sigma}^\dagger$ and $c_{j\sigma}$ are the creation and annihilation operators for electron at site i and j respectively, with spin σ . The jump or hopping term is denoted by t .

The first term in the Hamiltonian $\mathbf{H}_0$ gives the low-energy electronic structure where the Dirac points lie at the K points. The occupied states represent the bonding states and the states above the Fermi level are antibonding states; both are symmetrically situated away from the neutrality point of the electronic structure.

The Coulomb interaction term of the Hamiltonian for two electrons is given by:

$$\mathbf{H}_C = U \sum_i n_{i\uparrow} n_{i\downarrow}$$

In the above equation, the first term U represents the strength of on-site Coulomb repulsion and the spin-resolved electron density $n_{i\uparrow}$ is written as $c_{i\sigma}^\dagger c_{i\sigma}$.

Thus, the Hubbard Hamiltonian is given by:

$$\mathbf{H} = -t \sum_{i,j,\sigma} [c_{i\sigma}^\dagger c_{j\sigma} + h.c.] + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

Above Hubbard Hamiltonian can be solved using the mean-field approximation where the i^{th} site electron with either spin $\uparrow$ or spin $\downarrow$ interacts with the mean field electron density with opposite spin $\downarrow$ or $\uparrow$.

$$\mathbf{H}_{mean} = U \sum_i [n_{i\uparrow} \langle n_{i\downarrow} \rangle + n_{i\downarrow} \langle n_{i\uparrow} \rangle - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle]$$

The resultant magnetization or spin density obtained from solving the above mean-field Hamiltonian self-consistently is given by:

$$M_i = \frac{n_{i\uparrow} - n_{i\downarrow}}{2}$$

Thus, the magnetization is strongly dependent on U/t . We note that graphene is a special case of the Lieb's theorem for half-filled bipartite lattice. (33) Typically, the ratio is ≈ 1.2 – 1.3 for graphene. For a larger U/t of 2.3 eV, an antiferromagnetic ground state can be achieved. (34) Thus, introducing a strong on-site Coulomb interaction is one way to alter the short-range interaction among p_z electrons to generate an imbalance between the spin-polarized electron density ($n_\uparrow - n_\downarrow$). A simple way to achieve this would be through defect engineering which involves the injection of spin through foreign atom doping or careful introduction of vacancies.

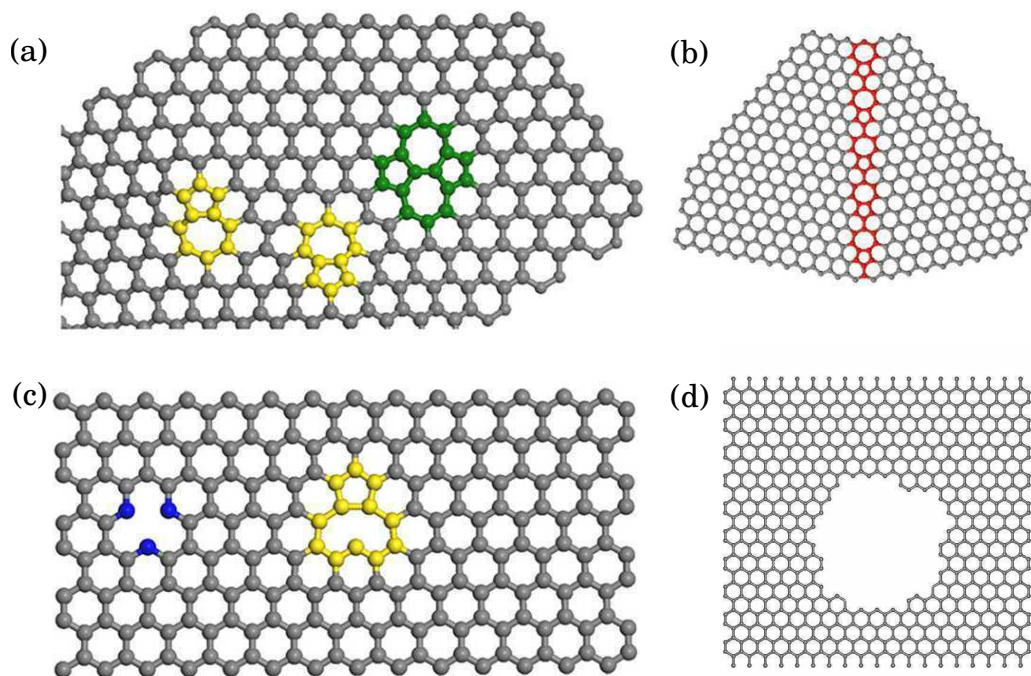


Figure 1.3: Defect types in graphene: (a) Topological defects such as dislocation dipole (yellow) and Stone-Wales (green) are formed due to the rearrangement of atoms. (b) Point defects such as monovacancy where a single atom is missing (from the center of triangle of blue), the local structural relaxation leads to distinct geometries such as 5|9 (yellow). (c) Line defect comprising of multiple dislocation dipoles. (d) Voids of $\sim$ nm and larger dimensions where a large number of carbon atoms are missing from the graphene sheet. (a-b) are point defects while (c-d) are extended defects. Figure reprinted from (36) by permission of Institute of Physics Publishing.

1.3 Magnetism in graphene via defects and doping

Imperfections in an otherwise periodic material are deemed as defects. These can be intrinsic defects (vacancy, interstitial) or extrinsic (foreign dopant); small (point defects) or large (line defects, void) [Figure. 1.3]. Depending on the defect type and their concentration, these defects can be 'vital or fatal' for the material. (35)

Defects are thermodynamically favored at finite temperature by the second law of thermodynamics [Figure. 1.4]. The configuration entropy ΔS lowers the Gibbs free energy ΔG of the material while the enthalpy ΔH increases with the addi-

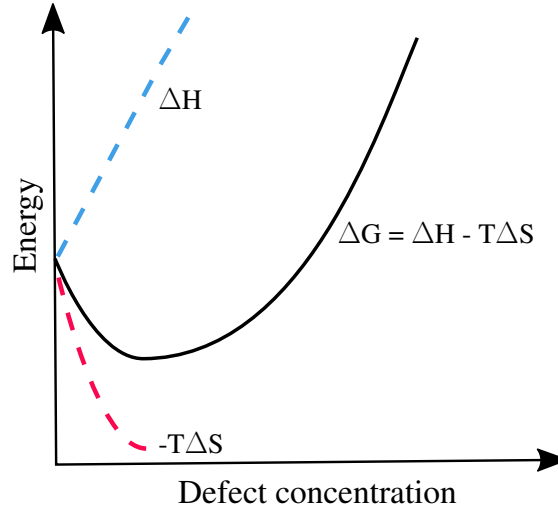


Figure 1.4: Defect concentration at the thermodynamic equilibrium of material for finite temperature. The configurational entropy $T\Delta S$ due to defects minimizes the Gibbs free energy ΔG of the material.

tion of disorder. For an optimal amount of defects, the lowering of energy due to change in entropy $T\Delta S$ will offset the gain through enthalpy ΔH . Thus, an equilibrium concentration of defects will be present in any given material. The number of ways a defect can be arranged is finite, and beyond a certain concentration of defects the enthalpic contribution is greater than entropic contribution. Although a variety of defects are possible [Figure. 1.3], the point defects and impurity atom doping are naturally common due to their high configurational entropy in comparison to voids or line defects. However, when the material is driven out of equilibrium for a considerable period of time, the point defects prefer to migrate and order themselves in complex arrangement such as line or void defects. Further, the defect formation also depends on the growth condition. In case of graphene, defect engineering is possible through TEM, STM or chemical functionalization that promote the formation of only particular defects. (37–39)

Among the multiple vacancy defects in graphene [Figure. 1.3], point vacancy defects with an odd number of missing atoms or line defects that form localized states are desirable for magnetism. In the first case, the absence of single atom

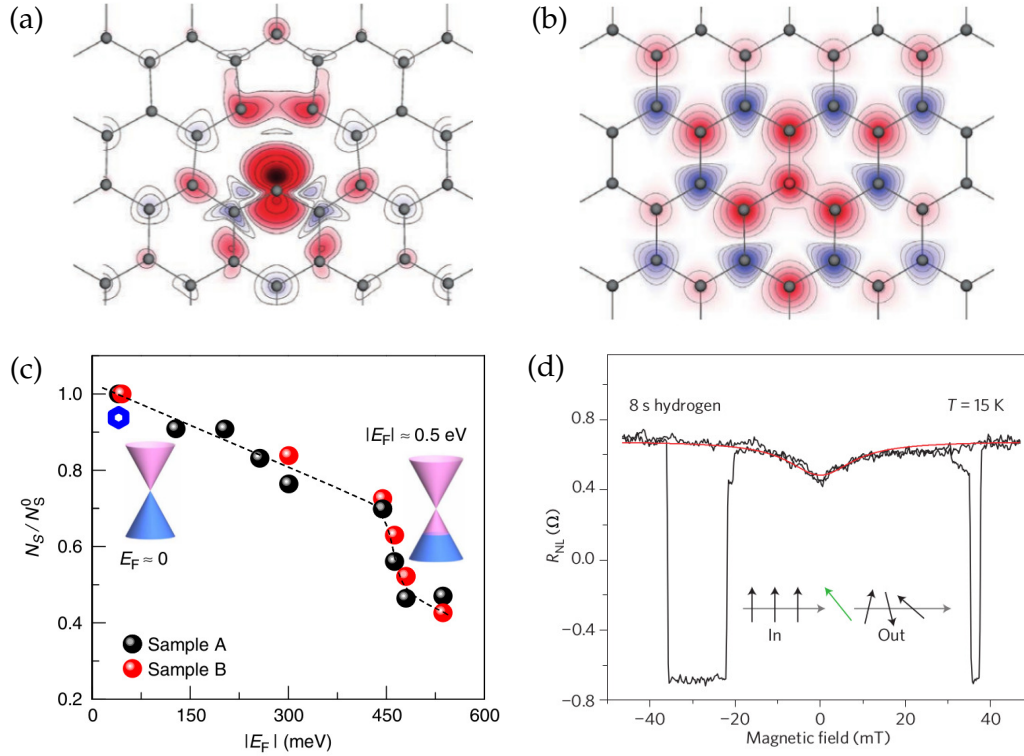


Figure 1.5: Magnetic moment in graphene from vacancy defect and foreign atom doping. (a) Magnetization density of single vacancy (SV) and (b) chemisorbed hydrogen from the density functional based calculations. Red (blue) denotes the spin-up (spin-down) spin density. Both localized and semi-localized magnetic moments are present in SV while only semi-localized spins are seen for chemisorbed hydrogen. (c) Magnetism of SV and its hole dependence: Normalized spin density in SV samples measured as a function of hole doping. N_S/N_S^0 is the ratio of spin concentration before and after doping. Measurements in sample B were carried for maximal doping followed by annealing at 373 K. Inset shows the neutral and hole-doped electronic structure of graphene. (d) The spin transport experiments show the moment formation from chemisorbed hydrogen at 15 K. The experimental data is shown by black line and the spin scattering (due to local magnetic moments) model fit is denoted by red line. A schematic of spin (black arrows) scattering by local moments (green arrow) is shown in the inset. The spin-polarized conducting electrons are denoted by grey arrows. Figures (a-b) reprinted from (27) by permission of Springer Nature, (c) reprinted from (40) by permission of American Physical Society, (d) reprinted from (41) by permission of Springer Nature.

gives rise to net spin density ($n_{\uparrow} - n_{\downarrow}$). The single vacancy (SV) [Figure. 1.5(a)] is interesting as it results in a magnetic moment of $2 \mu_B$, with contributions from local sp^2 and semi-localized p_z states. Thus, it was speculated that multiple SV defects

could lead to ferromagnetism in graphene. However, the randomly distributed SV are paramagnetic due to the cancellation of spin densities. (40) For SV defects occupying a single sublattice, magnetically ordered states have been theoretically predicted. (42) However, the spatial control of defects within experiments remains a major challenge. For similar reasons, the ferromagnetism reported in line defects for graphite has been scarcely replicated. (43) Manipulation of magnetism by tuning the semi-localized magnetism is achievable in SV [Figure. 1.5 (c)]. In this thesis, we discuss the magnetic moment of SV and its gate-dependence at length in Chapter 4.

The magnetism generated from foreign atom doping can be through (i) local magnetic moment intrinsic to the dopant such as $3d$ transition-metal atoms or (ii) semi-localized moment from the sub-lattice symmetry breaking such as hydrogen chemisorption. Transition-metal doping results in local moment formation, however, the experimental observations of adatom clustering and a paramagnetic ordering are unfavorable for robust magnetic ordering. (44; 45) Thus, it is necessary to investigate the diffusivity of dopants on 2D materials and identify suitable doping sites using computational methods as we have shown in Chapter 4 and Chapter 6 for graphene and phosphorene respectively.

The chemisorbed hydrogen atom provides a magnetic moment of $1 \mu_B$ from the semi-localized p_z states [Figure. 1.5 (b)]. In this case, the H atom is located above the central C atom. The C–H bond withdraws a p_z electron from graphene and introduces an imbalance in the spin densities. Measurements of local moment [Figure. 1.5 (d)] as well ferromagnetic coupling is limited to low temperatures. (39; 41) Nonetheless, hydrogen chemisorption demonstrates the potential of introducing dopants to generate ferromagnetism in graphene.

Boron and nitrogen are suitable dopant choices since their similar sizes allow easy substitution into the lattice. The doped atom is therefore robust to external

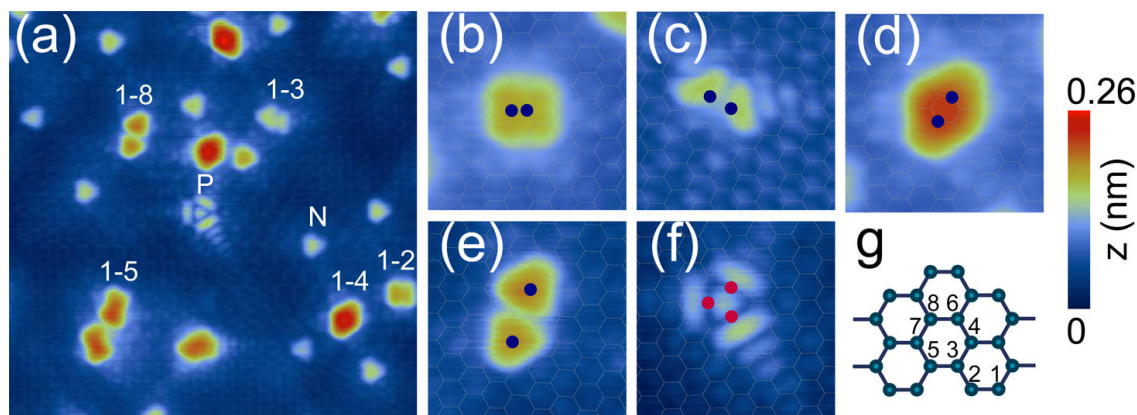


Figure 1.6: The diversity of N doping in graphene: The single graphitic nitrogen is labeled as N. Multiple graphitic N-pairs are observed in a large amount with a wide range of N–N separation. P refers to the pyridinic nitrogen defect. We show in Chapter 4 that the graphitic N complexes are promising for generating a ferromagnetic order. Details of STM imaging in (a) are: -0.5V , 400 pA , dimension of 10 nm . Figure reprinted from (46) by permission of American Chemical Society.

perturbations. Further, their doping results in n- or p- doped graphene, which provides conduction electrons for possible spin transport. It is also possible to open the gap at Dirac point depending on the N arrangement. (46; 47) Multiple techniques exist for the synthesis of N doped graphene where the N content and its bonding can be altered based on the growth method. (48) For example, Figure. 1.6 shows both substitutional and defected N complexes in close vicinity. Recently, several works have reported ferromagnetic behavior in N doped graphene with varying Curie temperatures that are prepared with different techniques. (49–52) Thus, N complexes and their concentration influence the magnetic behavior of N doped graphene. However, detailed knowledge of the suitable N complexes and their arrangement is not known. We carry out investigation of various N doped complexes in Chapter 4 and further identify the complexes that result in ferromagnetic behavior.

In addition to the above-discussed magnetism, graphene is an appealing spintronic material. The low mass of carbon atoms endows graphene with low spin-orbit coupling. As a result, the spin transport through graphene will not be scat-

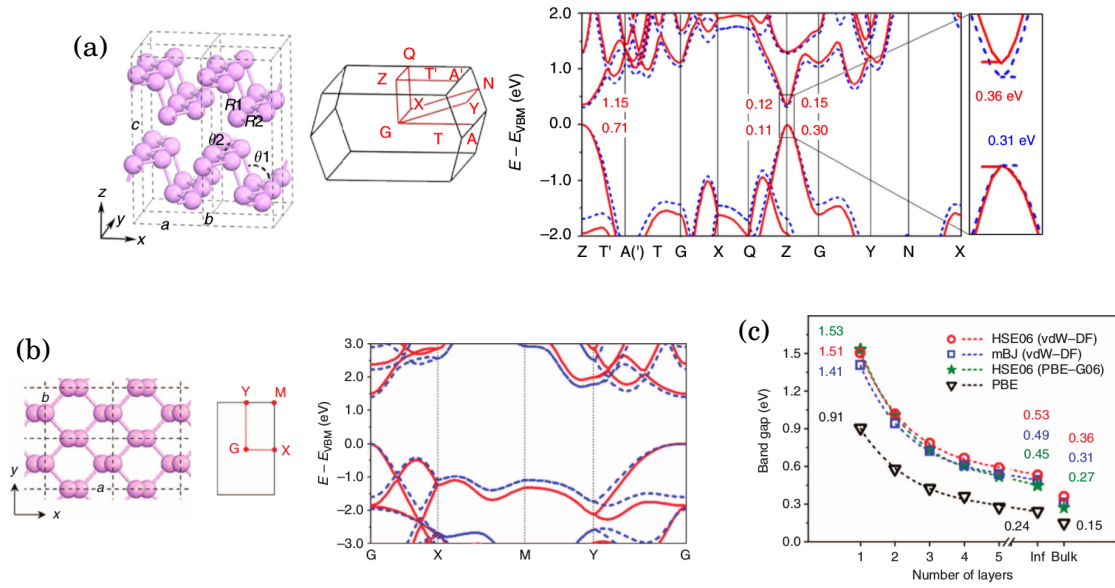


Figure 1.7: The Orthorhombic lattice of black phosphorus and phosphorene. (a) Crystal structure of black phosphorus consists of puckered layers of phosphorus atoms. The Brillouin zone and corresponding electronic dispersion. The valence and conduction band lie at Z point. (b) Crystal structure and Brillouin zone of single layer phosphorene. The band edges lie at the G or Γ point. Prominent anisotropy in electronic dispersion is observed along $G \rightarrow Y$ and $G \rightarrow X$ directions. (c) The layer dependent band gap of black phosphorus. Figure reprinted from (54) by permission of Springer Nature.

tered by carbon and will have a long spin relaxation time ($\sim$ ns) and diffusion lengths ($\sim \mu\text{m}$) at room temperature. (27; 53) Gate-voltage and electric field control can result in guided spin currents (spin Hall effect) on graphene. However, the absence of band gap is a major shortcoming of graphene as it hinders the magnetic stability of such systems.

1.4 Phosphorene: A two-dimensional semiconductor with anisotropy

The single layer of bulk black phosphorus was recently isolated by mechanical exfoliation. (3; 4) Much like bulk graphite, black phosphorus is a layered van der Waals material. Both bulk and the isolated layer are identifiable by their puckered hexagonal lattice. Although the stability of black phosphorus has been a challenge as it degrades rapidly under ambient conditions, air-stable monolayers have been fabricated. (55; 56)

The bulk black phosphorus has orthorhombic lattice with space group $Cmca$ [Figure. 1.7(a)], where covalently bonded puckered honeycomb layers are stacked together by weak van der Waals (vdW) interaction. (57) The bulk black phosphorus has a direct band gap which is measured to be 0.23 eV, (3) and in agreement with theoretical calculations [Figure. 1.7(a)]. (4; 54; 58; 59) Similar to graphite, the individual layers are held together via weak vdW interaction in black phosphorus, and thus it is easy to exfoliate single and few-layer phosphorene. (3; 4). However, the interlayer attraction in black phosphorus is stronger than graphite and the exfoliation energies are therefore higher for phosphorene.

The band gap of 1.45–2.05 eV in phosphorene (4; 54; 60) is larger than bulk black phosphorus. (3; 61–63) [Figure. 1.7(b)] First-principles calculations demonstrate that the band gap decreases with increasing layer thickness, (54) [Figure. 1.7(c)] and can also be tuned by external strain. (64) It is important to note that the valence and conduction bands are more dispersive or linear along $G \rightarrow X$ direction than along $G \rightarrow Y$ direction where the dispersion is parabolic. This is responsible for the anisotropic electrical conductance, which has been experimentally observed in both bulk and single layer. (3; 4; 54)

The large gap in phosphorene results in an on-off current ratio of 10^5 which is

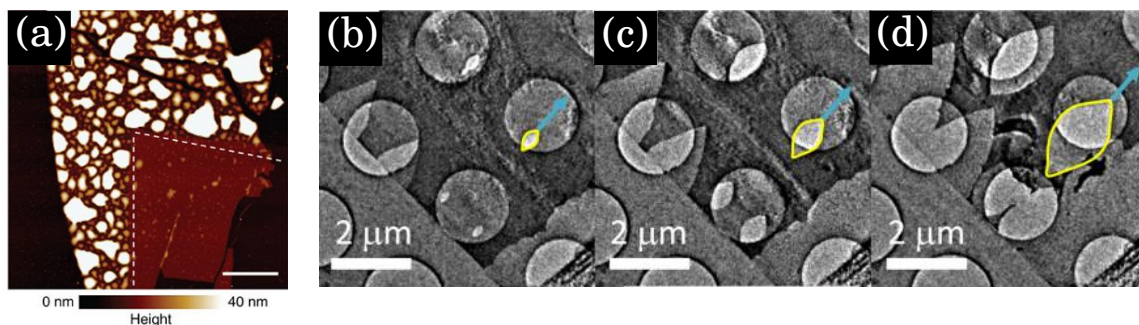


Figure 1.8: Degradation of phosphorene: (a) Chemical degradation at the surface of 10 nm black phosphorus from exposure to ambient condition for 5 days. The lower (dark brown) section of black phosphorus is covered by h-BN and does not undergo degradation. The scale bar represents $4\ \mu\text{m}$. (b-d) Structural degradation in the form of anisotropic voids (with yellow edges) occurs on heating black phosphorus. The snapshots are taken after 5, 8, 12 minutes of heating at 673 K. Upon further heating, black phosphorus undergoes sublimation. Figure (a) reprinted from (65) by permission of Springer Nature. Figures (b-d) reprinted from (66) by permission of American Chemical Society.

higher than MoS_2 . (3) Further, its carrier mobility of $1000\ \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is also better than MoS_2 . (3; 4) Thus, the semiconducting nature and the distinct behavior of phosphorene along the in-plane orthogonal directions leads to many interesting applications. (3; 4; 15; 16; 67)

However, both phosphorene and black phosphorus react with air and undergo degradation. The degradation results in severe loss of structural stability as oxygen, water, light combine to form oxide and acid compounds at the surface. (68–70) The interaction of the oxygen molecule with phosphorene is significant due to the strong $\text{P}=\text{O}$ bond. One way to prevent chemical degradation is to encapsulate phosphorene or black phosphorus [Figure. 1.8(a)] in a corrosion-free material such as h-BN. (65)

Further, black phosphorus undergoes structural degradation above 650 K [Figure. 1.8(b-d)]. (66) Vacancies and edges contribute heavily to the degradation process as the weakly bonded P atoms break away from phosphorene. As a result, the vacancy defects enlarge to form anisotropic voids. With further heating, phos-

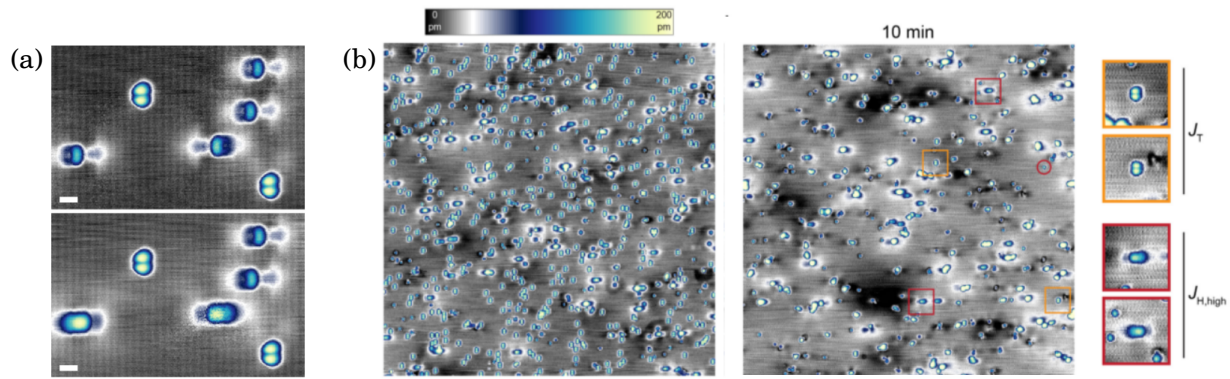


Figure 1.9: Cobalt deposition on black phosphorus: (a) Co absorbs in two distinct configurations identified by the highly directional lobes. The Co atom can be switched between two configurations via STM tip at 5 K ($V_s = -400$ mV, $I_t = 20$ pA, scale bar = 1 nm). (b) For $4 \rightarrow 300$ K annealing, the Co deposition dramatically changes within a short span of 10 minutes ($V_s = -400$ mV, $I_t = 20$ pA, scale bar = 80×80 nm). Thus, the potential application of Co atom as bistable memory state has practical limitations. Figure reprinted from (71) by permission of Springer Nature.

phorene is sublimated within few minutes. Both chemical and structural degradation limit the potential of large-scale use of phosphorene. Thus, it is necessary to identify ways to overcome these problems. In Chapter 5, we study the single vacancy diffusion, divacancy formation, adatom diffusion, sublimation and oxygen degradation process. The defect migration barriers provide an insight into the temperature-dependent defect activity in phosphorene.

Similar to graphene, doping of $3d$ transition-metal atoms can induce magnetism in phosphorene. A high carrier mobility and low spin-orbit coupling further improve the spintronics prospect of phosphorene. The semiconducting nature of phosphorene can be utilized in developing non-volatile magnetic semiconductors. In comparison to heteroatom 2D semiconductors, the absence of antisite disorder in phosphorene lead to prediction of Curie temperatures above 300 K. (72) Further, the anisotropic response of phosphorene imparts an additional degree of freedom. The exchange interaction is anticipated to be highly direction dependent. The undesirable scenario of metal atom clustering is prevented along the armchair direc-

tion due to high activation barriers. Thus, phosphorene offers enormous potential in engineering spintronic devices.

Co deposition on black phosphorus was shown to be switchable between two distinct valence states [Figure. 1.9(a)] when manipulated by STM tip at low temperatures of 5 K. (71) Thus, an individual atom can serve as orbital memory unit which can store the information without the need for a magnetic read-out. However, the Co atoms are highly mobile at room temperatures and the altered arrangement is undesirable for magnetic storage purpose. [Figure. 1.9(b)] Thus, a reliable control of induced spins is important to realize practical applications. We identify vacancies to be suitable doping sites where the induced spins will be pinned even at room temperature. The magnetic moment of $3d$ transition-metal atoms on both pristine and defected phosphorene is studied in Chapter 6. The divacancy defect is found to be very promising in this regard. Further, the semiconducting nature of phosphorene changes to half-metal/metal upon doping. The manipulation of electronic structure along with the overall magnetic properties is yet another exciting aspect of phosphorene.

The tunable electronic structure of black phosphorus has led to realization of anisotropic Dirac semi-metal through adatom doping as well as applied electric field. (73; 74) A topological insulator state is predicted in few-layer phosphorene for a critical electric field strength. (75) In Chapter 7, we demonstrate a distinct semiconductor to metal transition through Cr doping. A many-body Kondo state is engineered where the conduction electrons from phosphorene couple anti-ferromagnetically with the localized Cr- d electrons. The Cr doped phosphorene differs from previously reported Kondo state in graphene as the chemical potential of phosphorene is dramatically tuned to metallic state, whereas the manipulation of semi-metallic graphene to metal with varying carrier densities is easily achieved through doping or gating. (76; 77)

The anti-ferromagnetic coupling results in screening of the impurity moment at low temperature, and the associated screening length defines the Kondo cloud size. We find that the cloud dimension in phosphorene is orders of magnitude smaller than bulk. This observation has interesting ramifications as the Kondo cloud has remained undetected in bulk where the cloud size exceeds the typical device dimension. However, in case of phosphorene it could be possible to observe the hitherto undetected Kondo cloud experimentally.

CHAPTER 2

COMPUTATIONAL METHODS

“I understand that the density tells you everything; the cusps of the density tell you where the nuclei are, the gradient of the density at the nucleus tells you what the nucleus is, and the integral of the density tells you how many electrons you have – therefore you have specified everything about your system and Hamiltonian and hence all is known.”

– E. Bright Wilson upon hearing Hohenberg–Kohn theorems. (78)

This chapter presents a brief account of the computational methods employed in this thesis. We begin by describing the complexities in solving the many-body problem. Significant approximations that have led to the formulation of density functional theory (DFT) are discussed. A summary of electron–electron interactions used in this work, which are modeled across increasing hierarchies of functionals is provided. To correctly address the electronic structure for defected or doped materials, we have calculated the band structures using the band unfolding scheme. The crystal orbital hamilton population method is used in conjunction with DFT to distinguish among bonding, non-bonding, and antibonding states. Finally, we describe the nudged elastic band method, a procedure to estimate activation energies and migration pathways.

2.1 Tackling the many-body problem

A quantum mechanical description of materials remains a challenging problem on account of multitude of interactions among the constituents as well as emergent interactions in particular cases. The complexities become apparent when one writes the many-body Hamiltonian for a system comprising of ions and electrons -

$$\mathbf{H} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{I \neq J} \frac{e^2}{2} \frac{Z_I Z_J}{|R_I - R_J|} + \sum_{i \neq j} \frac{e^2}{2} \frac{1}{|r_i - r_j|} - \sum_{i,I} \frac{e^2 Z_I}{|R_I - r_i|}$$

where $I(i)$ denotes an ion (electron), $M(m)$ is the ion (electron) mass, $R(r)$ is the position of ion (electron). The first two terms of the Hamiltonian represent the kinetic energy of ions and electrons respectively; the third and fourth term describe the Coulomb interaction energy for ion–ion and electron–electron interaction whereas the electron–ion interaction is described by the final term. The solution to above system is given by the Schrodinger equation -

$$\mathbf{H}\Psi(r, R) = E\Psi(r, R)$$

where Ψ is the many-body wave function, and E is the eigenvalue of the system. The exact solution is almost impossible to obtain except for systems containing few electrons. The difficulty stems from the many-body interactions which need to be decoupled into independent set of equations.

The ionic contribution to the Hamiltonian can be separated from the electronic interaction on account of different timescales for their motion. The adiabatic nature of ions arises from the large mass of ions compared to electrons ($m/M \sim 2 \times 10^{-3}$ or less). Thus, the ions can be treated as static objects while the electrons relax to an equilibrium position. Above approach is known as adiabatic or **Born-**

Oppenheimer approximation. (79) The effective Hamiltonian can now be written as

$$\mathbf{H} = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i \neq j} \frac{e^2}{2} \frac{1}{|r_i - r_j|} - \sum_{i,I} \frac{eZ_I}{|R_I - r_i|} + V_{ion}$$

where the first term describes the kinetic energy of electrons, the second term is electron–electron interaction, the third term denotes the attractive Coulomb interaction among electrons and static ions. The last term is additive energy for the ion–ion interaction calculated using the Born–Oppenheimer approximation. Further simplification of the Hamiltonian requires decoupling of the electron–electron interactions.

Hartree proposed that the many-body electronic wave function be written as a product of single electron wave functions $\Phi(r_1, r_2, \dots, r_N) = \phi_1(r_1)\phi_2(r_2)\dots\phi_N(r_N)$. (80) Each wave function $\phi_i(r_i)$ has an independent Schrodinger equation and the effective potential experienced by an electron is the result of Coulomb interaction with remainder electrons and ions given by the second and third terms in the following Schrodinger equation,

$$-\frac{\hbar^2}{2m_i} \nabla_i^2 \phi_i(r) + V_{ion}(r_i) \phi_i(r) + e^2 \int \frac{\sum_{i \neq j} |\phi_j(r')|^2}{|r - r'|} dr' = \epsilon_i \phi_i(r)$$

and the total energy is given by:

$$E = \sum_i \epsilon_i - \frac{e^2}{2} \int \int \frac{\rho_i(r) \rho_j(r')}{|r - r'|} dr dr'$$

where the second term accounts for the doubly counted electron–electron interaction, also known as the Hartree energy. Note that $\rho(r) = |\phi(r)|^2$ denotes the electron density. Thus, a self-consistent solution of the Schrodinger equation is obtained by the variational approach, where the total energy is minimized with

respect to either wave function or electron density. The resultant eigen energy is the sum of many single-particle energies. However, the **Hartree approach** does not take into account the Fermi–Dirac statistics for electrons. The antisymmetric nature of electronic wave function Φ expressed using the Slater determinant is addressed within the Hartree–Fock approximation. The exchange interaction between two anti-parallel electrons lowers the Coulomb energy of the system due to a reduction in electron–electron repulsion, this energy gain is known as the exchange energy. The Schrodinger equation for **Hartree–Fock approximation** is

$$\left(-\frac{\hbar^2}{2m_i} \nabla_i^2 + V_{ion}(r_i) + \int \frac{\sum_{i \neq j} \rho_j(r')}{|r - r'|} dr' - e^2 \sum_{i \neq j} \int \frac{\phi_i^*(r) \phi_j(r')}{|r - r'|} dr' \right) \phi_i(r) = \epsilon_i \phi_i(r)$$

While the first two terms represent the Hartree approximation, the last term for the exchange energy contribution arises from the Pauli exclusion principle. Thus, Hartree-Fock approximation represents a remarkable simplification of the original many-body problem. However, electronic energies beyond the exchange interaction (for example, electronic correlation) are absent. This results in an underestimation of the chemical bond strength. Typically, the band gaps are overestimated due to the non-local nature of exchange interaction.

2.2 Density functional theory (DFT)

A significant breakthrough in remedying the many-body problem was to express the electron–electron interactions using electronic density $\rho(r)$ instead of wave function. This led to a drastic reduction in the degrees of freedom in the Schrodinger equation and the eigenvalue problem became tractable for systems containing a large number of ions and electrons.

Hohenberg and Kohn showed that the electronic density $\rho(r)$ uniquely deter-

mines the external potential $V(r)$ of the many-body system within a trivial additive constant. (81) Since the Schrodinger equation can be solved using $\rho(r)$, one can also obtain the wave function. Consequently, the identification of ground state electronic density results in complete information of physical observables of the system, in principle. Simply put, the electronic properties are a functional of the electronic density. Hohenberg and Kohn further demonstrated that the electronic density which minimizes the energy functional is the ground state density. However, in the absence of an exact form of the energy functional, the density functional approach remained impractical.

The energy functional was successfully computed by Kohn and Sham's non-interacting particle approach. (82) They considered an auxiliary system of non interacting particles with single particle wavefunction $\phi(r)$ that behaved in the same manner as the electronic density of many-body system. To achieve this, a new **Kohn-Sham energy functional** is defined where the kinetic energy of interacting electrons is combined with the correlation energy, and the non-interacting kinetic energy contribution is written explicitly. Thus, the Kohn-Sham functional is -

$$E_{KS}[\rho] = - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_x[\rho] + E_c[\rho]$$

where the first term is the kinetic energy functional of the non-interacting electrons, the second term is the Hartree energy, and the last two terms are the exchange and correlation energy functionals. Conveniently, these are treated together as $E_{xc}[\rho]$. Applying variational principle, the above energy functional is minimized with respect to the density $\rho(r)$ and wave function $\phi(r)$ to obtain the ground state properties in a self-consistent manner. Note that the single particle wave function in Kohn-Sham equations do not represent the actual electronic wave function. However these wave functions are crucial for constructing the elec-

tronic density within the self consistent loops (using the relation $\rho(r) = \sum_i |\phi(r)|^2$).

2.3 Exchange–correlation functional

The exact functional for exchange and correlation is unknown since these interactions inherently arise from many-body interactions and can only be approximated up to a certain limit. Thus, the results of a DFT based calculation are as good as the assumptions in the underlying exchange–correlation functional $E_{xc}[\rho]$. The $E_{xc}[\rho]$ is split into kinetic and potential energy terms - the kinetic energy part includes energy difference between the non-interacting and correlated system and the potential energy involves energy difference between many-body and Hartree energies. Since both exchange and correlation effects lower the energy of the system by increasing the distance (or decreasing the repulsion) between electrons, the exchange–correlation term is modeled as a ‘hole’ within DFT. Such exchange–correlation hole reduces the probability of finding an adjacent electron. The exchange part of the hole takes into consideration the Pauli exclusion principle as well as corrects for the spurious repulsive interaction of electron with its density (self-interaction) that is added to the Hartree energy in DFT formalism. The electronic density for real system is inhomogeneous and various approximations for the exchange–correlation functional have been proposed to either reduce the computational complexities or mimic the experimental results.

Local density approximation (LDA)

The LDA is the simplest approximation among all exchange–correlation functional which treats the electronic density as locally homogeneous. Thus, the density is locally constant and numerically accurate. The LDA E_{xc} is given as

$$E_{xc}^{LDA}[\rho] = \int \rho(r) E_{xc}^{homo} \rho(r) dr$$

where E_{xc}^{homo} is the exchange–correlation energy for homogeneous electron density. The LDA is successful for ideal metals such as Na, as well for non-homogenous materials where the exchange–correlation effects are short-range and sufficiently captured within LDA. The local nature of LDA does not completely cancel the self-interaction energy and can results in higher energy for obtaining a localized ground state. This can lead to excess delocalization, reduction in band gap, incorrect magnetization. The self-interaction error persists in GGA as well.

Generalized gradient approximation (GGA)

The extent of density localization is increased within GGA by considering the gradient of electronic densities:

$$E_{xc}^{GGA}[\rho] = \int \rho(r) E_{xc}(\rho(r)) dr + \int F_{xc}(\rho(r), \nabla \rho(r)) dr$$

The additional exchange contribution from the enhancement factor F_{xc} results in higher exchange energies than LDA for high and moderate electronic densities, which is consistent with the domination of exchange interaction over correlation for the above density regimes. For low densities, GGA behaves like LDA. In general, GGA improves the binding energy and overestimates the bond length over LDA. Majority of the calculations in this thesis are performed using the Perdew-Burke-Enzerhof functional (PBE), which is a widely used form of GGA. (83) The major drawbacks of the LDA and GGA functionals, especially for semiconductors and transition-metal doped systems, are overcome by the following functionals.

Strongly constrained and appropriately normed meta-GGA (SCAN)

Since GGA is a local functional, it does not perform well across all density regimes. The addition of kinetic energy functional τ , which is non-local in nature, to GGA is a common strategy among meta-GGA functionals. The SCAN functional differs from GGA/meta-GGA by the inclusion of kinetic energy τ to construct a semi-local exchange-correlation, which meets all known constraints placed on semi-local functionals and is appropriately normed. (84) This is expressed succinctly as

$$E_{xc}^{SCAN}[\rho] = \int E_{xc}(\rho(r), \nabla\rho(r), \tau(r)) dr$$

where kinetic energy τ is obtained from the Kohn-Sham single particle wave functions.

$$\tau = \frac{1}{2} \sum_{occupied} |\nabla\phi(r)|^2$$

A dimensionless parameter α based on kinetic energy contribution across different electronic densities is included in the SCAN meta-GGA functional. The kinetic energy density for local density (single and two-electron orbital) is given by

$$\tau_{loc} = \frac{1}{8} \frac{|\nabla\rho(r)|^2}{\rho(r)}$$

and for homogeneous density,

$$\tau_{homo} = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}$$

The dimensionless parameter α is defined as

$$\alpha = \frac{\tau - \tau_{local}}{\tau_{homo}}$$

which reproduces the GGA behavior for metals when $\alpha = 1$ ($\tau = \tau_{\text{homo}}$), covalent bonding for $\alpha = 0$ ($\tau = \tau_{\text{local}}$). In addition, the weak van der Waals bonding is obtained for $\alpha \gg 1$ (antibonding nature of τ exceeds both τ_{homo} and τ_{local}). SCAN meta-GGA is appropriately normed to homogeneous electronic density, H atom, rare gas atoms, etc. such that the exchange–correlation hole always lies in the vicinity of the reference electron, which is critical for minimizing the self-interaction error.

Importantly, SCAN functional successfully meets all the seventeen conditions for a semi-local functional in a non-empirical manner, which are [1] negativity*, [2] equality of spin-scaling*, [3] uniform density scaling*, [4] 4th order gradient expansion, [5] finite non-uniform density scaling limit, [6] tight lower bound in case of two-electron densities - above constraints are placed on the exchange part of the functional. For the correlation term, [7] nonpositive energy*, [8] 2nd order gradient expansion*, [9] uniform density scaling to the high-density limit*, [10] uniform density scaling to the low-density limit*, [11] vanishing correlation energy for one-electron density, and [12] finite non-uniform density scaling limit. The combined exchange–correlation constraints are [13] size extensivity*, [14] general Lieb-Oxford lower bound*, [15] weak dependence upon relative spin polarization for low-density limit*, [16] static linear response of the uniform electron gas*, and [17] Lieb-Oxford bound for two-electron densities. In comparison, the PBE-GGA functional meets a limited number of constraints denoted by an asterisk (*).

We use the SCAN meta-GGA functional to improve the magnetization in defected as well as boron- and nitrogen-doped graphene, which is underestimated in PBE-GGA functional due to the self-interaction error.

Hybrid functional (HSE06)

The shortcomings of LDA/GGA functional (DFT) and Hartree–Fock method

in estimation of band gap can be overcome by hybrid functionals. Typically, the exchange correlation functional of DFT is mixed with partial exchange contribution from Hartree–Fock method. The Hyde-Scuseria-Ernzerhof hybrid functional (HSE06) involves separation of the short range Hartree–Fock exchange and a rapid screening of the long range Hartree–Fock exchange terms. (85) Further, only $1/4^{th}$ short-range Hartree–Fock exchange is mixed with the $3/4^{th}$ short-range DFT exchange.

$$E_{xc}^{HSE} = \frac{1}{4}E_x^{HF(short)} + \frac{3}{4}E_x^{DFT(short)} + E_x^{DFT(long)} + E_c^{DFT}$$

DFT + U

The treatment of the d, f electrons present in strongly correlated materials is grossly delocalized in LDA/GGA functionals and underestimates the magnetic moments. A repulsive interaction between the localized d, f electrons forces the system to prefer localized states with high-spin configuration. Such an approach is synonymous to the Hubbard model and the repulsive interaction added to DFT is known as Hubbard U . The repulsive U is applied only for d, f electrons and the otherwise delocalized s, p electrons are treated with conventional DFT approach. The total energy for DFT + U is given by,

$$E^{DFT+U}[\rho(r), n_d] = E^{DFT}[\rho(r)] + E^U[n_d] - E^{double}[n_d]$$

where the first term calculates the total DFT energy, the second term is the on-site Coulomb repulsion based on the occupancy of the d (or f) orbital, and the last term compensates for the double-counting of repulsive interaction in DFT calculation. The spin-state are sensitive to the value of U . In this work, we implement Dudarev's rotationally invariant approach of DFT + U . (86)

2.4 Band unfolding method

Defect modeling as well as doping requires a supercell calculation to achieve a dilute concentration that approaches practical limits. The replication of primitive cell to form a supercell in real space is accompanied by downfolding of the Brillouin zone in reciprocal space. The resultant electronic structure calculation of supercell leads to a complex band structure, which makes the identification of impurity states from the host bands difficult. The supercell band structure can be reconstructed by unfolding of the band structure onto the primitive cell Brillouin zone. (87) However, a straightforward approach is ineffective since defects lower the supercell symmetry and in the absence of a translation vector, the correspondence between the primitive and supercell reciprocal space is incomplete. In this work, we have calculated the electronic band structure using the band unfolding technique implemented in the BandUP code. (88; 89) The supercell state for band m can be written as the sum of primitive cell states representing band n ,

$$|\mathbf{K}, m\rangle = \sum_n \sum_i^{N_K} F_u(\mathbf{k}_i, n; \mathbf{K}, m) |\mathbf{k}_i, n\rangle$$

where F_u denotes the unfolding of primitive cell states onto supercell. The primitive and supercell wavevectors are related by $\mathbf{k}_i = \mathbf{K} + \mathbf{G}_i$ where i spans the primitive cell Brillouin zone. The band unfolding is carried out by mapping the spectral weights of supercell Brillouin zone onto the primitive cell Brillouin zone. The contribution of primitive cell states to a particular supercell state (band m) is given by the spectral weight S ,

$$S = \sum_n \langle \mathbf{K}, m | \mathbf{k}_i, n \rangle = \sum_{\mathbf{g}} C_{\mathbf{K}, m}(\mathbf{g} + \mathbf{G})$$

The later expression for spectral weight S is rewritten using the plane wave expansion for $|\mathbf{K}, m\rangle$ ($|\mathbf{k}, n\rangle$) where $\mathbf{G}$ ($\mathbf{g}$) is the reciprocal lattice vector in supercell (primitive cell) Brillouin zone,

$$|\mathbf{K}, m\rangle = \left[\sum_{\mathbf{G}} C_{\mathbf{K},m}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \right] e^{i\mathbf{K}\cdot\mathbf{r}}$$

Thus, S can be evaluated independently of the primitive cell coefficients. In order to plot the band structure, the spectral weights are assigned to the primitive cell $\mathbf{k}$ -points using the spectral function,

$$A(\mathbf{k}, E) = \sum_m S \times \delta(E - E_{m,\mathbf{K}})$$

Here, the intensity of particular energy state is dependent on the spectral weight. Finally, the effective band structures obtained through the above unfolding method are comparable to angle-resolved photoemission spectroscopy (ARPES) measurements.

2.5 Crystal Orbital Hamilton Population (COHP)

A major drawback of the plane wave based DFT codes is their inability to distinguish between the bonding, anti-bonding and non-bonding electronic states. Detailed knowledge of the chemical bonding is necessary to identify the exact nature of the interaction between two atoms. In the present work, we have successfully used the crystal orbital Hamilton population (COHP) method to extract this information. For example, we explain the general trend of binding between transition metal dopant and host 2D materials via the bonding state analysis of $3d$ transition metal dopant and phosphorene. In another case, the necessary condition of hybridization between magnetic impurity and metallic host to realize a Kondo state

is shown to be true for Cr-doped phosphorene using COHP method. To achieve this the plane wave information must be projected to an appropriate orbital basis set where the plane wave-orbital overlap determines the electronic character.

The crystal orbital overlap population (COOP) method is a popular technique in quantum chemistry to distinguish between bonding and antibonding orbitals, which is determined by the overlap matrix O_{ij} between orbital i and j . The COOP is defined as

$$COOP_{ij} = \sum_{n,\mathbf{k}} C_i^* C_j O_{ij} \times \delta(\epsilon - \epsilon_{\mathbf{k}}),$$

where $C_{i/j}$ are the coefficient matrices of the orbitals i and j . A positive (negative) overlap matrix refers to bonding (antibonding) orbital and the bonding strength is measured from the orbital population weight. Within density functional theory, the energy (Hamiltonian) dependent crystal orbital Hamilton population (COHP) method can analogously distinguish between the different orbital types. (90; 91) The definition of COHP differs from COOP in the absence of orbital-wise information in DFT based codes. Here,

$$COHP_{ij} = \sum_{n,\mathbf{k}} T_i^* T_j H_{ij}^{proj} \times \delta(\epsilon - \epsilon_{\mathbf{k}}),$$

H_{ij}^{proj} refers to the projected Hamiltonian matrix elements and the transfer matrices $T_{i/j}$ are the analogs of coefficient matrices $C_{i/j}$. The transfer matrix is defined as the overlap between the plane wave function ψ_i and local orbital χ_j ,

$$T_i = \langle \psi_i | H^{proj} | \chi_j \rangle$$

and H_{ij}^{proj} is the projection of plane wave Hamiltonian H^{DFT} onto a localized basis set.

$$H_{ij}^{proj} = \langle \chi_i | H^{proj} | \chi_j \rangle$$

Thus, COHP allows the partitioning of DFT based band energies to real space orbitals (i.e., density of states). The negative (positive) energy states correspond to bonding (antibonding) states. Further, the integration of orbital energies up to the Fermi level (integrated COHP) gives the measure of binding energy.

2.6 Nudged Elastic Band (NEB) method

Defect diffusion and chemical reaction dynamics are activated processes which require an intimate knowledge of transition state energy and migration pathways. The transition state represents the highest point along the migration (or reaction) path curvature – the energy decreases along all directions except one, and this first-order saddle point is characterized by unique imaginary vibrational frequency. The search for transition state and minimum energy path between two stable configurations using density functional theory may appear counterintuitive considering its variational nature is designed to find the minimum energy configuration across multiple potential energy surfaces. The nudged elastic band (NEB) method employs a set of inter-connected images between the initial and final configurations that are selectively optimized towards the minimum energy path using density functional theory. (92)

The images $\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{n-1}\}$ are initially interpolated between the end configurations $\{\mathbf{r}_0, \mathbf{r}_n\}$ along a linear path.[Figure 2.1] Each image is connected to its adjacent image by an elastic band and the total arrangement is defined by the object function

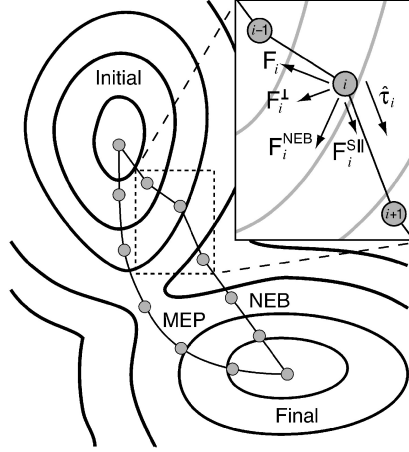


Figure 2.1: Transition state and minimum energy path optimization through the nudged elastic band (NEB) method. A linearly interpolated chain of images between the initial and final states is modified by the NEB force, $\mathbf{F}_{i,NEB} = \mathbf{F}_{i,true}^\perp + \mathbf{F}_{i,spring}^\parallel$ and approaches the minimum energy path. The force components acting on each image are shown in inset. Figure reprinted from (92) by permission of American Institute of Physics.

$$S(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{n-1}) = \sum_i E(\mathbf{r}_i) + \sum_i \frac{k}{2} (\mathbf{r}_i - \mathbf{r}_{i-1})^2$$

where $E(\mathbf{r}_i)$ and $\frac{k}{2}(\mathbf{r}_i - \mathbf{r}_{i-1})^2$ denote the internal and band (spring) energies respectively for the i^{th} image. The images are optimized to prevent (i) sliding of images towards either $\mathbf{r}_0$ or $\mathbf{r}_n$, and (ii) corner cutting which leads to deviation from transition state due to an excessive spring force. The NEB method provides a nudging force to ensure that images approach the minimum energy path. The resultant NEB force $\mathbf{F}_{i,NEB}$ comprises of a tangential component of the band force and a perpendicular component of the true force, where the tangent τ_i is defined along the path between adjacent images $\mathbf{r}_i$ and $\mathbf{r}_{i-1}$. The perpendicular component of the true force $\mathbf{F}_{i,true}^\perp$ acting on image i is,

$$\mathbf{F}_{i,true}^\perp = \mathbf{F}_{i,true} - \mathbf{F}_{i,true} \cdot \tau_i$$

and the tangential component of the spring force experienced by image i is,

$$\mathbf{F}_{i,spring}^{\parallel} = k(|\mathbf{r}_{i+1} - \mathbf{r}_i| - |\mathbf{r}_i - \mathbf{r}_{i-1}|) \cdot \tau_i \tau_i$$

Thus, the resultant NEB force acting independently on each image is

$$\mathbf{F}_{i,NEB} = \mathbf{F}_{i,true}^{\perp} + \mathbf{F}_{i,spring}^{\parallel}$$

and the NEB forces are minimized until the images converge to the minimum energy path or fall below the convergence criteria.

An improvement over the NEB method is achieved by forcing only the highest energy image to approach the saddle point using the climbing image NEB (CI-NEB) method. The spring forces are removed for this particular image and the perpendicular component of true force is inverted to push the image towards the saddle point.

$$\mathbf{F}_{i,CI-NEB} = \mathbf{F}_{i,true}^{\perp} - 2\mathbf{F}_{i,true}^{\perp} \cdot \tau_i \tau_i$$

The CI-NEB affects the spacing between images in the absence of spring forces. However, this leads to a better sampling of the transition state and the adjacent region.

CHAPTER 3

MICROSCOPIC MECHANISM OF VACANCY MIGRATION IN GRAPHENE

Kinetics of vacancy defect in graphene drives structural modifications leading to disorder, multi-vacancy complex and edge reconstruction. Within the first-principles calculations, we study the dynamic Jahn-Teller distortion and diffusion of a vacancy defect. Further, the intricate dependence of carrier doping is systematically investigated. The experimental observation of dynamic Jahn-Teller distortion is argued to be blocked by defect functionalization and charge doping. We demonstrate that lattice relaxation perpendicular to the graphene sheet along with the in-plane strain relaxation play predominant roles in predicting the correct microscopic mechanism for vacancy diffusion. The importance of quantum correction to the classical barrier is discussed. The calculated activation barrier increases upon both electron and hole doping and the observed trends are explained by the differential charge density distribution and hardening of the responsible low-energy phonon modes. Electron doping essentially freezes the vacancy motion, and thus any degradation mediated by it. While tracking and analyzing the vacancy diffusion experimentally in graphene is a difficult task, the present results will motivate new experimental efforts and assist interpretation of the results. The contents of this chapter have appeared in *Physical Review B* 98, 075439 (2018).

3.1 Introduction

Schottky lattice defects can significantly alter the physical, chemical and magnetic properties of graphene. (93–97) Lattice vacancies are thermodynamically created at a finite temperature, originate from non-equilibrium growth such as micro-mechanical cleavage, chemical vapor deposition, and growth on a substrate; and could also be generated by electron and ion irradiations. (95; 98–105) The single vacancy defect is the most important point defect, (94) and has been identified using aberration-corrected high-resolution transmission electron microscopy, (98; 106–109) and scanning tunneling microscopy. (103) While a single carbon atom is removed from the hexagonal graphene lattice, three dangling bonds are created on the adjacent atoms. This symmetric defect structure concurrently undergoes a spontaneous Jahn-Teller distortion to a symmetry-reduced 5–9 ring, where two of the neighboring atoms bond weakly leaving one unsaturated dangling bond. (100) Further, the Jahn-Teller distorted vacancy structure can easily switch between three equivalent orientations with a very small kinetic barrier, (110) however, which is debated experimentally. (108) With a σ contribution from the dangling bond, the π electron imbalance generates a semi-localized magnetic moment at the defect site according to the Lieb’s theorem for bipartite hexagonal lattice. (40; 42; 111; 112) This localized moment is also observed to undergo many-body Kondo screening due to the interaction with conducting electrons. (77; 113; 114)

The interaction between spatially scattered vacancy defects and their kinetics can drive structural modifications including the formation of disordered regions. (94) Migration of mono-vacancies and their eventual coalescence lead to multi-vacancy pores. (115; 116) A directional strain field can lead to the formation of line defects due to multiple vacancy mergers. (117) The biased vacancy migration toward the edge of a graphene flake alters the edge character at room

temperature and thus severely alter the electronic, magnetic and transport properties. (118–120) These defects act as strong scattering centers and disrupt the ballistic nature of electronic transport in graphene, and thus become crucial to device performance. (93; 94) As a result, the single vacancy diffusion acts as a microscopic unit process for the formation of higher order defect complexes. In this context, a profound understanding of the microscopic mechanism for vacancy propagation is necessary, especially at the device operating conditions.

While the vacancy diffusion in three-dimensional crystals is being studied for decades, the same for the two-dimensional materials are exceedingly difficult to track and interpret. The presence of a substrate, layer thickness, external perturbations, as well as the interaction with the experimental tracking device such as STM may play a significant role and the interpretation for the results become that much difficult. Thus, the experimental data on vacancy migration and simultaneous estimation of the barrier in graphene is absent. In contrast, vacancy diffusion on the graphite surface was studied by scanning tunneling microscopy. Using the measured vacancy jump frequency as a function of temperature, the activation energy of 0.9–1.0 eV was estimated assuming a pre-exponent factor of 10^{13} s^{-1} . (121) In the present context of vacancy diffusion on the single-layer graphene lattice, this estimated barrier on the basal plane of graphite should be treated as the upper bound, as we will argue below. In contrast, the vacancy defect has been studied within the first-principles calculations, though the microscopic diffusion mechanism is still debated. The theoretical activation energy for diffusion to the nearest lattice sites are estimated between 1.1–1.4 eV range. (122–126) The large inconsistency between the experimental activation barrier estimated from the diffusion data on the graphitic surface and the theoretical predictions on the single-layer graphene may arise due to the inappropriate consideration of strain relaxation during the vacancy migration, which eventually leads to the inaccurate transition

state.

Thus, thermally activated migration of point-defects causing degradation needs to be better understood, predicted and controlled. Here, we report a comprehensive study on the microscopic mechanism of vacancy diffusion. We elaborate the importance of strain relaxation during diffusion and the effects of the gate voltage in a device setup are investigated. We also investigate the dynamic Jahn-Teller distortion and discuss the impossibility of experimental observation due to defect functionalization by hydrogen and charge doping. The effect of applied gate voltage is studied through varied carrier doping within the experimentally realized carrier concentrations of $5 \times 10^{13} \text{ cm}^{-2}$. (127) We illustrate that both out-of-plane and in-plane strain relaxations are essential to predict the accurate mechanism and the corresponding activation barrier. The counterintuitive dependence of activation barrier on the gate voltage is explained through the low-energy phonon modes and differential charge density distribution. The quantum Wigner correction to the classical activation barrier at finite temperature is discussed. The present results suggest that vacancy migration will considerably slow down under both positive and negative gate voltage, and thus will decelerate the concurrent graphene degradation in a device setup.

3.2 Computational details

Calculations were carried out using the spin-polarized density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package. (128; 129) The ion core and the valence electrons were described within the projector augmented wave formalism, (130) and the wave-functions were expanded in the plane-wave basis with 500 eV cutoff for the kinetic energy. The exchange-correlation energy was computed using the Perdew-Burke-Ernzerhof (PBE) form of generalized gra-

dient approximation (GGA). (83) All the structures were allowed to fully relax until all the force components were less than $0.01 \text{ eV}/\text{\AA}$ threshold, where the Brillouin zone was sampled using a $2 \times 2 \times 1$ Monkhorst-Pack k -grid. (131) A finer $8 \times 8 \times 1$ k -grid was used to calculate the density of states (DOS). Calculations were carried out with a 10×5 supercell repeated with the rectangular $(\sqrt{3}, 3)a_0$ unit-cell, where a_0 is the nearest-neighbor distance between carbon atoms. Thus, this supercell consisted 200 carbon atoms without the vacancy, and all the results represent this supercell if not otherwise stated. We have also studied and analyzed our results with a smaller $6 \times 4 (\sqrt{3}, 3)a_0$ and a larger $13 \times 8 (\sqrt{3}, 3)a_0$ rectangular supercells consisting of 96 and 416 atoms respectively. A larger $4 \times 4 \times 1$ Monkhorst-Pack k -grid was used for the smaller $6 \times 4 (\sqrt{3}, 3)a_0$ supercell. The periodic images perpendicular to the graphene sheet were separated by $12 \text{ \AA}$ vacuum to cancel any spurious interactions. The phonon frequencies were calculated at the Γ -point for selected atoms around the vacancy using the density functional perturbation theory (DFPT). The effect of external gate voltage was simulated by varying the carrier (electron and hole) density. The microscopic mechanism for vacancy diffusion and the corresponding activation energy was determined using the climbing image nudged elastic band method (CI-NEB). (92) The minimum energy path was confirmed by the presence of a single imaginary frequency in the vibrational spectra for the transition state configuration.

3.3 Results and Discussion

We start our discussion with the thermodynamic stability of different vacancy structures and investigate the associated strain field. A monovacancy in graphene lattice is formed in the absence of a single C-atom during growth or under irradiation, and results in three dangling σ bonds. Subsequent relaxation of the under

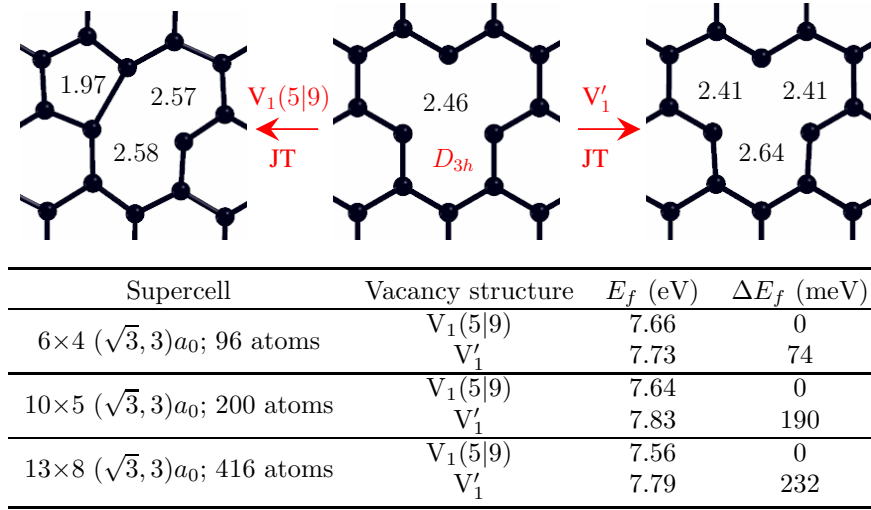


Figure 3.1: The symmetric D_{3h} vacancy undergoes different Jahn-Teller (JT) distortions to form distinct vacancy structures. The bond lengths for the two relaxed vacancies $V_1(5|9)$ and V'_1 are shown in Å. The variation in formation energy E_f and the difference ΔE_f between $V_1(5|9)$ and V'_1 is shown for different sized supercells.

coordinated atoms, which form an equilateral 2.46 Å vacancy structure, leads to different vacancy structures. There are two possible ways in which an equilateral triangle with D_{3h} symmetry could distort into isosceles C_{2v} triangle due to Jahn-Teller (JT) effect. In the JT distorted ground state, the two C-atoms form a weak σ bond while the dangling bond survives at the apical atom. The resultant vacancy structure thus consists of 5-9 ring structure $V_1(5|9)$, where the C-atoms at the pentagon are 1.97 Å apart and form an isosceles triangle with the apical atom that is 2.58 Å away. The other JT distorted metastable structure V'_1 has two shorter (2.41 Å) and one longer C–C distance. Different JT relaxation mechanisms and the respective formation energies are shown in the Figure 3.1 for varied supercell sizes. The formation energy E_f is calculated to be 7.64 eV, which is in agreement with the previous theoretical and experimental results. (108; 110; 132) Here, the E_f is calculated as $E_f = 1/n (E_{\text{vac}} - \frac{N-n}{N} E_{\text{pristine}})$, where n is the number of missing atom, and N is the total number of atoms in the supercell. The formation energy does not show a strong dependence on the supercell size. The other JT distorted

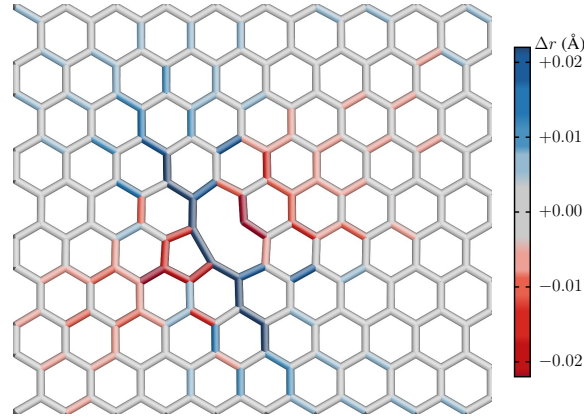


Figure 3.2: Defect induced strain field for $V_1(5|9)$ calculated as the difference in bond length Δr with defect free graphene lattice. Elongation and contraction of bonds are represented in blue and red colors, respectively. A significant strain field is localized in the proximity of the defect, while the amplitude decreases with distance from the defect and extends over 2 nm.

vacancy structure V'_1 is found to be metastable with ~ 0.2 eV higher energy.

In the context of vacancy diffusion, it is anticipated that the strain field generated in the graphene lattice due to the point-defect should play a critical role. Such strain field is predicted to be long-range in graphene and other carbon nanostructures. (119; 133–136) Further, complex defects such as dislocation in graphene generates substantial corrugation in addition to in-plane strain extended over several nanometers. (116; 137; 138) Moreover, it has been demonstrated earlier that defect-defect interaction could severely alter mechanical, electronic and physical properties of graphene. (136; 139) Thus, to study an individual vacancy, the defect-defect interaction which originates through long-range strain field must have an inappreciable effect.

We calculate the strain field produced in the lattice due to the $V_1(5|9)$ defect by calculating the difference in C–C bond distances in defect-free graphene without the defect (Fig. 3.2). The strain field in the vicinity of the point defect is evident and is extended over 2 nm as the amplitude decreases with the distance from the defect. Thus, a supercell extending over 2 nm is necessary to study an isolated point de-

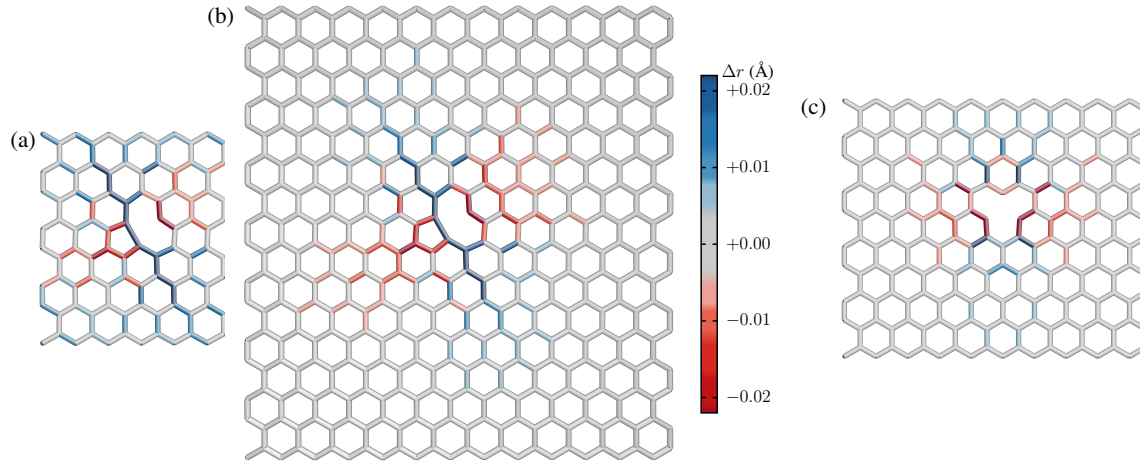


Figure 3.3: The defect induced strain field for $V_1(5|9)$ vacancy structure calculated with (a) $6 \times 4(\sqrt{3}, 3)a_0$ and (b) $13 \times 8(\sqrt{3}, 3)a_0$ supercells. (c) The same for the V'_1 vacancy structure calculated with a $10 \times 5(\sqrt{3}, 3)a_0$ supercell. The strain field is calculated as the difference in the bond length Δr with the defect-free lattice.

fect, and a rectangular $10 \times 5(\sqrt{3}, 3)a_0$ supercell is found to be sufficient. In this regard, a comparatively smaller 6×4 supercell is found to be insufficient due to finite strain field at the cell boundary, which will influence the isolated defect properties through interaction with the periodic image. In contrast, a larger $13 \times 8(\sqrt{3}, 3)a_0$ supercell is found to be redundant, which does not show any significant difference in the strain field while compared with the $10 \times 5(\sqrt{3}, 3)a_0$ supercell. (Fig. 3.3) In contrast to $V_1(5|9)$ defect, the strain field generated at the metastable V'_1 defect configuration is much localized. (Fig. 3.3) Such different strain fields generated by the two JT distorted defects are in good agreement with previous experimental observations. (108)

3.3.1 Rotational reconstruction dynamics of $V_1(5|9)$

There are three equivalent 120° rotated degenerate configurations for the $V_1(5|9)$ defect, which can be accessed by the dynamic JT reconstruction. The local stretching and concurrent reformation of a new pentagonal bond lead to these degenerate

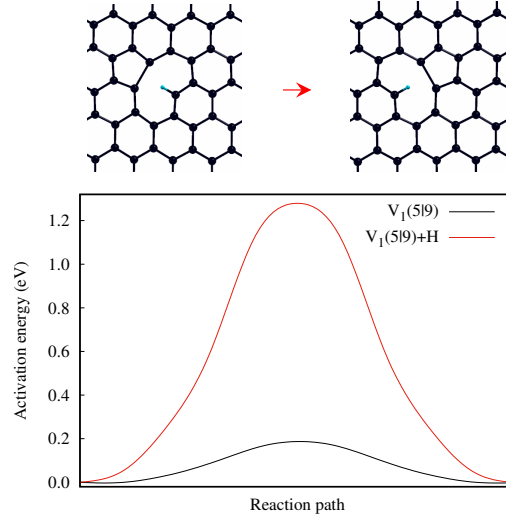


Figure 3.4: Calculated activation barrier for the dynamic JT distortion for the hydrogenated vacancy, $V_1(5|9)+H \rightarrow 120^\circ-V_1(5|9)+H$. The activation barrier is found to be much larger compared to the same for bare $V_1(5|9)$ vacancy.

configurations. Note that such reconstruction does not involve any mass diffusion, and the energy requirement for this bond reorientation mechanism is expected to be small. The barrier for this local swapping of the reconstructed bond is calculated to be 0.19 eV, with $V_1(5|9) \rightarrow V'_1 \rightarrow 120^\circ-V_1(5|9)$ as the mechanism. However, a wide range of barriers 0.13 – 0.78 eV have been reported earlier. (110; 126; 140; 141) The small energy cost indicates the $V_1(5|9)$ defect should undergo a continuous reconstruction at a moderate temperature. The cycle frequency for the dynamic reconstruction can be estimated $k \sim k_0 \exp(-\Delta E/k_B T)$, where $k_0 \sim 10^{13}$ Hz is the attempt frequency. Thus, the cycle frequency at 300 K is ~ 6 GHz, which considerably slows down at low temperature to ~ 4 Hz at 77 K. The corresponding time-scale is thus about 155 ps and 1 s, respectively, at these temperatures. However, these time-scales are much shorter compared to the experimental observations, which do not witness reconstruction for 150 s, (108) and would be interesting to address the discrepancy. One possibility could be that functionalization of the under-coordinated C-atom blocks the dynamic reconstruction. The other

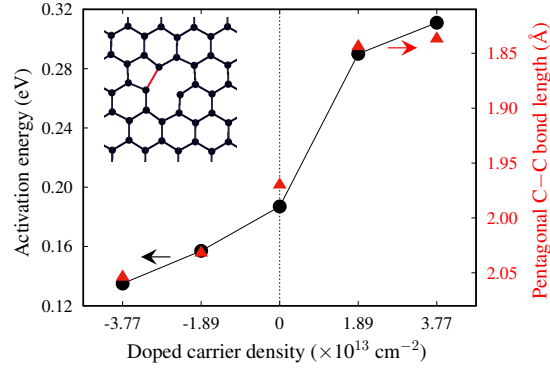


Figure 3.5: The activation energy for the dynamic JT reconstruction, $V_1(5|9) \rightarrow V'_1 \rightarrow 120^\circ\text{-}V_1(5|9)$, is strongly affected by carrier doping in the graphene lattice. The overall trend can be explained by the corresponding change in the pentagonal C–C bond (shown in inset) due to charge doping leading to strengthening or weakening of C–C bond upon electron and hole doping, respectively.

possibility is the charge transfer between the dielectric TEM grid and graphene, which could essentially hinder the dynamic reconstruction of the $V_1(5|9)$ defect. It is known that charge is transferred to graphene from the dielectric Si_3N_4 TEM grid as is used in the experiments. (108; 142)

Once a carbon atom is removed from the graphene lattice, the time-scale for D_{3h} to JT reconstruction is much shorter than the typical H diffusion on the graphene sheet. (143; 144) Thus, the $V_1(5|9)+\text{H}$ is the ubiquitous defect complex and survives at high temperatures even beyond 600 K. (145; 146) The earlier muon spin-resonance spectroscopy also indicates the presence of singly hydrogenated vacancies. (147) We, therefore, investigate the dynamic JT reconstruction in the presence of H. The H functionalization decreases the pentagonal C–C bond to 1.92 Å, and strongly influences the breaking and subsequent reformation of this bond. Therefore, the calculated activation energy for the dynamic JT distortion for the hydrogenated vacancy, $V_1(5|9)+\text{H} \rightarrow 120^\circ\text{-}V_1(5|9)+\text{H}$, is calculated to be much larger to 1.28 eV. (Fig. 3.4)

Now we study the effect of carrier doping on the dynamic JT reconstruction.

With the addition of electrons (holes) to the graphene lattice, the energy requirement for the dynamic JT reconstruction increases (decreases) as shown in Fig. 3.5. The doped carrier is semilocalized at the defect site as observed from the differential charge density [discussed later in (Fig. 3.11)], and strongly affects the pentagonal C–C bond. The overall trend in activation barrier can be explained by the change in pentagonal C–C bond in $V_1(5|9)$, which is reduced under electron doping, and conversely increased while doped with holes (Fig. 3.5). Thus, compared to the neutral $V_1(5|9)$ defect, strengthening (weakening) of the pentagonal C–C bond due to electron (hole) doping results in higher (lower) energy requirement for the local swapping of the reconstructed bond. The electron doped case is more relevant in the context of dynamic JT reconstruction than the hole doped situation as the charge is transferred from the TEM grid to graphene. However, one could still discuss the effect of hole doping where the barrier reduces to 0.16 eV for $1.89 \times 10^{13} \text{ cm}^{-2}$ density that corresponds to a time-scale of 10^{-3} s at 77 K.

The increased energy requirement due to H functionalization and electron doping has significant implications on the impossibility of experimental observation of dynamic JT reconstruction to date. With 1.28 eV activation barrier, the H functionalization essentially restricts the dynamic JT reconstruction process. In contrast, the energy cost for local reconstruction increases to 0.29 eV for $1.89 \times 10^{13} \text{ cm}^{-2}$ electron doping with a reconstruction time-scale of about 10^6 s at 77 K. Therefore, even though the dynamic JT reconstruction is possible, the vacancy functionalization or the charge doping in experimental situations may essentially lock the $V_1(5|9)$ defect structure, and hinder experimental observation of dynamic reconstruction.

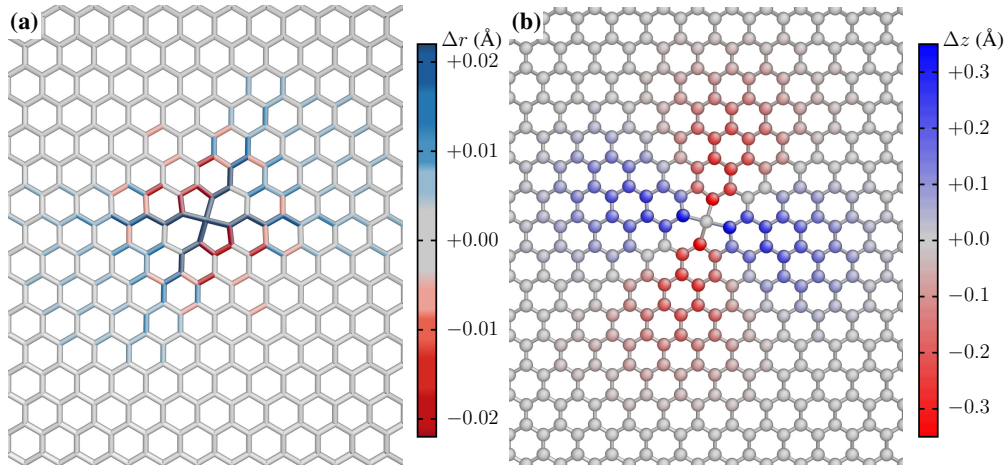


Figure 3.6: The complex in-plane and out-of-plane lattice relaxation at the transition state minimizes the activation barrier as shown for the $13 \times 8(\sqrt{3}, 3)a_0$ supercell. (a) Elongation and contraction of bonds around the moving atom are shown in blue and red colors, respectively. (b) The atoms around the moving C-atom are symmetrically displaced up (blue) and down (red) perpendicular to the graphene plane. The displacement field is extended over 2 nm.

3.3.2 Vacancy migration and complex lattice relaxation

Now we investigate the diffusion kinetics of an isolated $V_1(5|9)$ vacancy defect in graphene lattice, and the importance of intricate out-of-plane and in-plane lattice relaxation. The diffusion of planar $V_1(5|9)$ defect is predominantly dictated by the motion of a single undercoordinated C-atom. However, the concurrent response of surrounding graphene lattice is quite complex and intriguing. The activation energy E_v^a on the minimum energy path is calculated to be 0.72 eV. The corresponding first-order transition state is found to have a corrugated structure with complex in-plane and out-of-plane lattice relaxations. The migrating C-atom at the transition-state is bonded with four neighboring atoms resulting in sp^3 -like hybridization and long-range strain field [Figure 3.6(a)]. At the transition state, the atoms around the four-fold coordinated C-atom are symmetrically displaced up and down compared to the defected graphene plane. The out-of-plane displacement is found to be as large as $\Delta z = \pm 0.34$ Å for the C-atoms that are connected to the migrating

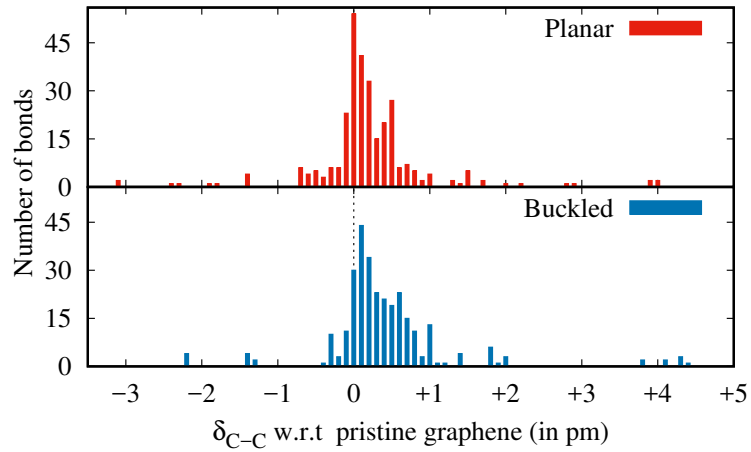


Figure 3.7: Distribution of C–C bonds for the (a) planar and (b) buckled transition states are shown for the $10 \times 5(\sqrt{3}, 3)a_0$ supercell. The difference in bond length is calculated with respect to the defect-free graphene. The out-of-plane lattice relaxation is important for minimizing the lattice strain generated during migration.

atom, and the displacement field is extended over 2 nm [Figure 3.6(b)]. Such complex lattice relaxations during vacancy migration minimizes the activation barrier. To further elucidate the mechanism and the differential dependence of such complex geometrical relaxation on the activation barrier, we investigate the transition state in further detail. First, we quantify the role of lattice relaxation perpendicular to the lattice by restricting the out-of-plane relaxation while allowing the in-plane relaxation. The planar migration path cannot relieve the residual strain, and thus the corresponding TS is much higher in energy. The calculated E_v^a is found to be 89% higher to 1.36 eV as compared to 0.72 eV, while lattice relaxation in all directions is allowed. A comparison of C–C bond distances for the transition state geometries of the planar and non-planar migration paths show that the strain relaxation in the case of unrestricted migration is easier through out-of-plane lattice relaxation.[Figure 3.7]

Next, we investigate the effect of in-plane relaxation through varied supercell size while the relaxation is without any constraints. As we have discussed earlier

that the long-range in-plane strain field could lead to spurious vacancy-vacancy interaction, a smaller $6 \times 4(\sqrt{3}, 3)a_0$ supercell causes the E_v^a to be 23% larger to 0.89 eV. In contrast, the E_v^a does not change for larger $13 \times 8(\sqrt{3}, 3)a_0$ supercell compared to $10 \times 5(\sqrt{3}, 3)a_0$. Thus, we conclude that the lattice relaxation perpendicular to the graphene sheet and the in-plane relaxation are extremely important, and the former substantially decrease E_v^a through the corrugation of TS.

We discuss the present results in the light of earlier theoretical and limited experimental results. In contrast to the present results, earlier first-principles calculations predicted a much higher activation barrier, in the range of 1.1–1.4 eV. (122–126) Having discussed the importance of strain relaxations, we argue this large discrepancy to originate mainly from the improper consideration of out-of-plane and in-plane lattice relaxation during the diffusion (Figure 3.2 and Figure 3.6). In a recent calculation, the barrier was calculated to be 0.87 eV within a similar theoretical hierarchy, (140) which is still much higher than the present classical barrier of 0.72 eV. This difference is due to the spurious vacancy-vacancy interaction owing to a much smaller supercell that was considered in the earlier calculation.

Moreover, a quantitative experimental data on the vacancy diffusion is still absent. While a $V_1(5|9)$ vacancy has been observed to move within an experimental time-scale of few hundred seconds, (108; 110) the prediction of diffusivity or activation barrier is difficult due to the lack of information about local temperature under TEM, and vacancy jump-rate as a function of temperature. However, we consider the vacancy diffusion on graphite surface that was studied through STM and discuss it in the context of present results on the vacancy diffusion in single-layer graphene. Using the experimental jump-rate and assuming a pre-exponent factor of 10^{13} Hz, the experimental activation energy was estimated to be 0.9–1.0 eV. (121) Based on the present results, we propose this barrier to be treated as the upper bound for vacancy migration in single-layer graphene. We have already demon-

strated that any restriction to the out-of-plane lattice relaxation during diffusion increases the barrier. Thus, as the complete out-of-plane relaxation is hindered on the basal plane of graphite, the measured activation barrier was expectedly higher than the same for single-layer graphene.

The present results also infer that in case of a subsurface vacancy in bulk graphite, the migration barrier is expected to be similar to the planar migration barrier of 1.36 eV as the out-of-plane lattice relaxation may be completely blocked. This claim is corroborated by the drop in vacancy kinetics that is observed through TEM for a vacancy in the middle layer of a trilayer graphene. (109) Similarly, a migration barrier of 1.8 ± 0.3 eV was attributed to the vacancy diffusion in irradiated graphite. (148) For bilayer graphene, a partial out-of-plane relaxation is still possible and the corresponding migration energies should have an intermediate value to graphite and single-layer graphene, closer to the vacancy in the basal plane of graphite. (109; 121; 149; 150)

In addition to the mechanism discussed above, a very different diffusion mechanism, migration by one zigzag lattice plane, was experimentally suggested by analyzing the TEM images. (108) In our calculation, such migration results in a very high migration barrier ~ 3.5 eV and thus unlikely to occur. In contrast, we argue that this new mechanism may be a combination of $V_1(5|9)$ rotation and migration that is discussed above. Further, there could be another possibility. In this experiment, the studied vacancy was separated approximately by 1 nm from a larger and more complex defect structure. Thus, the vacancy in question was under the influence of strain field generated by this complex defect and thus interacting strongly with it. In such a situation, the vacancy may migrate very differently, and the corresponding mechanism should not be considered as the case for an isolated one. Comparing with the other 2D materials such as hexagonal boron nitride, silicene, and phosphorene, (151–153) we conclude that the microscopic mechanism

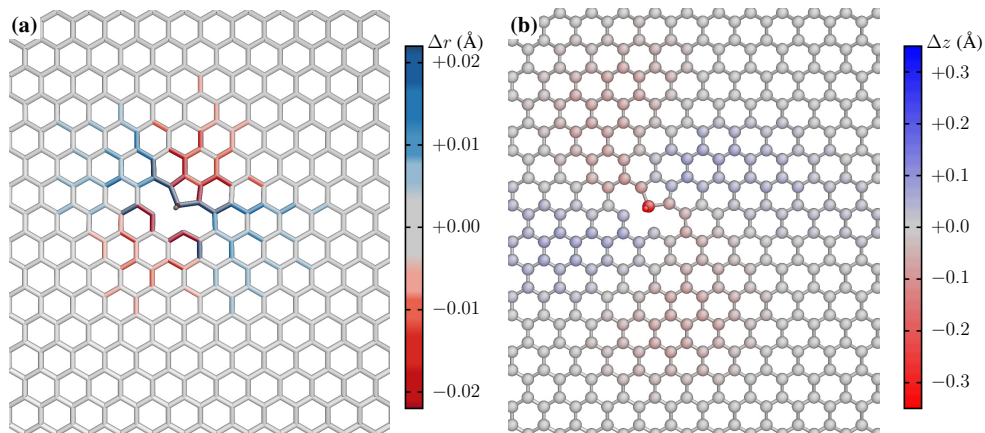


Figure 3.8: The in-plane (a) and out-of-plane (b) lattice relaxation at the transition state for the hydrogenated vacancy as shown for the $13 \times 8(\sqrt{3}, 3)a_0$ supercell. The transition state structure is completely different from the bare vacancy. The in-plane lattice deformation is much localized, and the out-of-plane relaxation is much smaller. The maximum Δz is found to be $0.09 \text{ \AA}$, compared to $0.34 \text{ \AA}$ for the bare vacancy case.

of vacancy diffusion in graphene is fundamentally different due to strong covalent bonding resulting in very different strain relaxation during migration.

Hydrogen functionalization changes the scenario completely and the concurrent migration barrier is increased to 2.3 eV . A closer investigation reveals that the respective transition state structure to be very different than that for the bare vacancy, where the migrating C-atom forms sp^3 -like bonds (Figure 3.6). The transition state, in this case, has an asymmetric structure and does not form such sp^3 -like bonds resulting in higher energy TS structure. (Figure 3.8) Further, while the transition state is compared with the same for the bare vacancy, the in-plane lattice relaxation is found to be much localized and the out-plane relaxation to be much smaller. All these put together increase the migration barrier for the functionalized vacancy.

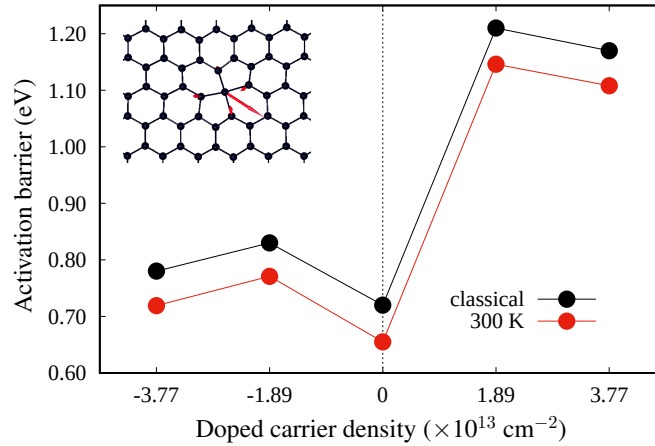


Figure 3.9: Calculated activation barrier for vacancy migration in graphene lattice, and its dependence on carrier doping. The increase in the activation barrier is much higher in case of electron doping than the corresponding hole doping. The qualitative trends with different electron and hole doping can be explained by responsible phonon modes for vacancy migration and differential charge density. At finite temperature, the classical barrier is corrected by Wigner quantum correction and shown for 300 K. Inset shows the eigenvector for the unstable phonon mode ($324i \text{ cm}^{-1}$ for the neutral case) at the TS which is a superposition of both in-plane and out-of-plane lattice vibrations.

3.3.3 Effect of carrier doping on vacancy diffusion

We investigate the effect of carrier doping that can be manipulated through applied gate voltage. Here we remain within the experimentally achieved limit of carrier doping $\sim 10^{13} \text{ cm}^{-2}$. (127) Though the pentagonal C–C bond of $V_1(5|9)$ is contracted or elongated upon electron or hole doping respectively, the nature of strain field remains unaffected with extra carriers and the overall migration mechanism remains the same. However, charge doping strongly affects the activation barrier and we observe a few critical trends (Fig. 3.9). (i) The E_v^a increases with both electron and hole doping, which appears to be counter-intuitive and cannot be explained by the simple change in the local pentagonal C–C bond. (ii) While electron doping substantially affects the E_v^a , hole doping has a comparatively lesser effect. (iii) The qualitative trend in E_v^a is non-monotonous and asymmetric for electron

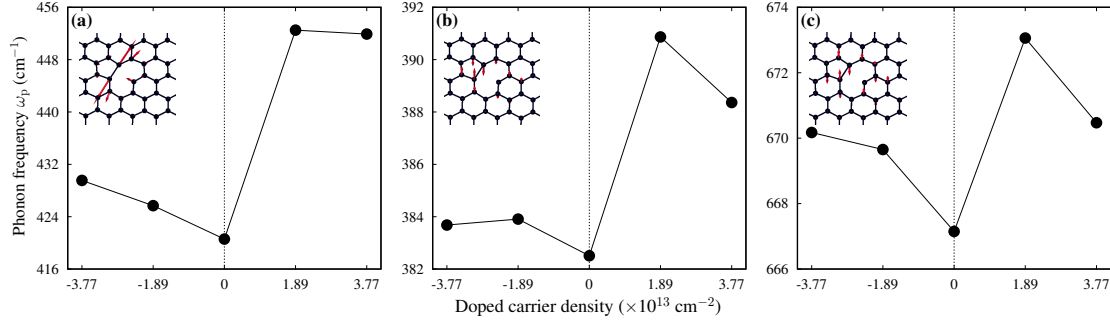


Figure 3.10: Frequency evolution of the defect induced (a) in-plane and (b, c) out-of-plane phonon modes for the $V_1(5|9)$ vacancy as a function of carrier doping. The corresponding eigenvectors are shown in the inset. The phonon modes shift to higher frequencies with carrier doping, and the effect of electron doping is stronger. Hardening of these phonon modes result in a commensurate increase in the corresponding activation barrier for a particular carrier type and concentration; and further explains the observed trends in activation barrier with varying density (Figure 3.9).

and hole doping. Electron doping substantially increases the E_v^a as much as by 68% to 1.21 eV for $1.89 \times 10^{13} \text{ cm}^{-2}$ density. Further electron doping does not alter the E_v^a , which is calculated to be 1.17 eV for $3.77 \times 10^{13} \text{ cm}^{-2}$ carrier density. Similarly, the E_v^a also increases due to the hole doping, however, the increase is only moderate in contrast to the electron doping. The E_v^a increases to 0.83 eV for $1.89 \times 10^{13} \text{ cm}^{-2}$ hole density, which changes to 0.78 eV while the doping is doubled.

To explain these qualitative trends in E_v^a with carrier doping, we systematically investigate the structural, electronic and phononic properties. The local bonding picture fails to render a comprehensive understanding of these observed trends, as the vacancy migration is a complex and collective motion of many atoms enclosing the vacancy center. Thus, we search for the low-energy phonon modes that are responsible for the vacancy migration and investigate how the frequencies of these modes change with carrier doping. We identify three defect-induced low-energy phonon modes with frequencies ranging from 380 to 675 cm^{-1} (Fig. 3.10). The eigenvector for the in-plane phonon mode explicitly indicates the character-

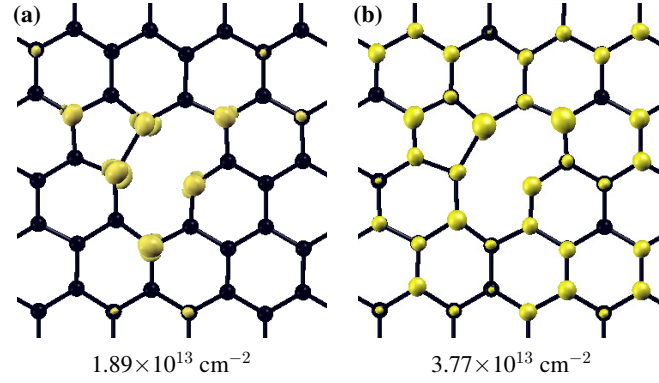


Figure 3.11: The differential charge density $\Delta\rho(r)$ calculated between the neutral and the charge doped graphene, and shown for different electron doping. (a) The doped electron is semi-localized at the $V_1(5|9)$ vacancy till $1.89 \times 10^{13} \text{ cm}^{-2}$, and (b) beyond which the charge is mostly distributed over the bulk π -state. While the π -states are located near the Fermi level, the σ -states are located much deeper in energy. Thus, only the π -states are affected due to charge doping designating p_z character of the differential charge density, and is localized on the atoms. This picture qualitatively explains the trends in phonon frequency with increasing electron doping and concurrent variation in activation barrier.

istic signature of vacancy migration [Fig. 3.10(a)]. The undercoordinated atom moves toward the pentagonal ring and the atoms on the pentagonal edge move apart simultaneously to accommodate it and form a hexagon. The two out-of-plane phonon modes [Fig. 3.10(b) and (c)] imply the necessary lattice relaxation perpendicular to the graphene sheet during vacancy migration, which we have substantiated in the previous discussions.

We notice the frequencies ω_p of these phonon modes increase with carrier doping (Fig. 3.10). Similar phonon hardening was observed experimentally for the C–C stretching G-mode due to both electron and hole doping realized by varied applied gate voltage. (127) Moreover, in the present case, the calculated ω_p show similar qualitative trends with varied carrier density as observed for the E_v^a (Fig. 3.9). The increase in ω_p is much higher for electron doping compared to hole doping, and a further increase in carrier concentration beyond $1.89 \times 10^{13} \text{ cm}^{-2}$ does not change ω_p much. Thus, hardening of these phonon modes for both elec-

tron and hole doping leads to a commensurate increase in the calculated E_v^a , and explains the qualitative trends.

The charge density distribution of the doped carrier could also qualitatively explain the trend in E_v^a as a function of carrier concentration. Vacancy defect in graphene lattice generates semi-localized π and σ states, namely V_π and V_σ , respectively. (40; 42; 103; 111; 154) Investigating the density of states, we observe that the Dirac point shifts by +310 meV compared to the Fermi level for the defected graphene with a vacancy. Thus, graphene with single vacancy defect refers to an intrinsically hole doped system with one hole. Further, the spin-split V_π states prevail in the vicinity of Fermi level. (42; 154)

In regard to this, we calculate the differential charge density $\Delta\rho(r)$ between the neutral and charge doped graphene with a single vacancy defect. The $\Delta\rho(r)$ determines the distribution of doped carriers, which is shown for electron doping in Fig. 3.11. While the lattice is doped with an electron, which corresponds to $1.89 \times 10^{13} \text{ cm}^{-2}$ density [Fig. 3.11(a)], the doped electron is semi-localized at the $V_1(5|9)$ vacancy. Moreover, the defect induced V_π state is populated, and the Fermi level coincides with the Dirac point. Thus, the semi-localized doped electron charge density distributed around the vacancy center in V_π state affects the low-energy phonon modes (Fig. 3.10) that are responsible for vacancy diffusion. However, upon further increase in the electron doping beyond $1.89 \times 10^{13} \text{ cm}^{-2}$, the charge is mostly distributed over the bulk π -state [Fig. 3.11(b)], and thus does not alter the responsible phonon modes further. This picture qualitatively explains the trends in E_v^a with increasing electron density (Fig. 3.9). Likewise, the trend in E_v^a with increasing hole doping could be qualitatively explained.

Table 3.1: Crossover temperature for quantum tunnelling in vacancy migration calculated for different doping level.

Doping level (cm^{-2})	ν^* (cm^{-1})	T^* (K)
$3.77 \times 10^{13} e$	376.44	86.20
$1.89 \times 10^{13} e$	361.68	82.82
Neutral	323.83	74.15
$1.89 \times 10^{13} h$	312.79	71.62
$3.77 \times 10^{13} h$	309.39	70.84

3.3.4 Quantum correction to the activation barrier and diffusivity

We next calculate the diffusivity of neutral and doped vacancy using both classical and quantum mechanical corrected transition state theory. The jump rate for vacancy diffusion in the classical transition state theory, where the vibrational modes are calculated within the harmonic approximation, is written as, (155)

$$\Gamma_c^{\text{hTST}} = \frac{\prod_i \nu_i^{\text{I}}}{\prod_i \nu_i^{\text{TS}}} e^{-E_v^a/k_B T},$$

where ν_i^{I} and ν_i^{TS} are the frequencies of harmonic vibrational modes at the initial and saddle point, respectively.

While the calculated activation barrier is valid at the high-temperature limit, the zero-point energy correction to the classical barrier should be invoked at very low temperatures, which can be written as,

$$\delta E_{v,\text{zpe}}^a = \sum_i \frac{\hbar \nu_i^{\text{TS}}}{2} - \sum_i \frac{\hbar \nu_i^{\text{I}}}{2}.$$

At any intermediate temperature, the Wigner correction and quantum tunneling should be considered. Below a critical temperature, $T^* = \hbar \nu^*/2\pi k_B$, the quantum tunneling becomes important. Here, ν^* is the magnitude of the imaginary

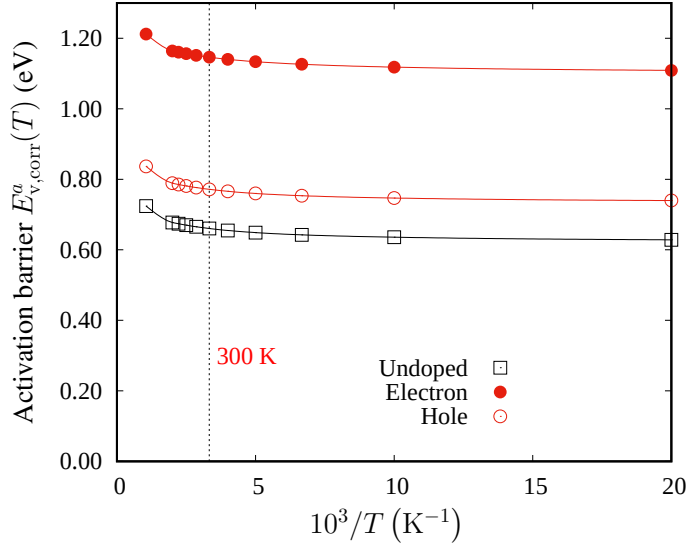


Figure 3.12: Quantum mechanical Wigner correction to the classical activation barrier for the $V_1(5|9)$ vacancy, $E_{v,corr}^a(T) = E_v^a - \delta E_{v,wig}(T)$ shown for the neutral and doped cases with $1.89 \times 10^{13} \text{ cm}^{-2}$ density. $E_{v,corr}^a(T)$ converges to the classical barrier E_v^a at a high temperature, while at very low temperature, the zero-point energy correction is sufficient. The quantum tunnelling correction is not included above 100 K.

frequency for the unstable phonon mode at the TS. Note that ν^* monotonically decreases with decreasing number of electrons as shown in (Table 3.1) This trend can be qualitatively explained as the variation in energy along the reaction path becomes slower with decreasing number of electrons. (156) For the neutral case, ν^* is found to be $\sim 324 \text{ cm}^{-1}$, which correspond to $T^* \sim 75 \text{ K}$. The calculated T^* monotonically changes with carrier doping and ranges between 70-86 K. Above this temperature, the Wigner correction is sufficient and the effective barrier converges to the classical value at a very high temperature.

The Wigner correction is given by, (157; 158)

$$\delta E_{v,wig}^a = -k_B T \ln \left[\frac{\prod_i \sinh(x_i^I)/x_i^I}{\prod_i \sinh(x_i^{TS})/x_i^{TS}} \right],$$

where $x_i = \hbar \nu_i / 2k_B T$ denotes the ratio of zero-point energy to the thermal energy

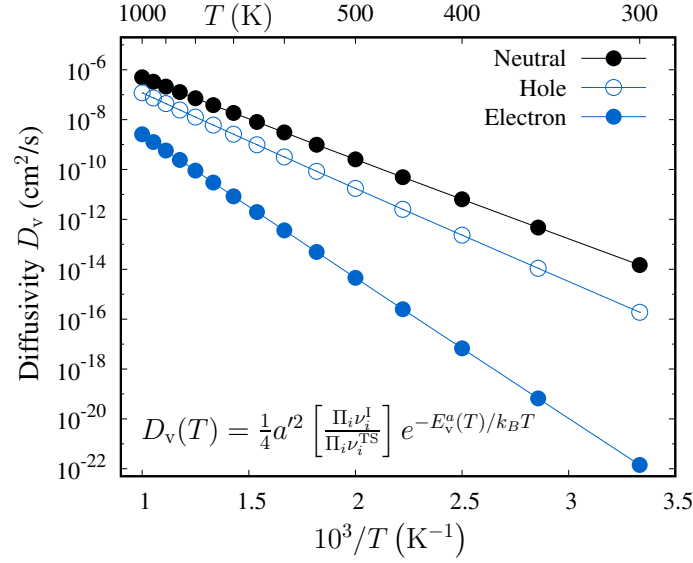


Figure 3.13: Diffusivity D_v calculated with Wigner corrected activation barrier $E_v^a(T)$ for neutral and carrier doped cases with $1.89 \times 10^{13} \text{ cm}^{-2}$ density. The diffusivity is substantially lower for both electron and hole doping.

for each vibrational mode. Thus, the corrected activation barrier $E_{v,\text{corr}}^a(T) = E_v^a + \delta E_{v,\text{wig}}^a(T)$, changes with temperature while the Wigner correction is incorporated (Figure 3.12). At room temperature 300 K, the $\delta E_{v,\text{wig}}^a$ is estimated to be about 70 meV. For example, the activation barrier for neutral vacancy decreases to 0.65 eV at 300 K compared to the classical barrier of 0.72 eV.

Using $E_{v,\text{corr}}^a$ we estimate the diffusivity D_v for temperatures $T > 300$ K (Figure 3.13), at which the quantum tunneling is not important. In two-dimension, D_v is given as, $D_v = \frac{1}{4}a'^2\Gamma$, where a' is the jump distance 1.84 Å and Γ is the jump rate. Due to the quantum Wigner correction, the D_v becomes one order of magnitude higher to $1.47 \times 10^{-14} \text{ cm}^2/\text{s}$ at 300 K than the classical diffusivity of $1.25 \times 10^{-15} \text{ cm}^2/\text{s}$ (Figure 3.14).

Carrier doping considerably slows down the vacancy diffusion through a significant increase in the corresponding activation barrier (Fig. 3.13). The corresponding D_v decreases by a factor of $\exp(\Delta E_v^a/k_B T)$ where ΔE_v^a is the increase in activation barrier under carrier doping. For $1.89 \times 10^{13} \text{ cm}^{-2}$ electron doping,

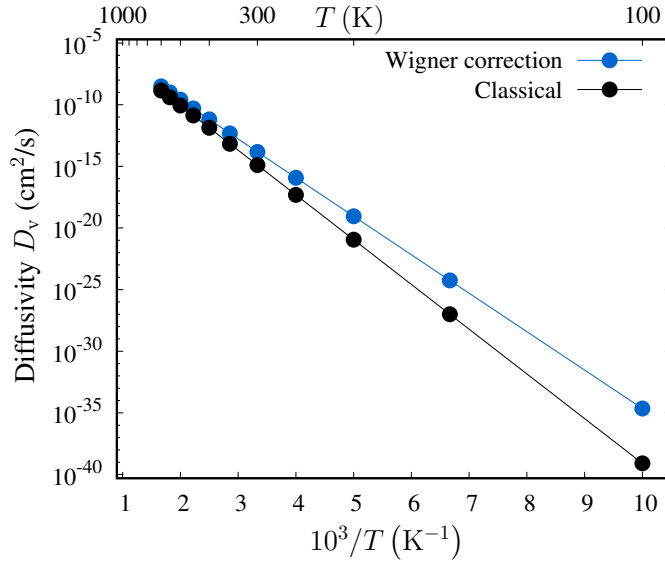


Figure 3.14: Diffusivity calculated using the Wigner corrected barrier for $T > 100$ K and compared with the diffusivity calculated with the classical barrier. At $T = 300$ K, the Wigner corrected diffusivity is one order of magnitude higher than the classical one.

the diffusivity is 10^8 times smaller than the undoped case at 300 K (Figure 3.13). In contrast, hole doping lowers the calculated D_v by two-orders of magnitude at the same density and temperature. Thus, while D_v decreases for both electron and hole doping, the dramatic drop in diffusivity under electron doping will effectively freeze the vacancy and restrict diffusion.

3.4 Summary

We investigate the dynamic Jahn-Teller distortion of vacancy defect and concomitant diffusion mechanism from the first-principles calculations. The discrepancy between the present results on the dynamic Jahn-Teller distortion and the experimental observations is explained by the possible defect functionalization and charge transfer between the graphene sheet and the dielectric TEM grid. These can hinder the observation of dynamic Jahn-Teller distortion within the experimental time-

scale. We illustrate that the lattice relaxation perpendicular to the graphene sheet, as well as the in-plane relaxation, are remarkably important to predict the diffusion mechanism accurately. While the Wigner correction to the classical barrier is important to consider, the quantum tunneling can be ignored above 100 K. Influence of the applied gate voltage on the vacancy diffusion has been systematically investigated through carrier doping. The substantial increase in the activation barrier under different electron and hole doping is explained through the hardening of low-energy phonon modes that are responsible for vacancy diffusion. The qualitative trends in the activation barrier are further explained by the differential charge distribution of the doped carrier. The substantial decrease in diffusivity under carrier doping will necessarily pin the vacancy, and any degradation that is mediated by vacancy diffusion will be severely slowed down under applied gate voltage.

Experimental investigation of vacancy diffusion in two-dimension is a challenging task and the consistent interpretation of the results are very complicated. Unintentional defect functionalization and substrate effects will alter lattice relaxation and may introduce charge doping, which will essentially play a significant role. Thus, at present, the experimental attempt to quantify vacancy diffusion in graphene remains scarce. We hope the present study will motivate further experimental efforts and help interpret the results.

CHAPTER 4

FERROMAGNETISM IN NITROGEN DOPED GRAPHENE

Inducing a robust long-range magnetic order in diamagnetic graphene remains a challenge. While nitrogen-doped graphene is reported to be a promising candidate, the corresponding exchange mechanism remains unclear and is essential to tune further and manipulate magnetism. Within the first-principles calculations, we systematically investigate the local moment formation and the concurrent interaction between various defect complexes. The importance of adatom diffusion on the differential defect abundance is discussed. The individual nitrogen complexes that contribute toward itinerant and local magnetic moment are identified. The magnetic interaction between the complexes is found to depend on the concentration, complex type, sublattice, distance, and orientation. We propose that the direct exchange mechanism between the delocalized magnetic moment originating from the itinerant π -electron at the prevalent graphitic complexes to be responsible for the observed ferromagnetism. We show that B co-doping further improves ferromagnetism. Present results will assist in the microscopic understanding of the current experimental results and motivate experiments to produce robust magnetism following the proposed synthesis strategy. This work has appeared in *Physical Review B* 99, 115442 (2019).

4.1 Introduction

The absence of intrinsic magnetism in graphene limits its application in spintronics and is being actively persuaded since it was first isolated. (1; 159) However, magnetism can be induced in graphene due to the p_z electron imbalance in bipartite hexagonal sublattice, (39; 41; 160) electron localization at the zigzag edge, (161–167) interaction with a spin-orbit coupled ferromagnetic substrate, (168–170) structural defect creation, (37; 42; 43; 103; 111; 154; 171), molecule adsorption, (172; 173) and heteroatom doping. (44; 49) However, a long-range magnetic order in graphene can only emerge through the exchange coupling between these induced local moments.

Hydrogen absorption on graphene creates an imbalance in p_z electrons between the two sublattices, which in turn generates a net magnetic moment. (39) Further, the spin-polarized state is observed to extend over several nanometers through the scanning tunneling microscopy (STM) experiment. This spatially extended magnetic state provides a channel for direct coupling between the induced magnetic moments at large distances. The half-filled flat band at the Fermi level produces localized magnetic moments at the zigzag edge of a graphene flake, (161) and a long-range order has been predicted. (162–167) However, the edge magnetism is predicted to be very intricate as it is strongly affected by the shape and size of the flakes, charge doping, chemical functionalization at the edge, and on-site Coulomb interaction. (164; 166) Proximity-induced exchange-coupled ferromagnetic order sets in graphene sheet at room temperature while placed on an atomically flat ferromagnetic thin film insulator. (168–170) The smallest structural defect, a lattice vacancy in graphene generates a semi-localized magnetic moment due to the π electron imbalance in addition to a σ contribution from the dangling bond. (37; 42; 103; 111; 154) Thus, proton irradiated graphene and graphene

with a network of point defects show magnetic ordering. (43; 171) Similarly, the larger lattice defects such as grain boundaries with dangling bonds are theoretically predicted to have magnetic moment. (174) However, the experimental evidence of a magnetic ordering remains scarce and controversial. (32; 43; 111; 175–177) While a room temperature ferromagnetism is predicted, (43; 175; 176) defected graphene with vacancies and other sp^3 defects lead to paramagnetism and devoid of any magnetic ordering down to low temperature. (32; 111; 177) Furthermore, in the cases where ferromagnetic signals have been detected, the origin of such long-range ordering remained unexplained. The presence of d -electrons in transition-metal impurities induces a local moment in pristine and defected graphene. (44; 178) However, only a paramagnetic ordering has been observed in this transition-metal doped graphene samples that were investigated through the X-ray magnetic circular dichroism measurement. (45)

In contrast, the substitutional and sp^3 impurities have attracted much attention with intriguing but elusive magnetic properties. The itinerant sp -electron Stoner ferromagnetism in a narrow impurity band is fundamentally different from the magnetism induced by the d -band of transition metals, where the large spin stiffness of sp -electrons ferromagnetism may lead to a higher Curie temperature. (179) The adatom impurities like hydrogen and fluorine exhibit strong absorption and induce magnetic moments (41; 160; 180; 181) due to sublattice imbalance in π -electrons following Lieb's theorem. (33) While the hydrogenated graphene show magnetic order at 5 K, (39) the fluorine doped graphene reveals paramagnetic behaviour. (37; 43) In this context, the substitutional N-doped graphene attracted much attention, which exhibits robust ferromagnetism. (49–52; 182; 183) However, the corresponding Curie temperature and saturation magnetization are reported to show a strong dependence on the growth, annealing strategies, and nitrogen concentration, which hinder a careful microscopic analysis. A variety of nitrogen com-

plexes are generated during the non-equilibrium synthesis, while N-concentration and the type of defect complex determines the electronic and transport properties. (47–52; 182–190) Recently, room-temperature ferromagnetism was reported in boron and nitrogen-doped turbostratic carbon films grown via pulsed laser deposition technique where the saturation magnetization is observed to increase with increasing N-doping. (191) However, even with such efforts, the nature and microscopic mechanism of magnetic interaction are not well understood in N-doped graphene, which is necessary to tune and manipulate magnetism toward its successful applications.

Within the first-principles calculations, here we systematically investigate the electronic and magnetic properties of various N-defect complexes in graphene. Further, how these defects interact with each other and lattice vacancies is studied to understand the mechanism responsible for the observed ferromagnetism. We report that the long-range magnetic interactions show a strong dependence on the N-concentration, complex type and on which sublattice they reside, distance, and orientation. We observe that the magnetism in the graphitic and vacancy containing N-complexes are fundamentally very different, and propose that the observed ferromagnetic order originates from the direct exchange between the extended magnetic states of the graphitic defects. Further, we investigate the crucial role of boron co-doping in the ferromagnetism.

4.2 Computational details

The spin-polarized density functional theory based calculations (128; 129) were performed within the projector augmented wave formalism, (130), and the wave functions were expanded in a plane-wave basis with 600 eV kinetic energy cut-off. The exchange-correlation energy was described using the conventional Perdew-

Burke-Ernzerhof (PBE) form for the generalized gradient approximation (GGA). (83) The structures were fully relaxed until all the forces became smaller than the 0.015 eV/Å threshold using the PBE functional. The Brillouin zone was sampled using a Γ -centered $8 \times 6 \times 1$ k -grid for the structural optimization, and a denser Γ -centered $24 \times 18 \times 1$ k -grid was used for the evaluation of density of states (DOS) and magnetization density. The subsequent N-doping was carried with the $4 \times 3(\sqrt{3}, 3)a_0$ and a larger $10 \times 5(\sqrt{3}, 3)a_0$ rectangular supercells, where a_0 is the C–C bond length in graphene. The periodic images of the supercell along the direction perpendicular to graphene sheet are separated by at least 12 Å distance. It is known that the self-interaction error inherent to the conventional GGA functional results in spurious electron delocalization and incorrect magnetic solutions for adatom doping and vacancy defects in graphene. (181; 192; 193) In this regard, we recalculated the electronic and magnetic properties using the Heyd-Scuseria-Ernzerhof (HSE06) (194) hybrid functional as well as using the strongly constrained and appropriately normed (SCAN) meta-GGA functional. (84) While the inclusion of fractional exact exchange for HSE06 hybrid functional improves the description of the electronic structure and the magnetization density, it is computationally expensive. In contrast, since the semilocal SCAN meta-GGA density functional satisfies all the known exact constraints for the exchange-correlation energy and the self-interaction error is reduced, it should better describe the thermodynamic, electronic and magnetic properties of materials. Indeed the SCAN functional predicts these properties correctly for diverse materials with a similar computational cost to the conventional GGA. (195; 196) In the present context of defect magnetism and the concurrent interaction between them, we further validate the applicability of the SCAN functional. The results are obtained within the SCAN functional if it is not otherwise stated.

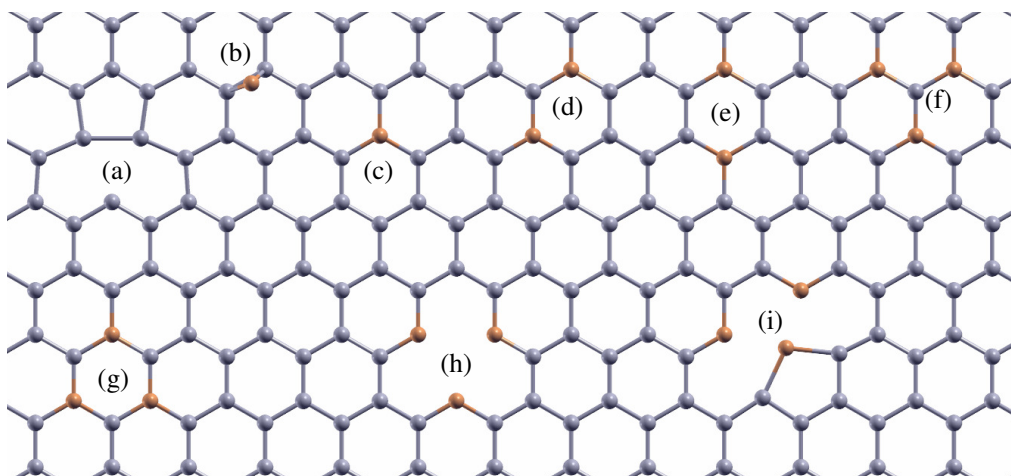


Figure 4.1: Schematic representation of defects in N-doped graphene. Apart from the lattice vacancies (a), chemisorbed (b), various graphitic [single graphitic N (c), meta-graphitic N pair N_{AA} (d), para-graphitic N pair $N_{AB'}$ (e), graphitic 3N (f), triazine (g)], and different vacancy containing N-complexes [pyridinic (h), pyrrolic (i)] are investigated. A and B represent the two graphene sublattice.

4.3 Results and Discussion

Before we investigate the magnetic interactions between the moment generating defect complexes in N-doped graphene, we first address the local magnetism produced by these individual defects. In addition to the lattice vacancies, the common defects in N-doped graphene are chemisorbed, graphitic and vacancy containing nitrogen complexes (Figure 4.1). (46–49; 49–52; 182–186; 188; 189) As the treatment of exchange-correlation may affect the electronic and magnetic description of these defects, here we compare the PBE, hybrid HSE06, and SCAN meta-GGA functionals.

4.3.1 Magnetism of individual defects

Single vacancy Magnetic properties of single vacancy defect in graphene are still studied and debated. (37; 42; 111; 192; 193) The Jahn-Teller distorted $V_1(5|9)$ vacancy [Figure 4.1(a)] generates defect induced localized σ and π states, V_σ and V_π

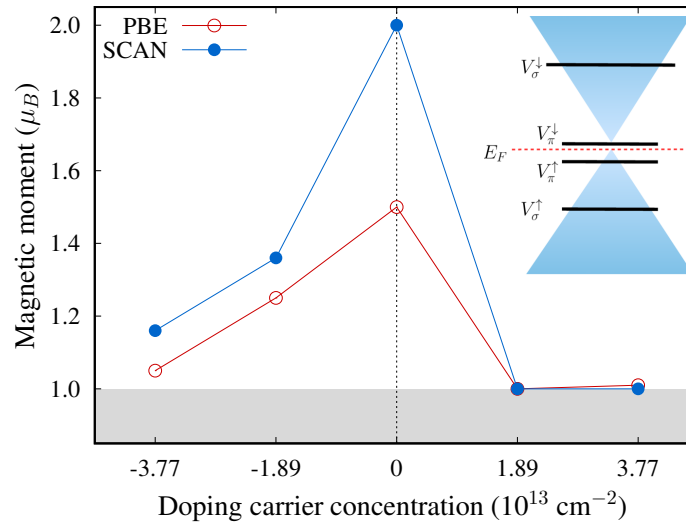


Figure 4.2: The dual origin of vacancy magnetism in graphene and its evolution with carrier doping. Positive (negative) concentration indicates electron (hole) doping. While the π -component of the magnetic moment is quenched under carrier doping, the σ -component remains protected. The inset represents a schematic energy diagram indicating defect induced and spin-split localized π and σ states along with the bulk π bands for the Jahn-Teller distorted $V_1(5|9)$ vacancy. This schematic picture explains the evolution of the magnetic moment of a lattice vacancy with varied carrier doping. While the magnetism is correctly described by the SCAN meta-GGA exchange-correlation functional, the PBE-GGA functional underestimates the moment.

(Figure 4.2). Earlier in Chapter 3 (Figure 3.1), we have discussed the structural details and formation energy of single vacancy for different vacancy concentration. Thus, the magnetic moment of $V_1(5|9)$ vacancy has two components. (37; 154) The π -electron imbalance in the bipartite graphene lattice should generate $1 \mu_B$ moment according to the Lieb's theorem. Additionally, the singly occupied dangling σ -bond should provide with another $1 \mu_B$ moment, leaving the total vacancy moment to $2 \mu_B$. However, the π -magnetism is suppressed within the conventional GGA description of exchange-correlation due to improper delocalization of electrons in the V_π orbital. Thus, the magnetic moment of $V_1(5|9)$ is underestimated to $1.5 \mu_B$ within the PBE exchange-correlation functional (Figure 4.2, Table 4.1), similar to that predicted earlier. (42) Further, the moment depends on the super-

cell size, and thus on the vacancy concentration. The picture is slightly improved while a fraction a_{HF} of Hartree-Fock exact exchange is considered in the HSE06 functional and $1.6 \mu_B$ moment is predicted at the vacancy for $a_{\text{HF}}=0.25$. A further increase in a_{HF} to 0.4 ensures a $2 \mu_B$ moment at the vacancy. In contrast, treating the exchange-correlation with SCAN meta-GGA functional describe the magnetism correctly with $2 \mu_B$ moment for the vacancy (Figure 4.2, Table 4.1).

Similarly, the corresponding electronic structure depends on the exchange-correlation functional. While a metallic solution emerges within PBE and HSE06 functionals, the SCAN functional correctly predicts a gapped band structure. This result is consistent with the diverging resistivity observed in irradiation induced defected graphene with about 10^{12} cm^{-2} vacancy concentration, which indicate insulating behaviour. (96) This was latter theoretically corroborated in graphene with high vacancy concentrations and an insulating solution with a large bandgap was proposed. (139; 197) Further, while the defect induced V_σ state shows a large spin-splitting above 2 eV originating from the JT reconstruction, the splitting for the V_π is small, about 250 meV (Figure 4.2). This prediction is consistent with the recent STM experiment, where the spin-polarized π density of states (DOS) peaks at the defect site are observed to be separated by 20-60 meV. (154) It should be noted here that in such experiments the V_π spin-splitting may be affected by a metastable vacancy geometry or by its interaction with the substrate. We find the vacancy magnetism to be robust against carrier doping with a realistic concentration, (198) as the position of the Fermi level is tuned (Figure 4.2). The graphene with a neutral $V_1(5|9)$ defect is intrinsically hole doped, and one extra electron on a large $10 \times 5 (\sqrt{3}, 3)a_0$ supercell corresponds to $1.89 \times 10^{13} \text{ cm}^{-2}$ carrier density. The extra electron occupies the unfilled $V_\pi^\downarrow$ state destroying the π -electron imbalance in the two bipartite sublattices. Thus, the π -component of the vacancy moment is completely quenched (Figure 4.2). In contrast, the σ -component of the

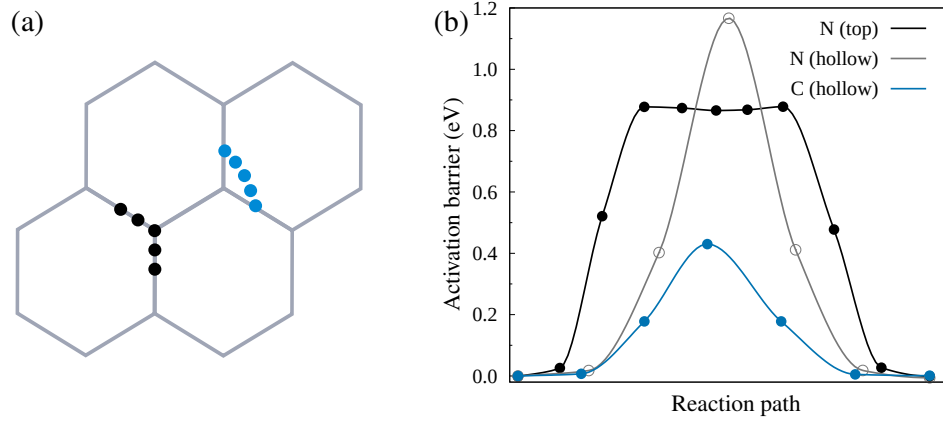


Figure 4.3: Migration pathways (a) and activation energies (b) for C and N adatom diffusion on graphene. The two species follow separate migration path: carbon adatom prefers moving through the hollow region in the hexagon with low barrier of 0.43 eV while N adatom has a high barrier of 1.16 eV along the same path. The movement of N adatom parallel to the C–C bond has a substantially lower activation barrier at 0.83 eV.

magnetic moment is protected against carrier doping. Increasing the electron doping beyond $1.89 \times 10^{13} \text{ cm}^{-2}$ does not further affect the magnetic moment (Figure 4.2). At higher electron density the unoccupied bulk π -states get filled, while the unoccupied $V_{\sigma}^{\downarrow}$ state lies much higher in energy and is impossible to populate with any realistic carrier density. The carrier concentration dependent differential charge density corroborates this picture. (199) The scenario with hole doping is different only qualitatively. The σ -component is unaffected, and hole doping does not quench the π -moment completely indicating the particle-hole asymmetry in defected graphene (Figure 4.2). The semi-localized $V_{\pi}^{\uparrow}$ state is only partially depopulated and a fractional π -moment survives. (37; 200) Therefore, while the π magnetism in graphene vacancy could be completely quenched with sufficient carrier doping, the spin- $\frac{1}{2}$ σ -magnetism is robust.

In the context of differential defect abundance in N-doped graphene, it is relevant to investigate the C and N adatom diffusion on graphene lattice. The C and N adatoms are absorbed at the bridge site with 1.51 and 0.9 eV binding en-

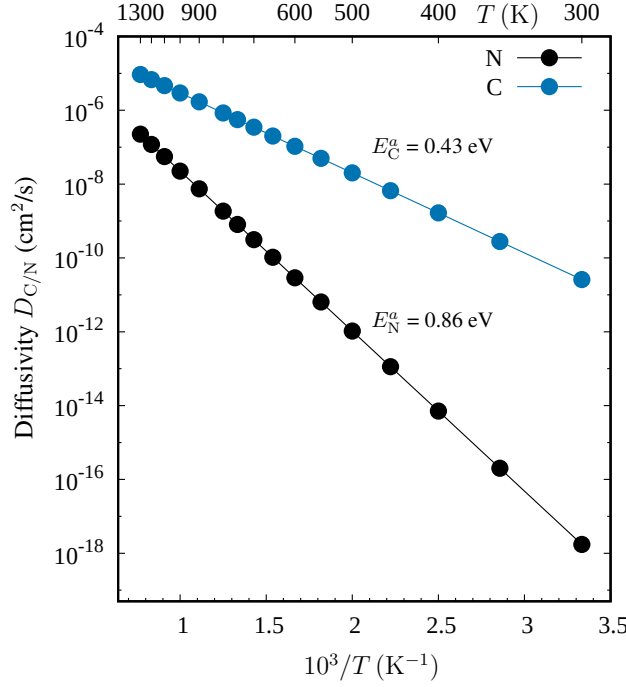


Figure 4.4: Adatom diffusivity $D_{C/N}$ calculated within the harmonic approximation, $D_X = \frac{1}{4}a'_X\Gamma_0 e^{-E_X^a/k_B T}$, where a'_X is the jump distance for the $X = C/N$ diffusion, and E_X^a is the corresponding activation barrier. $\Gamma_0 (= \Pi_i \nu_i^I / \Pi_j \nu_j^{TS})$ is the jump prefactor, where ν_i^I and ν_j^{TS} are the frequencies of harmonic vibrational modes corresponding to the structures at the initial and saddle point. Very high diffusivity of C and N adatoms on graphene, especially in the temperature range 800-1300 K relevant to growth and annealing conditions, (46–49; 49–52; 182–186) indicates self-healing of the vacancy defects and promotes the formation of graphitic N-complexes. Both adatoms are absorbed at the bridge-site, and the two different diffusion mechanisms are shown in the inset.

ergy. We calculate the activation barrier for adatom diffusion within climbing image nudged elastic band method. (92) In agreement with the previous calculations, (201; 202) the calculated activation barriers are found to be 0.43 and 0.86 eV, respectively, for C and N diffusion (Figure 4.3). Such low activation barrier results into a very high diffusivity $D_{C/N}$ at the experimental growth and annealing temperatures (Figure 4.4), and the adatoms will quickly recombine with the graphene vacancies. Therefore, due to high adatom mobility, it is expected that the graphene vacancies will be annihilated to decrease in concentration and form graphitic N-

Table 4.1: Magnetic moment of the defect complexes in Figure 4.1 severely depends on the treatment of exchange-correlation energy. We compare the moments calculated with conventional PBE, hybrid HSE06 ($a_{\text{HF}}=0.25$) and SCAN meta-GGA functionals, where the later better describes the moment. While the HSE06 calculations were carried out with $4 \times 3 (\sqrt{3}, 3)a_0$ supercell, the $10 \times 5 (\sqrt{3}, 3)a_0$ supercell was used for the calculations with PBE and SCAN density functionals.

Defect	Magnetic moment (μ_B)				
	$4 \times 3 (\sqrt{3}, 3)a_0$			$10 \times 5 (\sqrt{3}, 3)a_0$	
	PBE	HSE	SCAN	PBE	SCAN
(a) Monovacancy	1.2	1.6	2.0	1.5	2.0
(b) N adatom	0.8	1.0	1.0	0.9	1.0
(c) Graphitic N	0.0	0.1	1.0	0.0	1.0
(d) Meta-graphitic N pair (N_{AA})	0.0	0.4	2.0	0.0	2.0
(e) Para-graphitic N pair ($N_{AB'}$)	0.0	0.0	0.0	0.0	0.0
(f) Graphitic 3N (G3N)	0.5	1.0	1.0	0.9	1.0
(g) Triazinic N (T)	0.8	1.0	1.0	0.9	1.0
(h) Trimerized pyridinic N (TPY)	0.3	1.0	1.0	0.2	1.0
(i) Trimerized pyrolic N (TPI)	0.9	1.0	1.0	1.0	1.0

complexes, while annealed at high-temperature or non-equilibrium growth conditions. (46–49; 49–52; 182–186) This prediction is consistent with the experimental observation of pyridinic to graphitic defect conversion during postannealing at high-temperature. (47) Further, the diffusion mediated self-healing has been observed in scanning transmission electron microscopy. (38; 203)

N-adatom The chemisorbed N-adatom (Figure 4.1(b)) is a p-type defect with the impurity state above the Fermi level (Figure 4.5). Here, the C–N separation is 1.48 Å. A localized magnetic moment of 1 μ_B is generated from the in-plane N-orbitals (Table 4.1). However, due to the high N diffusion on graphene (Figure 4.4), such adatom defect may not be present and effectively contribute to magnetism in graphene samples that are prepared and annealed at high-temperature. In contrast, high N diffusion will further promote the formation of graphitic N-complexes.

Graphitic nitrogen defects The appearance of Dirac point (DP, E_D) in graphene band structure is very sensitive to external perturbations, and the breaking of sublattice symmetry induces a substantial gap at the DP. (204–206) Thus, all the graphitic N-defects are expected to generate a gap at E_D . Single graphitic nitrogen (Figure 4.1(c)) introduces an impurity state near the Fermi level and induces a 0.60 eV gap at E_D . The C–N bond length is 1.41 Å. An overall semiconducting electronic structure emerges (Figure 4.5) and the results are consistent with the STM measurement. (46) Further, an exchange splitting of 18 meV is observed between the majority and minority spin channels, which results in itinerant π -magnetism along with a small $0.06 \mu_B$ moment localized at the N-site. However, the total moment generated by this defect strongly depends on the treatment of exchange-correlation energy and defect concentration (Table 4.1). While the SCAN functional correctly generates $1 \mu_B$ moment, the moment strongly depends on the fractional exact exchange a_{HF} in HSE06 functional. The conventional HSE06 functional ($a_{HF} = 0.25$) underestimates the moment (Table 4.1), although it gradually increases with increasing a_{HF} and generates $1 \mu_B$ moment for $a_{HF} = 1$. In contrast, in agreement with an earlier report, (207) the conventional PBE functional fails to produce any spin-splitting and a non-magnetic solution emerges. Therefore, the SCAN meta-GGA functional provides the correct magnetic picture over other exchange-correlational functionals. A higher a_{HF} within HSE06 functional indicate that itinerant and localized magnetism are described by different exchange interactions.

The graphitic complexes with two nitrogens N_{AA} and $N_{AB'}$ have been experimentally identified [Figure 4.1(d) and (e)]. (46; 185; 186; 190) Due to the sublattice asymmetry in these n-type complexes, the DP is destroyed, and within the SCAN functional a 0.31 and 0.50 eV gap emerges at the E_D for N_{AA} and $N_{AB'}$ complexes, respectively. The overall electronic structure is found to be defect specific as a half-metallic (semiconducting) solution is observed for the N_{AA} ($N_{AB'}$) defect in the

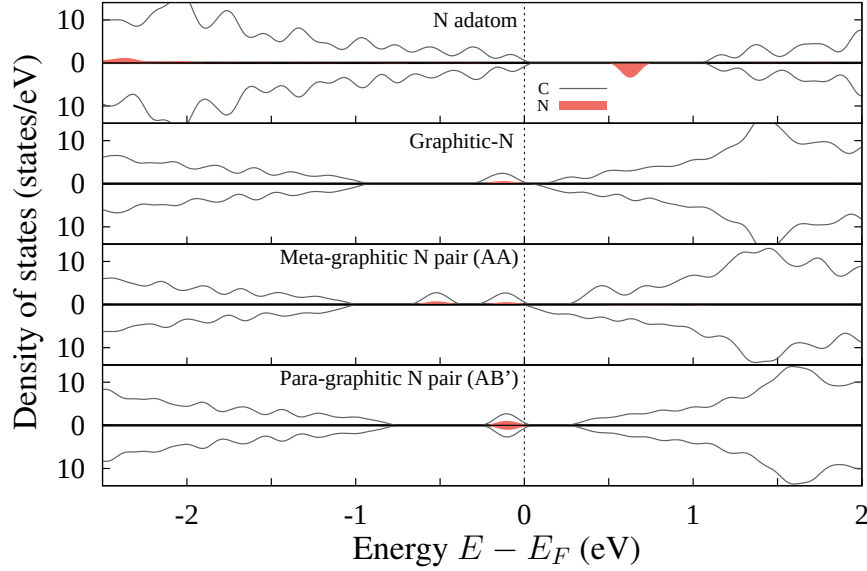


Figure 4.5: Spin-polarized projected density of states calculated using the $(10 \times 5) - (\sqrt{3}, 3)a_0$ supercell for the N adatom and graphitic N-complexes containing single or pair of N atoms. N adatom results in p-type electronic structure while the graphitic N-complexes show n-type behavior. Gap opening at the Dirac point E_D is a constant feature across the defect complexes. The N (C) states are denoted by shaded red region (black line).

large $10 \times 5 (\sqrt{3}, 3)a_0$ supercell (Figure 4.5). The overall results here are in agreement with the experimental results as the character of electronic DOS near the Fermi level is consistent with the STS measurements. (46; 185) The exchange-split bands generate itinerant magnetism and a small moment of $0.06\text{--}0.08 \mu_B$ is generated at the N-sites, which are coupled ferromagnetically (antiferromagnetically) while the nitrogen atoms occupy the same (different) sublattice. This fact results into 2 and $0 \mu_B$ moments for the N_{AA} and $N_{AB'}$ pairs, respectively (Table 4.1). We find the results across different exchange-correlation functionals are similar to that observed for the single graphitic N-defect.

While the triazine (T) complex [Figure 4.1(g)] is thermodynamically slightly more favorable over the graphitic-3N (G3N) complex [Figure 4.1(g)], both of these defects are formed at the non-equilibrium growth conditions. The graphitic-3N complex could also be produced when a highly mobile carbon adatom diffuses

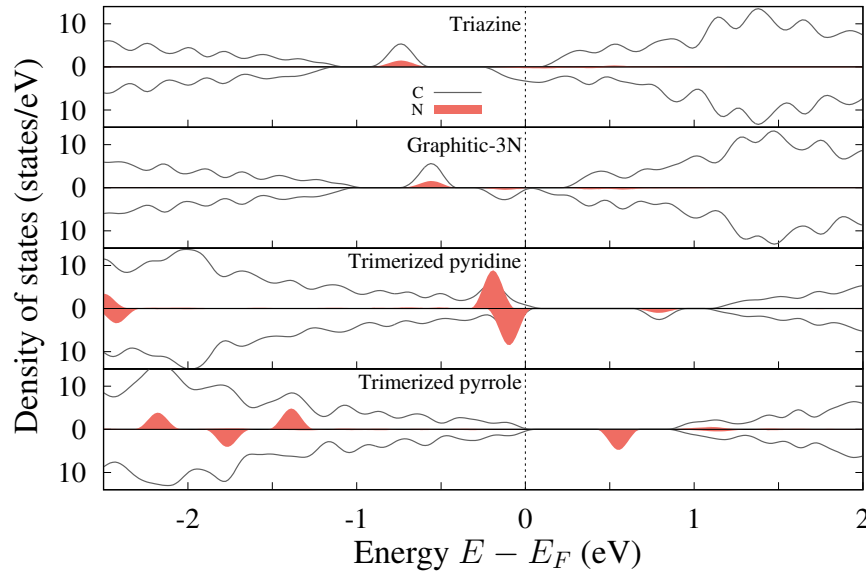


Figure 4.6: Spin-polarized projected density of states calculated using the $(10 \times 5) - (\sqrt{3}, 3)a_0$ supercell for the graphitic and vacancy containing N-complexes. Substitutional N-doping opens up a gap at the Dirac point E_D and the electronic structure becomes n-type. In contrast, the vacancy containing defects display p-type semiconducting behaviour.

into the lattice vacancy in the trimerized pyridinic and pyrrolic complexes in the bulk regions of graphene. In both the defects [Figure 4.1(f) and Figure 4.1(g)], all three nitrogen atoms occupy the same sublattice leading to a sublattice asymmetry, which in turn destroys the DP and consequently open up a gap at the E_D (Figure 4.6). The overall electronic structure is half-metallic for the T-complex, and the same is found to be semiconducting for the G3N-complex (Figure 4.6). It is important to note that such half-metallicity induced asymmetric electron transport for different spin components could have significant implication in spin-based devices. To gain further insight into the magnetism, we investigate the differential charge density and the corresponding magnetization density (Figure 4.7). The $C \rightarrow N$ π -electron transfer creates Lieb's imbalance and an exchange split π -band emerges, which is responsible for the itinerant magnetism that is confirmed from the magnetization density [Figure 4.7(a) and (b)]. In addition, a hybridized nitro-

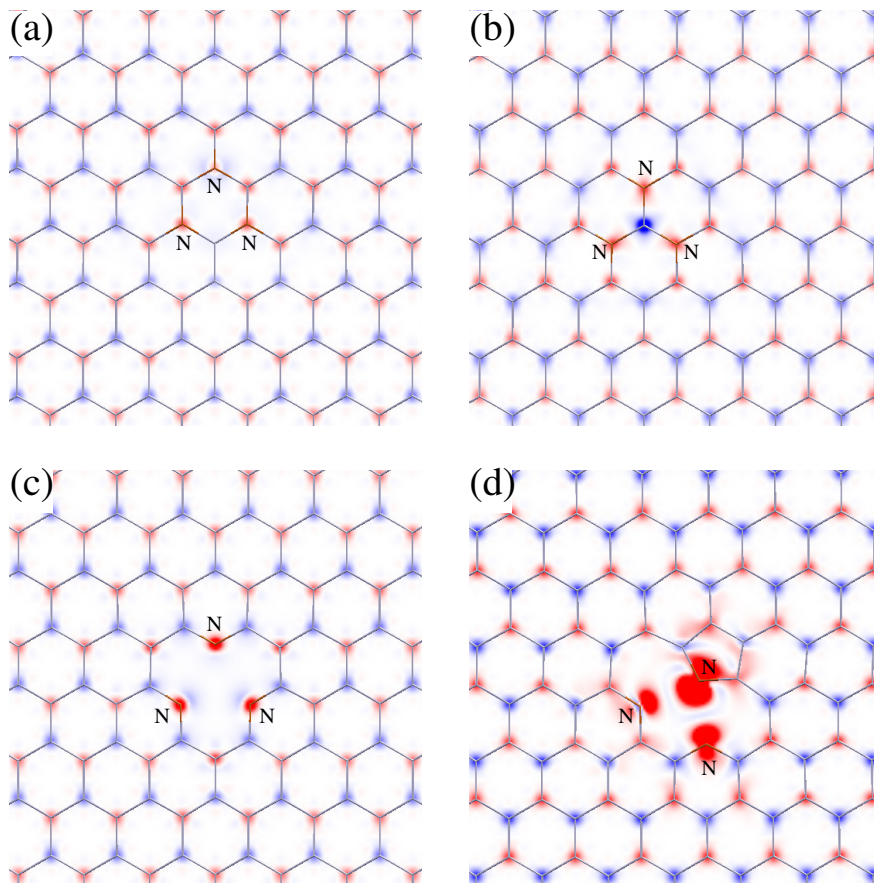


Figure 4.7: Magnetization density for graphitic and vacancy containing N-complexes: (a) triazine, (b) graphitic-3N, (c) trimerized pyridine and (d) trimerized pyrrolic defect. Red and blue colour indicate the up and down spin density, respectively. While the magnetism in graphitic N-complexes is mostly itinerant in nature, the magnetization density demonstrates that a very significant fraction of the moment is localized at the N-sites for the vacancy containing N-complexes.

gen impurity state is observed near the Fermi level, which is responsible for a tiny N-moment of $\sim 0.05 \mu_B$. Note the C-atom at the centre of G3N-defect acquire a comparatively larger localized moment of $0.25 \mu_B$ [Figure 4.7(b)]. These together result into a total moment of $1 \mu_B$ for these graphitic defect complexes (Table 4.1).

Thus, in general, the electronic and magnetic structure of the different graphitic defect complexes are remarkably similar. First, all of them open up a gap at the E_D due to sublattice asymmetry, which is consistent with the the angle-resolved photoemission spectroscopy results. (47) Second, the exchange-split π -band generates

Table 4.2: Formation energies for the graphitic complexes calculated with SCAN functional. The formation energy per N dopant is calculated as $E_f = \frac{1}{x}(E(C_yN_x) - [E(C_{y+x}) - yE(C) + xE(N)])$ where $x(y)$ denotes the number of N (C) atoms in graphene, and $E(C_{y+x})$ is the total energy of pristine graphene while $E(N/C)$ is the single atom energies of N/C respectively.

Defect	E_f (eV)
(a) Graphitic N	2.64
(b) Meta-graphitic N pair (N_{AA})	3.66
(c) Para-graphitic N pair ($N_{AB'}$)	3.47
(d) Graphitic 3N (G3N)	3.82
(e) Triazinic N (T)	3.81

itinerant magnetism, while the localized moment at the N-site is small about 0.03–0.09 μ_B . While the overall electronic structure of the graphitic complexes are defect specific, all of them are found to be n-type, which are in overall agreement with the STS results. (46; 185) Further, the preference for graphitic complexes is also evident from the calculated formation energies which are remarkably lower than $V_1(5|9)$ (6.08 eV) due to the robust, covalent C–N bonding (Table 4.2).

Vacancy containing nitrogen defects Now we explore the defect complexes wherein the N atoms are incorporated in a vacancy. The trimerized pyridine (TPY), where three N atoms occupy the same graphene sublattice surrounding a vacancy [Figure 4.1(h)] is energetically favoured over the mono and dimerized pyridines. (188) The 1.33 Å C–N bonds are consistent with experimental values for pyridinic complexes. The N atoms form an equilateral triangle with 2.61 Å sides, which is larger than the triangular unrelaxed vacancy with 2.46 Å. Further, this complex is found to be p-type and the Bader analysis indicates a 0.9-1.12 e/N charge transfer to nitrogen from carbon.

The magnetism in such vacancy containing nitrogen defects is rather intricate, and a detailed investigation into the electronic DOS (Figure 4.6) and the magneti-

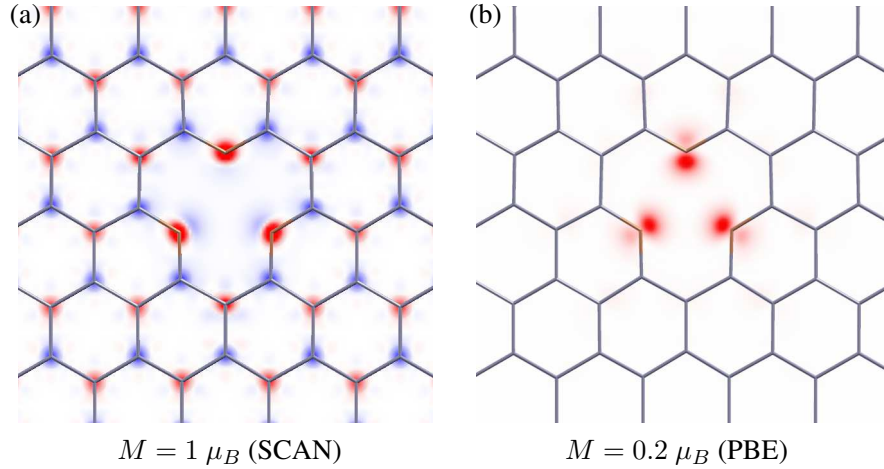


Figure 4.8: Contrasting magnetization density for trimerized pyridine obtained with (a) SCAN and (b) PBE functional. The itinerant nature of magnetism from C- p_z states is correctly captured by SCAN functional which includes a substantial contribution from localized moment on N atoms. The C- σ magnetism from PBE functional is in disagreement with Lieb's theorem as well as STM/STS observations.

ization density [Figure 4.7(c)] unravel the origin of $1 \mu_B$ moment for this complex. Unlike the bare vacancy, the σ component to the moment is completely ruled out due to the presence of occupied σ -state that originates from the undercoordinated N atoms (Figure 4.6). In contrast, the moment has entirely π character and originates from the localized N- p_z and itinerant C- p_z states with an exchange-splitting of 11 meV. As a result, a sizeable localized moment of $0.15 \mu_B$ is observed at the N-sites for this complex and a fraction of the total moment originates from the itinerant magnetism [Figure 4.8(a)]. In contrast to the SCAN functional, the PBE results provide a very contrasting picture. First, the moment is substantially underestimated [Figure 4.8(b)], and further, the moment originates from the localized σ -state at the N-sites without any π contributions. However, the STM and STS investigations of the monomerized and trimerized pyridine reveal an electron density distribution that is consistent with the p_z states of the vacancy defect and thus corroborate the results obtained with the SCAN functional. (46; 154; 208)

The trimerized pyrrolic (TPI) complex is formed when a single N atom is absorbed in a divacancy to form a pentagon and rest of the undercoordinated C atoms are also substituted by N in Figure 4.1(i). The pentagonal C–N bonds (1.41 Å) are larger in comparison with the other C–N bonds (1.33 Å). Similar to the TPY-complex and bare vacancy, this complex has p-type character. The electronic DOS calculated within the PBE and SCAN functionals show qualitatively similar features, and the unoccupied σ -states originating from the N-impurities appear just above the Fermi level (Figure 4.6). The calculated magnetization density indicates that a large fraction $\sim 80\%$ of the total $1 \mu_B$ moment is localized on the nitrogen atoms and only a small fraction originates from the delocalized π -band [Figure 4.7(d)]. Further, due to the proximity of the unoccupied σ -states to the Fermi level, a slight perturbation through the charge doping will adversely affect this localized σ component of the moment.

Therefore, the magnetism in the vacancy containing N-complexes is fundamentally different from the graphitic defects. While the magnetism in graphitic defects is entirely itinerant, a very significant fraction of the moment is localized at the N-sites in vacancy containing N-complexes. Thus, in the absence of a strong exchange path, one would not expect that such localized magnetic moments in these vacancy containing defect complexes to contribute significantly to the high-temperature ferromagnetism. Indeed, the role of this particular defect on the observed ferromagnetism has remained controversial. (49; 52; 182)

4.3.2 Magnetic interactions among nitrogen defects

Although nitrogen-doped graphene is reported to show ferromagnetism, the microscopic mechanism is not yet understood and resulted in conflicting arguments. (49–52; 182; 183) The appearance of a diverse Curie temperature with varied growth and annealing conditions makes the microscopic analysis very complicated as the

differential defect abundance may fluctuate drastically in the samples. A long-range magnetic order in nitrogen doped graphene can only emerge when the moment generating defects are exchange coupled. Thus, we investigate the magnetic interactions between the abundant defect complexes.

The single vacancy in graphene lattice generates a robust semi-localized moment. However, the interaction between the vacancy moments is sublattice dependent. Vacancies in the same sublattice are coupled ferromagnetically, whereas they prefer antiferromagnetic alignment when placed on different sublattices. Further, the magnetic interaction sharply falls to zero below 1 nm distance due to semi-localized nature of the moment. (209) Thus, a randomly distributed vacancy in graphene will not lead to any magnetic ordering, which is consistent with the results predicting paramagnetism. (32; 111; 177) Moreover, it should be noticed in this context that, the existence of a vacancy in the N-doped graphene is rare due to the very high C and N adatom mobility at the high-temperature growth conditions (Figure 4.4), which leads to self-healing of vacancy or the formation of graphitic N-defect.

Single graphitic nitrogen defect is similar to the pristine vacancy. For two substitutional atoms on the (different) same sublattice, the spin-configuration is (anti-) ferromagnetic. Moreover, the interaction strength decays fast with increasing separation and follows an inverse power law, and the long-range interaction may develop through Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. (207) Thus, a statistically random distribution of single graphitic nitrogen will not result in high-temperature ferromagnetism that has been reported so far. (49–52; 182; 183)

A very complex picture emerges when we explore the interactions between the larger defects. Here, we address two distinct regimes of N-doping that is motivated by several experimental observations. (49–51; 191) It has been unanimously pointed out in the literature that ferromagnetism emerges at a critical N-

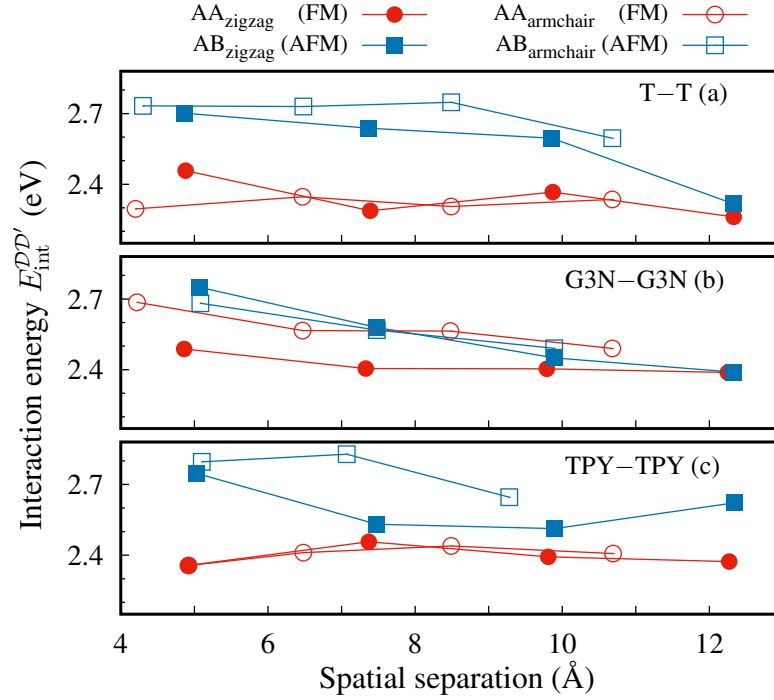


Figure 4.9: Interaction energy between the N-complexes $E_{\text{int}}^{\mathcal{D}\mathcal{D}'}$ in graphene is calculated in the low concentration limit (3 at. %) with varying distances and orientations along the zigzag and armchair directions. Independent of the interacting defect types, the magnetic coupling is observed to be sublattice depended. The defects on the equivalent (opposite) sublattice are coupled ferromagnetically (antiferromagnetically). Such sublattice dependent magnetic interaction will not lead to the observed ferromagnetism in nitrogen-doped graphene. In contrast, these complexes interact very differently in the high N-concentration limit, which is discussed in the text.

concentration around 5 at. % and above which the saturation magnetization and coercive field increase further with increasing the concentration. Thus, we consider N-concentration below 5 at. % and in the 8–13 at. % range, and investigate how the concentration influences the magnetic interaction. In this regard, we calculate the interaction energy $E_{\text{int}}^{\mathcal{D}\mathcal{D}'}$ between two magnetic defects $\mathcal{D}$ and $\mathcal{D}'$ as, $E_{\text{int}}^{\mathcal{D}\mathcal{D}'} = (E_{\text{m}}^{\mathcal{D}\mathcal{D}'} - E_{\text{nm}}^{\mathcal{D}\mathcal{D}'}) - (E_{\text{m}}^{\mathcal{D}} - E_{\text{nm}}^{\mathcal{D}}) - (E_{\text{m}}^{\mathcal{D}'} - E_{\text{nm}}^{\mathcal{D}'})$ and shown in the Figure 4.9. The energies corresponding to the magnetic and non-magnetic solutions for the interacting defects are $E_{\text{m}}^{\mathcal{D}\mathcal{D}'}$ and $E_{\text{nm}}^{\mathcal{D}\mathcal{D}'}$, while $E_{\text{m}}^{\mathcal{D}/\mathcal{D}'}$ and $E_{\text{nm}}^{\mathcal{D}/\mathcal{D}'}$ represent magnetic and non-magnetic energies of the isolated defects.

First, we discuss the long-range magnetic interaction between the graphitic defects in the low N-concentration limit and investigate how it is affected by the spatial separation and direction between the defects (Figure 4.9). Two interacting T–T, G3N–G3N, and mixed T–G3N defects in a $(10 \times 5) - (\sqrt{3}, 3)a_0$ supercell represents 3 at. % N-concentration. At such a low concentration and for all these types of defect interactions, we notice some general trends [Figure 4.9(a) and 4.9(b)]. (i) These defects mostly prefer to occupy the same graphene sublattice, (ii) owing to the itinerant nature of the individual moments in these graphitic defects, the interaction between them is long-range, and (iii) the nature of magnetic interaction between the defects is entirely dictated by their respective sublattice [Figure 4.10(a)–(d)]. For the defects on the equivalent (opposite) graphene sublattice, the magnetic interaction is found to be ferromagnetic FM (antiferromagnetic AFM). The picture remains unaltered regardless of the spatial separation and relative orientation between the defects along the armchair and zigzag directions (Figure 4.9). Although the nature of the magnetic moment in these defects is completely different, the sublattice dependent magnetic interaction is in complete agreement with results predicted by the RKKY interaction between the localized moments on the bipartite graphene lattice. (210; 211) While these defects mostly prefer to occupy the same sublattice $\mathcal{D}_A \mathcal{D}'_A$ over the $\mathcal{D}_A \mathcal{D}'_B$ configuration, during the non-equilibrium growth process the defects are equivalently distributed over the two graphene sublattice. Therefore, the sublattice dependent FM and AFM interaction will restrict the observation of FM order at such a low concentration of nitrogen. This picture is consistent with the experimental observation that FM ordering is not found below 5 at. % N-concentration. (49)

Now we turn our attention onto high N-concentration, and two interacting T–T, G3N–G3N, and mixed T–G3N defects in a $(4 \times 3) - (\sqrt{3}, 3)a_0$ supercell correspond to 12.5 at. % N-doping. The sublattice dependent magnetism for such

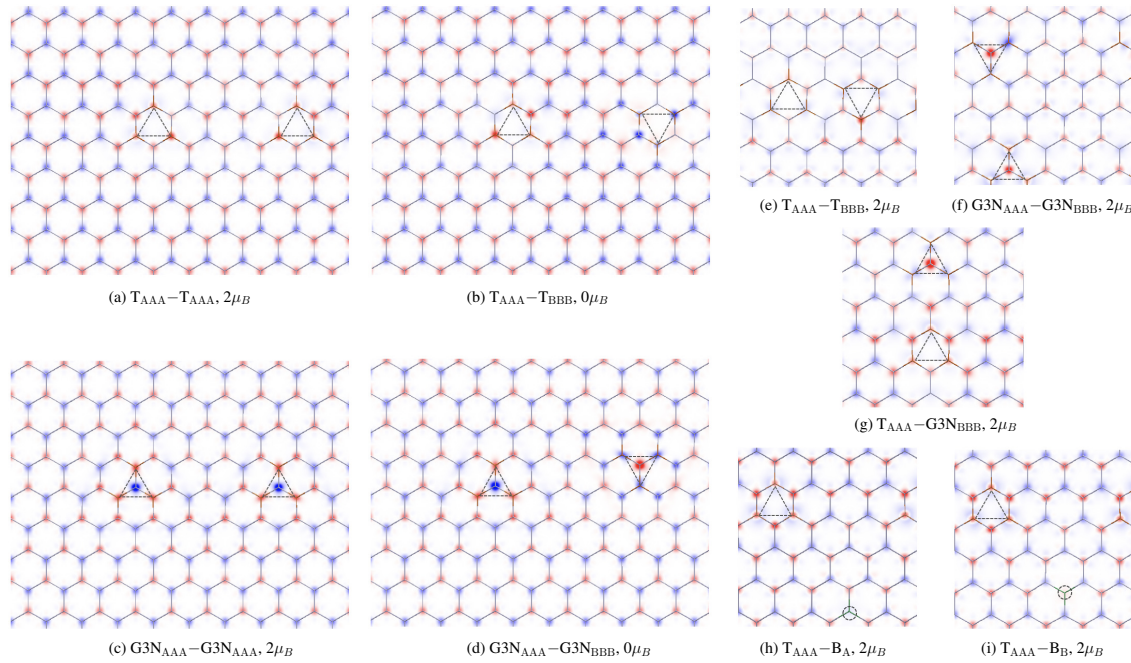


Figure 4.10: The calculated magnetization density reveals the corresponding magnetic interactions between the defects, which are highlighted with a triangle or circle. In the low N-concentration limit of 3 at. %, the graphitic defects follow the usual sublattice dependent magnetic interaction. (a)–(d) The defects on the (opposite) same sublattice are (anti-) ferromagnetically coupled. However, the picture changes at the high N-concentration limit (12.5 at. %) and crucial exceptions to the usual sublattice dependent magnetic occur. (e)–(g) In specific crystallographic direction of graphene lattice, the defects are coupled ferromagnetically, regardless of their sublattice. Such ferromagnetic interaction between the graphitic N-defects is responsible for the observed ferromagnetism. (h)–(i) The interaction between the T-complex and the single graphitic B-defect is always ferromagnetic, independent of the sublattice. Thus, B co-doping promotes ferromagnetism in N-doped graphene and increase the saturation magnetization, which is consistent with the recent experimental observation. (191) Red and blue colour indicate the up and down spin density, respectively.

high N-concentration changes dramatically. In contrast to the AFM interaction, a FM interaction with spontaneous magnetization emerges while the defects that are placed on the different sublattice [Figure 4.10(e)–(g)]. However, such FM structure is found when the defects are interacting along a particular direction, which is along the zigzag direction for T–T interaction [Figure 4.10(e)] and along the armchair direction for the G3N–G3N [Figure 4.10(f)], and mixed T–G3N [Fig-

Table 4.3: Concentration, sublattice and direction dependent magnetic exchange for interacting triazine–triazine (T–T), graphitic 3N–graphitic 3N (G3N–G3N) and triazine–graphitic 3N (T–G3N) complexes. These interactions follow the usual sublattice dependent FM and AFM coupling of local moments on a bipartite hexagonal lattice. The defects on the equivalent (opposite) sublattice are coupled ferromagnetically (antiferromagnetically). However, at the high N-concentration limit, exceptions to this generic trend appear. At high concentration, the moments may couple ferromagnetically even when they are on different sublattice, leading to an effective ferromagnetism. The exceptional case of FM for high N-concentration are denoted with (*).

Defect	T				G3N			
	armchair		zigzag		armchair		zigzag	
	AA	AB	AA	AB	AA	AB	AA	AB
T	FM	AFM	FM	AFM (*)	FM	AFM (*)	FM	AFM
G3N	FM	AFM (*)	FM	AFM	FM	AFM (*)	FM	AFM

ure 4.10(g)] defect interactions. Thus, at high N-concentration, the graphitic T and G3N defects are responsible for the observed ferromagnetism [Table 4.3]. Further, the concentration of the graphitic T-complex may be increased by using the triazine-based precursor during the growth using the chemical vapour deposition technique. (212) Moreover, a suitable postannealing strategy may convert the vacancy containing pyridinic and pyrrolic defects to graphitic G3N-complex. (47) Therefore, we conclude that such sample preparation strategies may give rise to robust ferromagnetism with improved Curie temperature. This discussion is consistent with the recent observation of room-temperature ferromagnetism in turbostratic N-doped graphene films, where the T-defect is found to be the most abundant complex. (191)

Further, in the high concentration limit of 8.3 at. % N-doping, we investigate the interactions between the two N_{XX} defects, and between the T-complex and a single graphitic N-defect. Both these interactions follow the usual sublattice dependent magnetic couplings. While the $N_{AA} - N_{AA}$ and $T - N_A$ interactions are

found to be ferromagnetic, the $N_{AA} - N_{BB}$ and $T - N_B$ are observed to be antiferromagnetic. Therefore, such defect-defect interactions are not responsible for the observed ferromagnetism in the N-doped graphene.

In contrast to the graphitic N-defects, the vacancy containing complexes do not contribute to ferromagnetism. Moreover, in accordance with the experimental observation, (47) we have discussed earlier that the C-adatom is highly mobile on the graphene lattice (Figure 4.4), and thus the vacancy containing TPY-defect complex will be converted into the graphitic G3N-complex during high-temperature growth and annealing. Therefore, the concentration of this defect will be negligibly small. However, for completeness, we have investigated the magnetic interaction between two TPY-complexes in both the low and high concentration limits. Unlike the graphitic T- and G3N-complexes and independent of N-concentration, the TPY–TPY magnetic coupling is AFM (FM) for defects on the opposite (equivalent) sublattice. Further, the picture is independent of defect orientation and separation [Figure 4.9(c)]. Thus, this vacancy containing defect will not play any role in the ferromagnetism in N-doped graphene.

4.3.3 Effects of boron co-doping

Motivated by the recent observation of room-temperature ferromagnetism in boron and nitrogen doped turbostratic carbon films, (191) we further investigate the effect of B co-doping on the ferromagnetism. Notably, we consider a small B co-doping in the limit of high N-concentration that is responsible for the observed ferromagnetism. Due to very-low B-concentration, we have only considered graphitic single B-defect and ignored the possibility of the larger B-complexes. We also ignored the chemisorbed B-defect, as in this configuration, the B-adatom is expected to be very mobile similar to the C and N adatoms (Figure 4.4), and consequently form single graphitic B-defect.

In contrast to the single N-defect, the graphitic B-defect leads to p-type behaviour due to electron deficiency. The C–B bonds are found to be elongated (1.49 Å) compared to the C–N bonds (1.41 Å) in the graphitic N-defect and a B $\rightarrow$ C charge transfer takes place. However, similar to the single graphitic N-defect, the B-defect also results in an itinerant magnetism with $1 \mu_B$ moment, where a very small $0.03 \mu_B$ moment is localized at the B-site. In contrast to the repulsive and sublattice dependent N–N magnetic interactions, the N–B interaction is found to be attractive, and a completely compensated AFM structure emerges, which is independent of the sublattice. Further, we investigate the interaction between this graphitic B-defect and the prevalent graphitic N-defects, T and G3N complexes with $1 \mu_B$ moment each. Surprisingly, the $B_{A/B}$ affects the overall picture significantly. The interaction between these graphitic defects and the $B_{A/B}$ is found to be attractive, which is opposite to their interaction with single graphitic N-defect. Independent of their respective sublattice, the interacting T– $B_{A/B}$ [Figure 4.10(h)–(i)] and G3N– $B_{A/B}$ configurations generate a total moment of $2 \mu_B$, while for all cases, the compensated AFM magnetic structure is found to be energetically much unfavourable. A closer look at the magnetization density reveals that the resultant $2 \mu_B$ moment arises due to the sublattice imbalance of the itinerant C- p_z electrons. This finding is consistent with the recent experimental observation of increased saturation magnetization in N-doped graphene due to B co-doping. (191) Therefore, we argue that small B co-doping will enhance ferromagnetism in nitrogen-doped graphene.

4.4 Summary

The microscopic origin of ferromagnetism that is observed in N-doped graphene has remained elusive. (49–52; 182; 183) The difficulty to comprehend arises due to

the complex dependence of magnetism on N-content and on the corresponding differential defect distribution originating from the varied growth and annealing details. In this context, we systematically investigate the moment formation and the intricate magnetic interaction between various defect complexes within the first-principles calculations. The C and N adatom diffusion on graphene plays a very important role in healing vacancy containing defects and generating graphitic N-complexes. The magnetism in the graphitic N-complexes are found to be fundamentally different from the vacancy containing complexes. While an itinerant magnetism emerges in the graphitic N-complexes, a very significant fraction of the moment is localized at the N-sites for the later. By comparing the results with PBE and HSE06 exchange-correlation functional and available experimental data, we conclude that the SCAN semilocal meta-GGA density functional provides a better description of the electronic structure and magnetism in defected graphene. We further demonstrate that the vacancy magnetism is robust against carrier doping.

The magnetic interaction between the defects are found to be intricate and complex, which depends on the defect type, N-concentration, defect orientation and the corresponding distance between them. Regardless of the defect type and at low N-concentration, the magnetic interaction shows a generic sublattice dependence independent of defect orientation and distance. In agreement with the RKKY interaction leading to sublattice dependent magnetic interaction in bipartite graphene lattice, (210; 211) the long-range coupling is found to be FM (AFM) for the defects on the equivalent (opposite) sublattice. Thus, at low N-content, the statistical distribution of defects on both graphene sublattice will not produce FM ordering. This result is consistent with experimental observation. (182) Interestingly, the picture drastically changes at the high N-concentration owing to a direction dependent and sublattice independent FM interaction with spontaneous magnetization for the interaction between the graphitic T and G3N defects. While we reject

the other type of defects through a comprehensive investigation, we conclude that graphitic T and G3N defects are predominantly responsible for the observed ferromagnetism. Further, we predict that an experimental strategy to increase the concentration of these graphitic defects will produce robust ferromagnetism with improved Curie temperature. Finally, we demonstrate that a small amount of boron co-doping will further enhance the ferromagnetism in N-doped graphene. Thus, while the present results help us to understand the scattered and often controversial experimental results, an overall microscopic understanding and a concurrent experimental synthesis strategy provided here will motivate new experiments to control magnetism in nitrogen and boron doped graphene.

CHAPTER 5

DEFECT-DRIVEN DEGRADATION IN PHOSPHORENE

Although phosphorene is a promising candidate for novel semiconducting devices, it is limited by its structural degradation at elevated temperatures leading to sublimation near 700 K and chemical degradation in ambient conditions. Intrinsic point defects and edges have been experimentally observed to be decisive in increasing the rate of degradation process. Using first-principles calculations, we investigate the migration of various point defects such as single vacancy, adatom, and interstitial, and also investigate the oxygen molecule dissociation. We demonstrate that the single vacancy migration within and across few-layers of phosphorene is highly anisotropic. The merger of adjacent single vacancies takes place through bond rotation that leads to divacancy formation. Further, the rate-limiting process in the onset of anisotropic voids is identified. We find that the rapid sublimation is attributed to desorption of phosphorus atoms upon aggregation. The chemical degradation due to oxygen molecule dissociation at single vacancy is found to be a barrierless process and thus happens spontaneously. The present results should have significant bearing in identifying the suitable conditions for fabrication of degradation-free phosphorene and operation of phosphorene devices. A manuscript based on the above results is currently under preparation.

5.1 Introduction

Few-layered black phosphorus has garnered significant attention due to a layer-tuneable band gap of 0.3–2.0 eV and an anisotropic response. (3; 4; 16; 19; 64; 213–215) Similar to graphite, the individual layers of black phosphorus consist of phosphorus atoms arranged in a staggered hexagonal lattice that are bound by van der Waals interaction. The isolated layers of black phosphorus, phosphorene, offer significant advantage over contemporary two-dimensional materials such as graphene and MoS₂ in realizing novel semiconducting and optoelectronic devices due to a moderate current on-off ratio, high carrier mobility, ambipolar transport, band gap within visible-light range, and an anisotropic electronic dispersion. (3; 4; 60; 215–217) Moreover, high flexibility and retention of band gap under strain allow heterostructure engineering possibilities with other semiconductors. (64; 218–220) However, the performance of two-dimensional as well as bulk semiconductors is affected by the presence of intrinsic point defects. (35; 221–223) Phosphorene is no exception to above observation.

Both surface and bulk vacancy defects have been frequently observed on account of their low formation energies, and are a likely source of the intrinsic p-type conductivity. (4; 58; 224; 225) Similar to graphene, the point defects in phosphorene relax in multiple configurations. (226; 227) The defects act as anisotropic scatterers and have been manipulated to form a many-body state with excited carriers. (224; 228) Vacancies in phosphorene induce mechanical degradation as well as structural changes under increasing strain, temperature, or vacancy concentration. (66; 229; 230) Strained phosphorene with vacancies is prone to loss in fracture strength and structural integrity along the zigzag axis due to bond distortion and breakage. Regions with high defect density are predicted to initiate crack formation followed by material failure under the transverse force generated by an atomic

force microscopy nanoindentation. (231)

Thermally activated diffusion of defects results in significant structural changes. Vacancy transformation and aggregation leading to complex defects and grain boundaries have been extensively studied in the case of graphene, (232) where the weak bonding at edges and vacancies initiate such changes. Few-layer phosphorene is observed to undergo anisotropic degradation, amorphization, and sublimation when heated above 650 K. (66; 233) Among the multiple bond breaking mechanisms which cause degradation, the current understanding stands at the diffusion of isolated vacancy within a single layer. (153)

However, complex processes involving defect-defect interaction, vacancy and adatom migration, surficial atom desorption, that result in larger defect formation are not known and need to be investigated in detail. A detailed understanding of how damage is initiated in phosphorene is necessary to identify the optimal conditions for defect-free phosphorene as well as improving the lifespan of devices.

Oxidation of phosphorene poses another significant challenge towards its stability. Phosphorene undergoes degradation in an ambient environment due to the combined effect of oxygen, water and light. Although the exact mechanism continues to be investigated, it is clear that the strong chemical bonding between lone pair electrons of phosphorus and π^* electrons of oxygen initiate the chemical degradation of phosphorene. (68–70; 234–240) Oxidation increases the hydrophilicity of phosphorene and accelerates the degradation process. (70; 234; 240) Edges and steps undergo rapid degradation in few-layered samples where the role of vacancy defects is understandably negligible. (236; 237) As the oxidation rate increases with a reduction in phosphorene layers, (69; 235) the interaction between oxygen and surficial defects will become significant with increasing surface-to-volume ratio. However, the nature of oxygen–defect interaction in phosphorene is a subject of debate among first-principles calculations. While oxidation is pro-

posed to be more favorable at vacancy over pristine surface, (241) another study claims the vacancy diffusion is unaffected by oxygen, due to weak interaction between them. (227) In the present study, various configurations for the physisorbed and chemisorbed oxygen at the vacancy site are investigated, and the oxygen molecule dissociation mechanism is elucidated for both pristine and defected phosphorene. We find the oxygen dissociation to be a barrierless process on single vacancy defect, whereas oxidation on both pristine surface and divacancy defect remains an activated process. Post-dissociation, the strong binding of oxygen atoms with both layers of phosphorene makes their removal difficult.

5.2 Computational details

The spin polarized density functional theory calculations were performed with Vienna ab initio simulation package (VASP) (128; 129) using the projector augmented wave formalism. (130) The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional describes the exchange and correlation. (83) The kinetic energy cutoff for the plane waves was set to 500 eV. Structural relaxations were performed until the ionic forces were below 0.01 eV/Å. Monolayer phosphorene calculations were performed on two sets of supercells, 6(zigzag)×4(armchair) supercell containing 96 atoms and 9(zigzag)×5(armchair) supercell containing 180 atoms. A periodic boundary condition of 15 Å was maintained along the direction of vacuum. The divacancy and interacting monovacancy migration calculations were carried out with the larger supercell whereas the remaining calculations were performed on 6(zigzag)×4(armchair) supercell. The reciprocal space integration for the two supercells was evaluated for 4×4×1 and 3×4×1 k-point grid respectively. Multi-layer calculations were performed for 6×4× n supercells ($n \leq 3$). The nonlocal van der Waals functional (optB88-vdW) of Langreth and Lundqvist

was used throughout the calculations to describe the oxygen–phosphorene and interlayer interactions. (242) The vacancy migration barriers were calculated with climbing-image nudged elastic band method (CI-NEB). (92) The true nature of the transition state is confirmed by obtaining the single imaginary vibrational mode.

5.3 Results and Discussion

Pristine phosphorene: The staggered geometry of phosphorene consists of two half-layers of P atoms that can be derived by two-fold operation on a hexagonal lattice: cleaving followed by an upward shift of one half of the hexagon. The in-plane atoms are arranged in zigzag fashion with bond lengths of 2.23 Å (along the zigzag axis), whereas the atoms across two half-layers have a slightly larger bond lengths of 2.27 Å (along the armchair axis). The half-layers are separated by a distance of 2.13 Å. Thus, every P atom is bonded to two in-plane and one out-of-plane P atoms. Given that each P atom has five valence electrons, three electrons participate in the above described bonding whereas two electrons form a lone pair cloud. The repulsion among the neighboring lone pairs leads to a staggered, anisotropic arrangement of P atoms with comparatively soft bonding. Evidently, the Young's modulus for phosphorene is substantially lower than graphene. (30; 243)

Single Vacancy: The removal of single P atom introduces dangling electrons on the undercoordinated atoms. Following their rearrangement, phosphorene relaxes to form two distinct vacancy configurations [Fig. 5.1]. The single vacancy SV(5|9) configuration involves inward displacement of the two atoms along the armchair direction to form a new P–P bond between the two half-layers, while the third P atom remains undercoordinated [Fig. 5.1(a)]. A similar (5|9) relaxation is observed for vacancy in graphene. (199) In contrast, the second configuration SV(55|66) undergoes minor displacement of atoms to form pentagon and hexagon

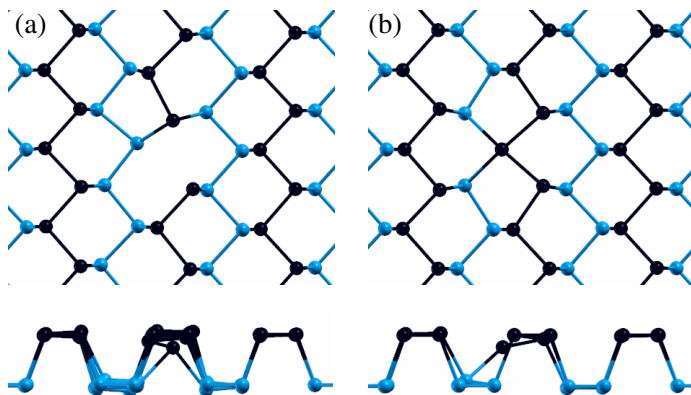


Figure 5.1: Top and side view of the two possible relaxations for single vacancy configuration in phosphorene: (a) SV(5|9) and (b) SV(55|66). The atoms surrounding the vacancy relax within the half-layers. SV(5|9) configuration is energetically favored over SV(55|66) by +0.35 eV. Black (blue) spheres denote P atoms from the top (bottom) half-layers.

pairs[Fig. 5.1(b)]. The P–P bond along the armchair direction (2.57 Å) are weaker than both pure (2.27 Å) and SV(5|9) (2.41 Å) configurations. Such four-fold coordination can occur in rippled graphene due to an increasing sp^3 character. (244)

The SV(5|9) configuration with a formation energy E_f of 1.68 eV is energetically favored over the metastable configuration SV(55|66) with a formation energy of 2.03 eV. The formation energy is calculated as $E_f = E_{total} - N_P \times E_P$ where E_{total} is the total energy of the defected supercell, E_P is the total energy of single P atom in pristine supercell, and N_P is the total number of P atoms in defected supercell. In contrast to graphene ($E_f = 7.65$ eV), it is easier to form vacancy defects in phosphorene. (199) Although the vacancy formation energies in transition metal dichalcogenides are comparable ($E_f = 1 - 3$ eV), the interstitial defects are energetically favored. (245) Further comparison with monoelemental bulk semiconductors such as Si and Ge ($E_f = 3.0 - 4.5$ eV) also highlight the defect-prone nature of phosphorene samples. (246; 247) The electronic and magnetic properties of SV(5|9) and SV(55|66) are discussed in Chapter 6 where we investigate the spintronic functionality of phosphorene.

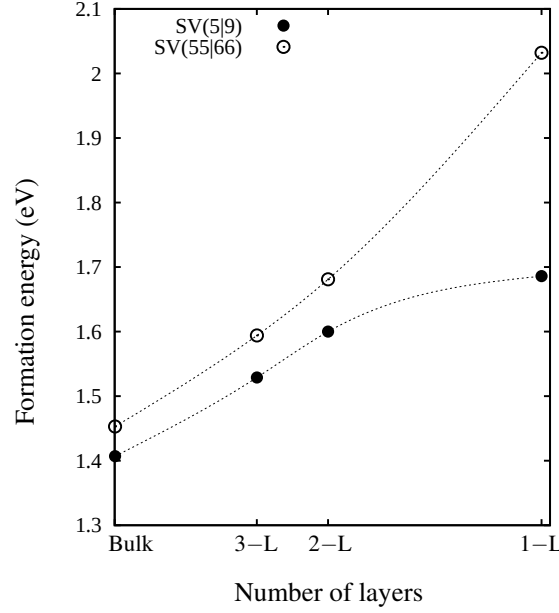


Figure 5.2: Formation energy for surficial SV(5|9) and the metastable SV(55|66) defects decreases with increasing layer thickness of phosphorene. The energy difference between SV(5|9) and SV(55|66) decreases from 350 meV in single layer (1–L) phosphorene to 48 meV within bulk phosphorene. Thus, the metastable defect SV(55|66) is likely to appear along with SV(5|9) in low temperature STM observations. (224; 225)

Distinct STM/STS signatures have been reported for SV in black phosphorus where (i) SV(5|9) and its mirror configuration ($\sigma_{armchair} / \sigma_{zigzag}$ – such that the missing atom lies on the adjacent P site within the same half-layer) were present in disparate proportion (7:4), and (ii) the two defects were identified by unique electronic states near the Fermi level. (224; 225) Above observations have been attributed to a loss of symmetry at the surface. To verify this behavior, we consider two SV(5|9) defects separated by ~ 2 nm in a supercell containing 312 atoms with defect concentration of 0.6%. Identical formation energies are obtained for both orientations of SV. The SV arrangement along armchair direction is energetically favored over zigzag ($E_{f(armchair)} = 1.71$ eV and $E_{f(zigzag)} = 1.73$ eV per SV). Thus, we do not find evidence for preferential arrangement of SV due to symmetry breaking. Since surface and bulk SV exhibit multiple charge states and relaxations, (58; 248) it

is plausible that the STS-reported distinct electronic signatures are due to coexisting SV configurations. To address this, we compare the formation energies of the two SV defects in single and multi-layered phosphorene. Here, the defect is placed on the topmost layer in case of few-layered phosphorene. The formation energy is lowered with increasing number of layers, and importantly, the difference in formation energies for the two defects also decreases [Fig. 5.2]. This supports the case for the presence of SV defects with distinct configurations.

5.3.1 Defect migration in phosphorene

Understanding the migration behavior of a vacancy in phosphorene becomes important due to their significant presence in commercial samples on account of their low formation energies. (225) Vacancy jump is a thermally activated process, and identification of temperature ranges suitable for annealing and prevention of degradation is necessary. In the following discussion, vacancy migrations in multiple layers of phosphorene are studied, including both inter- and intra- layer migration. Jumps along both the armchair and zigzag directions are considered to understand the effect of structural anisotropy on migration activity. Lastly, the activation energy to form complex defects is calculated to understand the void formation and sublimation seen during the thermal decomposition of phosphorene.

5.3.2 Anisotropic SV migration

Firstly, vacancy migration along the armchair direction is considered. The SV(5|9) overcomes a migration barrier (E_a) of 0.38 eV to translate by half lattice vector along the armchair direction [Fig. 5.3(a)]. The undercoordinated atom is displaced locally to form a bond while the vacancy jump occurs primarily by switching of bonds. The shift along the armchair direction is accompanied by a vertical movement of pentagon bond to the other half-layer. An identical barrier is obtained for

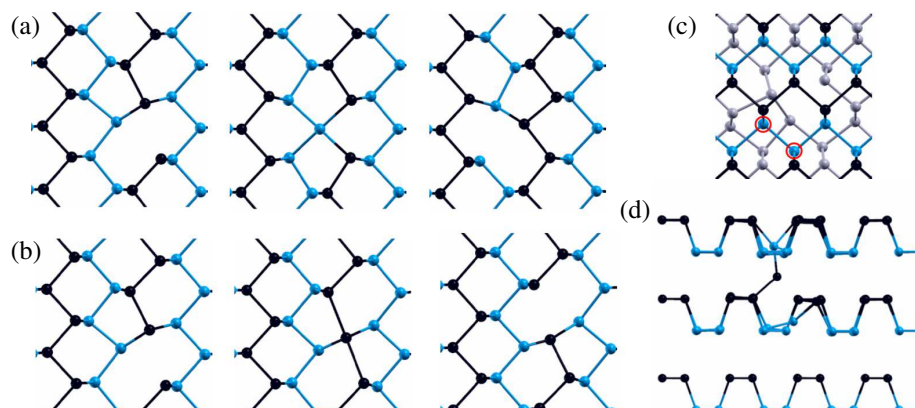


Figure 5.3: Intra-layer and inter-layer SV(5|9) migration path. The initial, transition state, and final configurations are shown for the intra-layer SV migration along the (a) armchair and (b) zigzag directions. Note that the pentagon bond switches its position along the direction of migration. Vacancy jump along the zigzag direction is found to be more favorable. (c) Inter-layer SV migration is considered for two different pathways where the nearest and next-nearest neighbor atom jump to the defected layer (migrating atoms are encircled in red). The grey P atoms belong to the second phosphorene layer. (d) P–P bonding across the two layers for the transition state configuration.

an armchair jump within the same half-layer. The migration along zigzag direction is more facile with a smaller E_a of 0.12 eV [Fig. 5.3(b)]. The undercoordinated atom is approached by the pentagon edge P atom belonging to the same half-layer. The above calculated barriers are in good agreement with previous reported values ranging between 0.18–0.40 eV. (153; 227; 249) Interestingly, the zigzag migration in phosphorene resembles the local vacancy reconstruction seen in graphene ($E_a = 0.2$ eV) [Fig. 5.4] and discussed extensively in Chapter 3. (199) The planar structure of graphene allows C_3 rotation of pentagon bond without translation of vacancy whereas, in phosphorene, a similar switch within the half-layer is not possible. Thus, a C_2 rotation of SV in phosphorene is equivalent to the rotational reconstruction in graphene. In addition to the anisotropic migration barriers, the vacancy jump mechanism discussed so far is peculiar as the undercoordinated P atom is typically considered to be weakly bonded and most likely to migrate. However,

phosphorene prefers to preserve the sp^3 bonding (staggered structure) through reorganization of P–P bonds along the half-layers. The overall vacancy migration by unit lattice vector in either direction is a combination of the anisotropic half-lattice shifts. Thus, the armchair E_a of 0.38 eV is the rate-limiting step for SV migration. In contrast, a relatively high barrier is observed in graphene ($E_a = 0.72$ eV). (199) The aggregation of vacancy defects in an anisotropic environment will lead to formation of line defects and grain boundaries, which in turn will act as sink for diffusing vacancies. (249)

The subsurface vacancies are known to behave differently from their surface counterparts across the spectrum of materials. (199; 250–252) In case of phosphorene, both types of vacancies have been observed in STM/STS studies, (224; 225) and the subsurface vacancies are predicted to have a lower formation energy. (58; 248) The subsurface vacancy migration along both directions are considered in a $6 \times 4 \times 2$ bulk supercell containing 191 atoms. The armchair SV migration has a barrier of 0.20 eV whereas the zigzag barrier is significantly lowered to 0.04 eV. Diffusion in the interior layers is clearly more favorable than the surface vacancy migration. This is in contrast to layered graphene where the vacancy migration barrier increases for subsurface vacancies and is discussed in Chapter 3. (121; 148; 199) For a single layer of graphene, the strain generated in the course of vacancy migration is countered by an out-of-plane buckling of neighboring atoms whereas the corresponding strain in phosphorene is released by relaxation along the half-layers [Fig. 5.4]. The out-of-plane buckling is restricted in multilayered graphene by neighboring sheets resulting in a higher E_a . The low migration energy for subsurface vacancies in case of phosphorene is due to the reduction in formation energies. Such correlation between formation energy and migration barrier has been reported in other bulk semiconductors. (250; 253)

The inter-layer vacancy migration is modeled with a trilayer phosphorene where

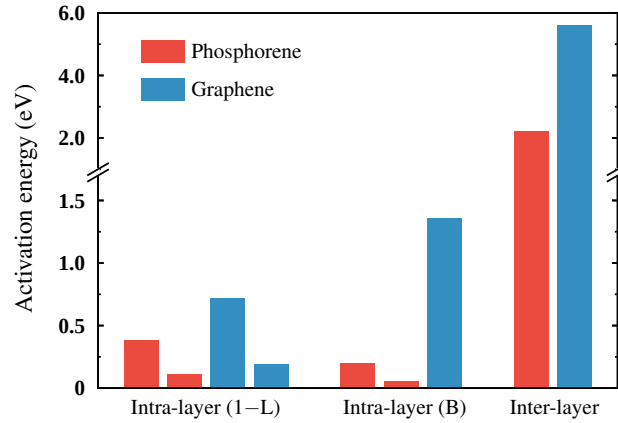


Figure 5.4: Contrasting behavior of activation energies for SV migration in phosphorene and graphene. The vacancy migration in phosphorene (shown in red) is more facile compared to graphene (blue) due to ease in P-P bonding between half-layers (or layers in case of inter-layer migration). The anisotropic structure of phosphorene results in two distinct migration pathways along the armchair and zigzag direction. Armchair migration barriers are significantly higher in both single (1-L) and multi-layered (B) phosphorene, and the SVs will preferentially migrate along the zigzag direction. Such anisotropy is absent in graphene although an on-site bond reconstruction ($E_a = 0.2$ eV) orients the SV in different directions. The SV migration in graphene induces an out-of-plane buckling, and its absence for layered graphene results in two-fold rise in activation energy. The inter-layer migration activity in both phosphorene and graphene is relevant only at high temperatures. The migration barrier energies for graphene SV are taken from (199; 254).

SV(5|9) migration between the lower half-layer of top phosphorene layer and upper half-layer of middle phosphorene layer is considered. Due to the AB alignment of individual layers, vacancies in layered phosphorene do not align vertically and diagonal jumps from the nearest neighbor atoms in the adjacent layer must be considered [Fig. 5.3(c)]. The migration energies were calculated for two separate pathways where the nearest and next nearest atom from adjacent phosphorene layer moves towards the vacancy. The migrating P atom forms a Wigner defect-like inter-layer P-P bonding along the migration path. (255) The formation of Frenkel or vacancy-interstitial pairs (discussed later) is another possibility although these complexes do not remain stable at high temperatures due to their

low activation energies [Fig. 5.7(a-b)]. The inter-layer migration barrier for nearest P atom jump is 2.17 eV while a higher barrier of 2.80 eV is obtained for the next nearest P atom. The large migration barriers for inter-layer vacancy jumps imply that such events can occur only at high temperatures and they do not play a major role in the annealing process that occurs above 473 K. (66) The barrier for inter-layer SV migration in few-layered graphene is 5.6 – 7.0 eV, and the estimated temperature at which such jumps become frequent is 2000 K. (254; 256) However, the inter-layer migration activity in graphene layers occurs at temperatures lower than 2000 K due to the formation of complex inter-layer structures and lowered migration barriers for these defects. A similar argument explains the inter-layer bonding observed in layered phosphorene. (233)

5.3.3 Vacancy-driven degradation, void formation and sublimation

Heating of few-layer phosphorene leads to formation of oblate or eye-shaped voids in individual layers, followed by inter-layer P–P bonds. Further degradation occurs by amorphization and eventual sublimation at 673 K. (66; 233) In addition to the vacancy migration discussed earlier, a better understanding of the structural degradation mechanisms is obtained from the SV $\rightarrow$ divacancy and SV $\rightarrow$ (divacancy-interstitial) pair transformations.

The divacancy defect DV(5|8|5) is formed by removal of two adjacent P atoms from the same half-layer [Fig. 5.5(a)]. A structural relaxation to pentagon–octagon arrangement ensures that every atom is three-fold coordinated, resulting in a formation energy of $E_f = 1.59$ eV which is lower than SV(5|9). Although the DV(5|8|5) has not been observed in low-temperature experiments, (224; 225) it plays an important role in the formation of metastable DV defects via bond rotations. (227) We discuss the structural and electronic properties of metastable DV defects at length

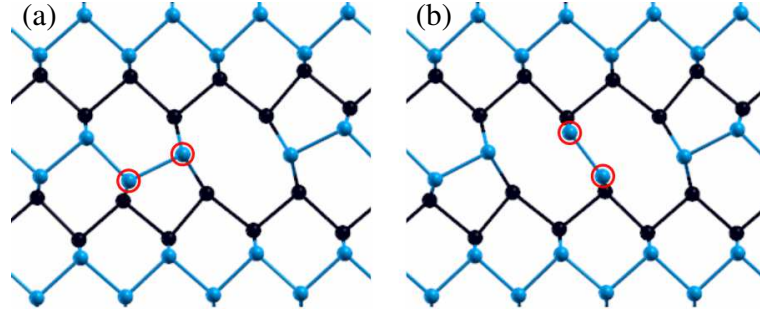


Figure 5.5: Transformation between divacancy and single vacancy defects. (a) The divacancy defect DV(5|8|5) transforms into (b) single vacancy pairs SV(5|9)-SV(9|5) via bond rotation (encircled in red) with an activation energy of 1.64 eV [Fig. 5.6(a)]. The reverse process of coalescence of the two SV(5|9) defects into DV(5|8|5) requires 0.68 eV. Thus, SV(5|9) defects in close proximity will preferentially combine to form DV(5|8|5), however at high temperature the DV(5|8|5) will split into SV(5|9).

in Chapter 6. In addition to the defect formation during growth, the DV(5|8|5) can also be formed by merger of two SV(5|9) defects [Fig. 5.5(b)]. The migration barrier for transformation of adjacent SV(5|9)+SV(9|5) $\rightarrow$ DV(5|8|5) is merely 0.68 eV while the dissociation of DV(5|8|5) $\rightarrow$ SV(5|9)+SV(9|5) has a higher barrier of 1.64 eV. Here, the clockwise rotation of the bond in [Fig. 5.5(a)] has a lower activation energy. Thus, the neighboring SV defects will coalesce and form DV(5|8|5) with relative ease. The DV dissociation barrier [Fig. 5.6(a)] is significantly higher than the previous estimate of 1.05 eV which was based on the energy differences between SV and DV configurations. (227) In fact, the local structural relaxations in SV(5|9)+SV(9|5) result in a difference of 0.93 eV with respect to DV(5|8|5) [Fig. 5.6(a)]. We propose the absence of DV(5|8|5) may be attributed to its dissociation into highly itinerant SV defects during annealing. The DV defects in graphene are stable due to a high barrier for dissociation (> 5 eV). (122; 257)

Next, we investigate the anisotropic void formation in layered phosphorene observed above 650 K. (66; 233; 258) It is proposed that the removal of an edge atom of point defect is the microscopic origin of such behavior. (66) However, the rate-

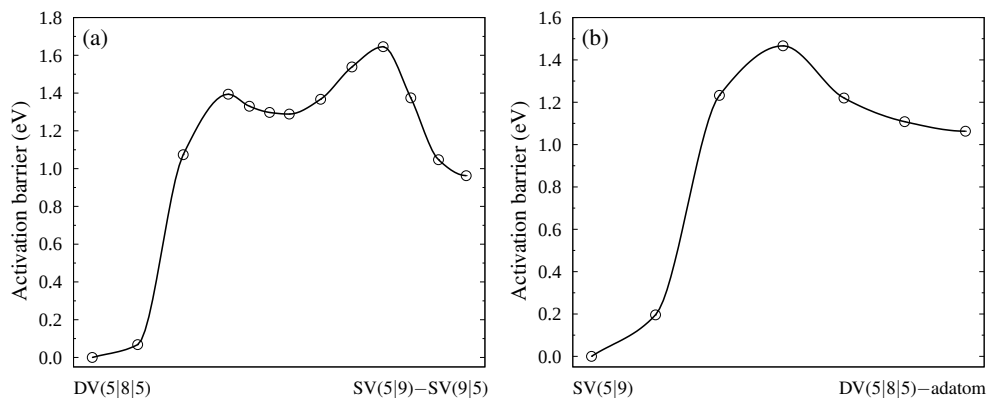


Figure 5.6: Energy profile for the transformation between (a) DV(5|8|5) and SV(5|9)+SV(9|5) complex. The low activation barrier of 0.68 eV for SV(5|9)+SV(9|5) $\rightarrow$ DV(5|8|5) favors coalescence of neighboring SV(5|9) defects while the dissociation of DV(5|8|5) $\rightarrow$ SV(5|9)+SV(9|5) requires a high barrier of 1.64 eV. (b) SV(5|9) and DV(5|8|5)+adatom complex. The undercoordinated atom of SV(5|9) can dissociate from its original site by overcoming an activation barrier of 1.46 eV and form a divacancy+adatom complex. The reverse process of DV(5|8|5) healing through adatom can easily occur at room temperature due to a low activation barrier of 0.46 eV.

determining atomistic process leading to void formation is not known. We study the transformation of SV(5|9) $\rightarrow$ DV(5|8|5)+adatom complex, where the undercoordinated P atom of SV(5|9) migrates to the nearest bridge site on pristine surface [Fig. 5.7(d)]. An activation barrier of 1.46 eV is required for the displacement of undercoordinated atom [Fig. 5.6(b)], which is in good agreement with the experimental estimate of 1.64 ± 0.1 eV. (258) The peripheral atoms of subsequent vacancy defect complexes will be displaced with similar or lower activation energies due to weak bonding at the edges, and result in an anisotropic void formation. The adatoms formed in the above process will diffuse along the zigzag direction with extremely low migration barriers ($E_a = 0.19$ eV).

Further increase in temperature accelerates the degradation and results in rapid sublimation of phosphorene layers. We address the sublimation process by considering the desorption of single and paired phosphorus adatoms from the pristine

surface. The single P adatom binds at the bridge site connecting two armchair edges with $E_f = 1.43$ eV. The adatom-surface separation of 2.19 Å is shorter than the ideal bond lengths for pristine phosphorene, highlighting the strong role of lone pair electrons in bonding. Desorption is modeled by separating the adatom 6 Å above the surface. In this case, the desorbed P atom is not bonded with the pristine phosphorene and has a high formation energy of 3.56 eV. Thus, the desorption of P adatom which is bound to phosphorene surface requires overcoming a minimum energy barrier of 2.13 eV. In contrast, we find the desorption of paired adatoms energetically favorable. The arrangement of two P adatoms adjacent to each other along the zigzag direction is found to be the most favorable ($E_f = 2.01$ eV). Compared to single P adatom, the formation energy per atom (1.0 eV) as well as adatom-surface separation (2.11 Å) in paired adatoms is significantly lower. Thus, the aggregation of P adatoms is clearly energetically preferred. Next, we investigate the desorption of paired adatoms to form a physisorbed P_2 molecule. Surprisingly, desorption decreases the energy by 0.83 eV. Further, the transformation from paired adatoms to physisorbed P_2 molecule was found to be a barrierless process. Thus, we conclude that aggregation of P atoms is critical to the rapid sublimation of phosphorene. Above observation is corroborated by the pair-wise sublimation of atoms reported for the phosphorene edges and voids. (258)

5.3.4 Defect healing and the role of adatoms

In the following discussion, we consider defect+adatom (interstitial) complexes and the activation energies to heal defects by adatoms. Frenkel defects or intimate vacancy-interstitial pair in SV(5|9) and SV(55|66) [Fig. 5.7(a-b)] are stable with formation energies of $E_f = 1.50$ and 1.87 eV respectively. The interstitial-adjacent P atoms separation (2.10 – 2.20 Å) is shorter than pristine phosphorene bond lengths. Such defects are absent in graphene due to the dominant nature

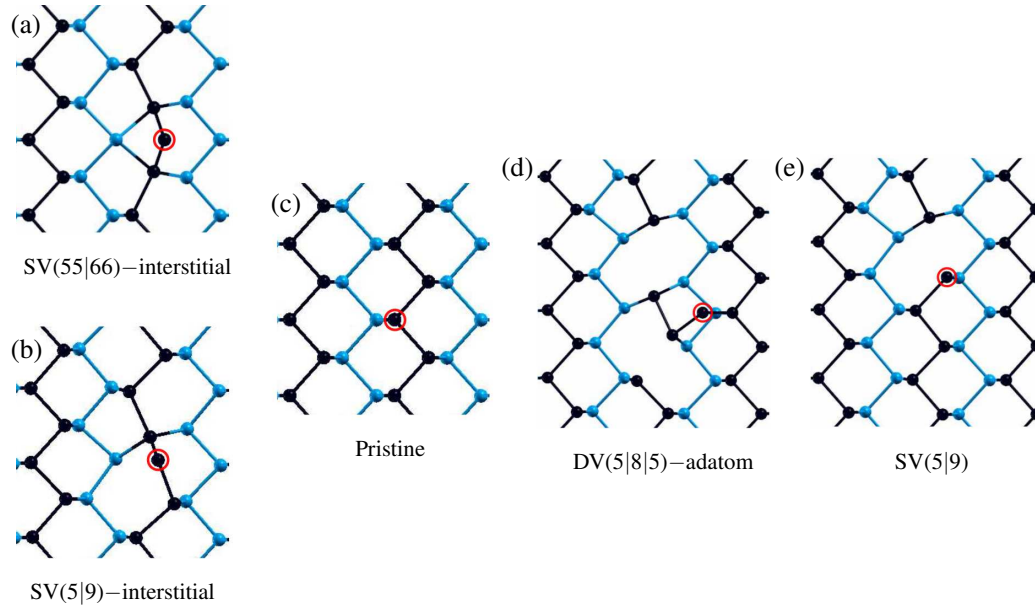


Figure 5.7: Vacancy-adatom (interstitial) complexes and their healed counterparts after recombination: Frenkel defects at the (a) SV(55|66) and (b) SV(5|9) defect complex recombine to form (c) pristine phosphorene. The interstitial atom in Frenkel defects preferentially bonds along the zigzag direction and these defect complexes are thermodynamically stable above room temperature. (d) The DV(5|8|5)-adatom complex is healed when the adatom migrates to occupy the undercoordinated atom site in (e) SV(5|9). The divacancy healing occurs at room temperature as it requires a low activation energy of 0.46 eV. The migrating atom is highlighted by red circle.

of sp^2 bonding which prevents an out of plane relaxation of adatom within vacancy. The healing of SV(5|9)+interstitial Frenkel defect requires a moderate $E_a = 0.66$ eV, whereas the SV(55|66)+interstitial Frenkel defect overcomes $E_a = 0.33$ eV to form SV(5|9)+interstitial pair. In contrast, the transformation of pristine $\rightarrow$ SV(5|9)+interstitial Frenkel defect requires a substantially high barrier of 2.20 eV and as a result, such defects can form and remain stable only at low temperatures in the course of healing process of SV(5|9). Next, we consider the healing of DV(5|8|5) defect. The DV(5|8|5)+adatom $\rightarrow$ SV(5|9) requires a barrier $E_a = 0.46$ eV, which can easily occur at 300 K [Fig. 5.7(d-e)]. Whereas, for graphene the DV(5|8|5)+adatom complexes are observed to be stable at room temperature

Table 5.1: The formation and activation energies for defect complexes in single layer phosphorene discussed in the present study.

Defect complex	Formation energy E_f (eV)	Activation barrier E_a (eV)
SV(5 9)	1.68	0.12 [zigzag], 0.40 [armchair]
SV(55 66)	2.03	–
DV(5 8 5)	1.59	0.68 [$\rightarrow$ SV(5 9)-SV(9 5)]
SV(5 9)+SV(9 5)	2.52	1.64 [$\rightarrow$ DV(5 8 5)]
Single adatom	1.43	0.19 [zigzag], 1.05 [armchair] > 2.13 [desorption]
Paired adatom	2.01	barrierless [$\rightarrow$ P ₂ molecule]
SV(5 9)+interstitial	1.50	0.66 [$\rightarrow$ pristine] 2.20 [$\leftarrow$ pristine]
SV(55 66)+interstitial	1.87	0.33 [$\rightarrow$ SV(5 9)+interstitial]
DV(5 8 5)+adatom	2.68	0.46 [$\rightarrow$ SV(5 9)] 1.46 [$\leftarrow$ SV(5 9)]

and the calculated barriers exceed 0.9 eV. (98; 257; 259) Thus, room temperature annealing of DV defects from P adatoms is possible in phosphorene.

The anisotropic diffusion of adatoms is critical for healing defects via phosphorization and annealing. Adatom migration along the zigzag direction ($E_a = 0.19$ eV) is more favorable than armchair ($E_a = 1.05$ eV). As a result, defects along the zigzag direction will be easily healed at room temperatures. However, the high annealing temperatures above 473 K are partly due to the high activation energy for an adatom to migrate along the armchair direction. (66)

The defect formation energies and migration pathways discussed so far [Table. 5.1] provide an insight into which defects are energetically favorable and how these defects undergo structural changes to form more complex structures. To further understand the defect activity and its temperature dependence, we investigate the defect hopping rate across a wide range of temperatures [Fig. 5.8]. The hopping rate ν is calculated using the Arrhenius rate equation $\nu = \nu_0 \exp(-E_a/k_B T)$,

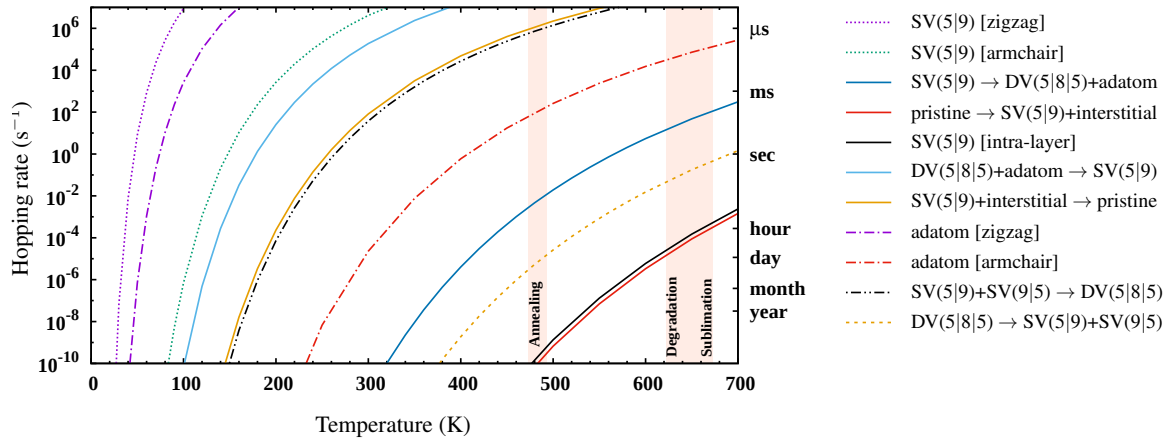


Figure 5.8: Defect activity in phosphorene at different temperatures. The defect hopping rate determines the defect migration and transformation process that takes precedence at given temperature. The annealing, degradation and sublimation temperatures are taken from (66; 233).

where ν_0 is the Debye frequency (10^{13} s^{-1}).

It must be made clear that a high hopping rate may not necessarily lead to structural modification. For instance, the DV(5|8|5) formation through merger of two SV(5|9) will occur when the SV(5|9) defects are adjacent to each other. Further, defects will diffuse randomly unless they are biased by strain or an external field. Therefore the hopping rates are indicative of defect activity and not conclusive.

We explore the temperature range and identify the dominant defect activity at different temperatures. At low temperatures, only the adatom and SV(5|9) jump in the zigzag direction have a considerable hopping rate. The hopping rates at 4 K are extremely slow (~ 1 jump per year) and such events will be absent in STM measurements. However the SV(5|9) jump along the armchair direction will occur within a measurable timescale in case of STM operating at 77 K. At 300 K, the hopping rate of SV(5|9)+interstitial $\rightarrow$ pristine healing and merger of SV(5|9)-SV(9|5) $\rightarrow$ DV(5|8|5) is high. The absence of DV(5|8|5) can also be explained from the hopping rates. The DV(5|8|5)+adatom $\rightarrow$ SV(5|9) healing rates exceeds the SV(5|9)+SV(9|5) $\rightarrow$ DV(5|8|5) coalescence rate. Further formation of DV(5|8|5) is

unlikely since it would require the randomly diffusing SV(5|9) defects to approach each other. With increasing temperature, the frequent adatom jumps along the armchair direction will heal defects and contribute to the annealing process. The observation of rapid void formation and degradation which occurs within few minutes of heating, (66; 233) is supported by the high hopping rate of SV(5|9)→DV(5|8|5)+adatom. The inter-layer SV(5|9) jump is not significant in either healing or degradation process.

5.3.5 Oxidation of pristine and defected phosphorene

Phosphorene undergoes chemical degradation in ambient environment where oxygen binds strongly with phosphorene. To understand the degradation process, we investigate the dissociation of oxygen molecule on pristine and defected phosphorene. We begin our discussion with the dissociation of O₂ on pristine surface [Fig. 5.9(a)]. The physisorbed O₂ molecule is weakly bound to the pristine surface at a height of 3.17 Å and with a binding energy (E_b) of -0.09 eV [Table. 5.2]. The binding energy is calculated as $E_b = E_{(P-O)} - E_P - E_O$ where $E_{(P-O)}$ is the total energy of the oxygen–phosphorene system, E_P is the total energy of phosphorene, and E_O is the total energy of oxygen molecule. The molecule undergoes a triplet to singlet conversion with increasing proximity to phosphorene. The O₂ molecule overcomes an activation barrier $E_a = 0.48$ eV to chemisorb on phosphorene, which is in good agreement with previous calculation. (70) Further, O₂ chemisorbs with a binding energy of $E_b = -0.18$ eV. The O atoms are weakly bonded to P atoms across the armchair direction with an increased O–O bond length. The dissociation of chemisorbed O₂ into individual dangling P–O bonds has a lower barrier of 0.13 eV. The lone pair electrons of P and divalent O electrons form a strong bond resulting in $E_b = -4.22$ eV.

In presence of puckered SV(5|9), the O₂ molecule is physisorbed above the de-

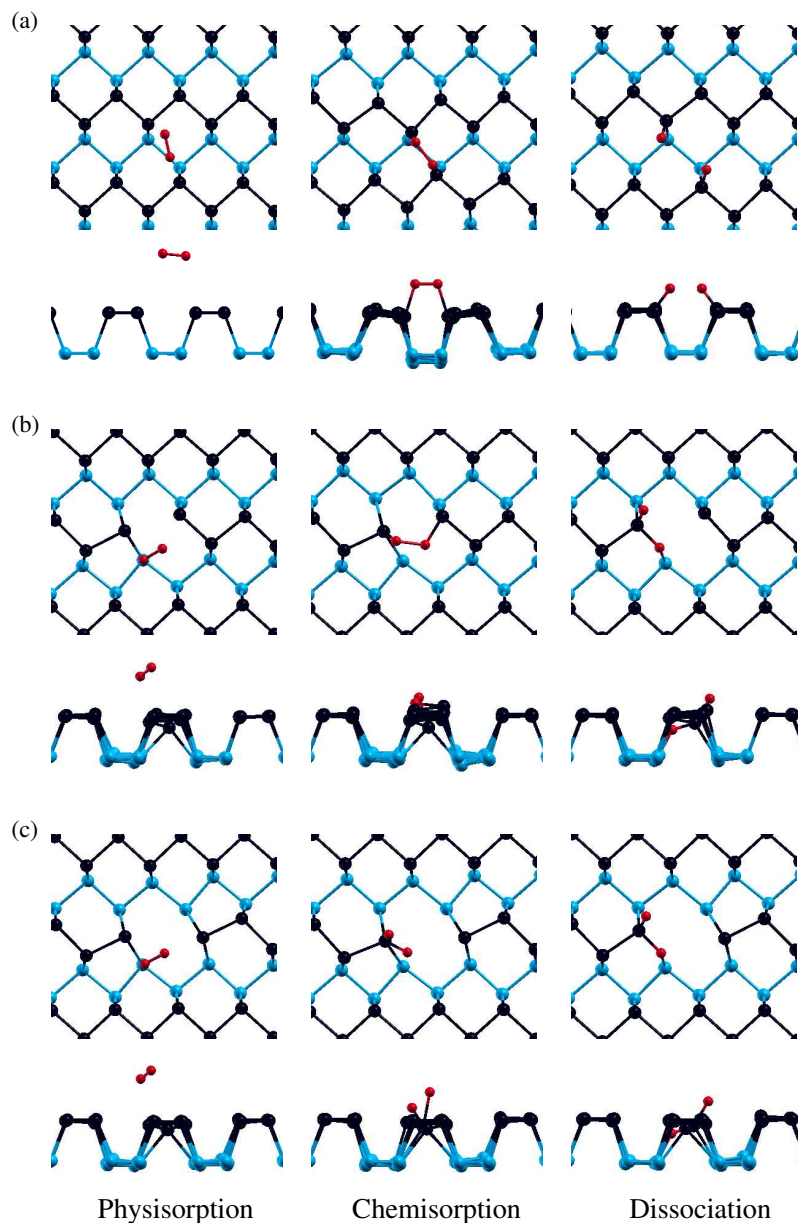


Figure 5.9: Top and side view of chemical degradation of phosphorene through O_2 dissociation on (a) pristine surface (b) SV(5|9) and (c) DV(5|8|5) defect complexes. The physisorbed and chemisorbed O_2 molecule rotate in order to bond favorably with the P lone pair electrons. While the physisorption $\rightarrow$ chemisorption process in case of pristine and DV(5|8|5) requires an energy barrier of 0.48 eV and 0.56 eV respectively, the above process on SV(5|9) proceeds without an activation barrier. Dissociated O atoms bind with the P atoms from both half-layers resulting in strong gain in binding energies.

Table 5.2: The binding energy E_b (eV), spin state S and activation energy E_a (eV) for physisorbed, chemisorbed, and dissociated O_2 molecule on pristine surface, SV(5|9) and DV(5|8|5) defect complexes.

	Physisorption E_b (S)	$\longrightarrow$ E_a	Chemisorption E_b (S)	$\longrightarrow$ E_a	Dissociation E_b (S)
Pristine	-0.09 ($S = 1$)	0.48	-0.18 ($S = 0$)	0.13	-4.22 ($S = 0$)
SV(5 9)	-0.21 ($S = \frac{3}{2}$)	–	-1.17 ($S = \frac{1}{2}$)	–	-5.47 ($S = \frac{1}{2}$)
DV(5 8 5)	-0.15 ($S = 1$)	0.56	-0.58 ($S = 0$)	–	-5.66 ($S = 0$)

fect at a height of 2.06 Å, and binds strongly ($E_b = -0.21$ eV) [Fig. 5.9(b)]. Remarkably, physisorption $\rightarrow$ chemisorption proceeds without an activation barrier. This is in contrast to the previous study where the barrier was calculated to be 0.59 eV for a different physisorbed site. (241) However, we find the physisorbed site in (241) to be a metastable configuration with $E_b = -0.16$ eV. The SV(5|9)+ O_2 system undergoes a spin-3/2 to spin-1/2 conversion, where SV(5|9) contributes spin-1/2 to the system due to the unoccupied defect states. The chemisorbed structure has a significantly higher binding energy ($E_b = -1.17$ eV) than O_2 -pristine phosphorene due to a strong P–O bond which is evident from the increased puckering at SV site [Fig. 5.9(b)]. Unlike pristine phosphorene, the dissociated O atoms embed within the lattice resulting in large gain in binding energy ($E_b = -5.47$ eV) [Table. 5.2]. Oxygen dissociation on SV(55|66) and DV(5|8|5) proceeds with an activation barrier of 0.53 and 0.56 eV respectively [Fig. 5.9(c)]. The wide range of annealing temperatures (523–643 K) for removing the oxygen impurities clearly indicates the presence of P–O bonds of varying binding strength. (260) At 643 K, the removal of O impurities will be accompanied by a plethora of intrinsic defect activities including void formation. While the O defects in multi-layered phosphorene can be removed by sublimation of surface phosphorene layer, a similar strategy is not possible in single or few-layered phosphorene.

5.4 Summary

In summary, we investigate the structural and chemical degradation of phosphorene within first-principles calculations. The point defect diffusion is found to be highly anisotropic, with lower activation barriers along the zigzag direction. The highly mobile adatom and single vacancy migration in the zigzag direction can occur below room temperature. Coalescence of neighboring single vacancies will result in divacancy defect DV(5|8|5) although the defect will dissociate to single vacancies when heated to annealing temperatures. Frenkel defect formation is possible in phosphorene and a moderate activation barrier ensures their stability at room temperature. We identify the microscopic mechanism leading to the formation of anisotropic void. Further degradation and sublimation of phosphorene occurs by aggregation of phosphorus atoms followed by their desorption. The high mobility of adatoms along the zigzag direction plays a significant role in healing defects. Oxidation on pristine surface and divacancy defect will occur at ambient conditions with a nominal activation barrier while in single vacancy defect, the oxidation is a barrierless process. The present work sheds light on the contemporaneous defect activity occurring in phosphorene and offers possible solutions to overcome its intrinsic limitations.

CHAPTER 6

INDUCING MAGNETISM IN SEMICONDUCTING PHOSPHORENE

Inducing magnetic moment in otherwise nonmagnetic two-dimensional semiconducting materials is the key first step to design spintronic materials. Here, we study the absorption of transition-metals on pristine and defected single-layer phosphorene, within density functional theory. The high diffusivity of transition-metal atoms on pristine phosphorene prevents a controlled magnetism at room temperature whereas the point-defects will anchor metals and exponentially reduce the diffusivity. Similar to other 2D materials, metals bind strongly on both pristine and defected phosphorene, and we provide a microscopic description of bonding, which explain the qualitative trend with increasing number of valence electrons. We further argue that the divacancy complex is imperative in any practical purpose due to their increased thermodynamic stability over monovacancy. For most cases, the defect-transition metal complexes retain the intrinsic semiconductor properties, and also induce a local magnetic moment with large exchange-splitting and spin-flip energies, which are necessary for spintronic applications. Specifically, the V/Mn/Fe absorbed at the divacancy have tremendous promise in this regard. Further, we provide a simple microscopic model to describe the local moment formation in these transition metal and defect complexes. This work has appeared in *The Journal of Physical Chemistry C* 120, 14991 (2016).

6.1 Introduction

Atomically thin two-dimensional (2D) materials have been a subject of intense research due to the unique physical properties originating from 2D confinement of electrons, and concurrent applications in electronic and optoelectronic devices. (8; 31; 261–266) In this regard, graphene has attracted much attention due to very high carrier mobility, $\sim 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. (8–10) However, graphene is semimetal, (8; 31; 261; 262; 267) and the lack of a band gap severely limits its application in field-effect transistor due to insufficient on-off current ratio. Thus, although without much success, extraordinary efforts have been given to induce a semiconducting gap without compromising the exceptional carrier mobility by structural modification of graphene (259; 268–270) or by external perturbations such as electric field and strain. (271; 272) In contrast, other 2D materials such as chalcogenides, (264; 265; 273) oxides, (274) and III-VI semiconductors (275) possess sizeable band gaps around 1–2 eV. Many transition metal dichalcogenides monolayers are natural direct band gap semiconductors. (273) For example, monolayer MoS_2 has a direct band gap of $\sim 1.8 \text{ eV}$, (2) which corresponds to a device on-off current ratio of 10^8 . (11) Although the carrier mobilities are much lower ($200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) than in graphene, it is still remarkably high compared to the thin-film semiconductors. (11) In contrast, the recently exfoliated single layer of black phosphorus, phosphorene, offers a better trade-off between carrier mobility and on-off ratio over existing 2D materials.

Phosphorene is a 2D semiconductor with a direct band gap of 1.45–2.05 eV, (4; 60) which is significantly larger than the bulk counterpart, 0.2–0.35 eV. (3; 61–63) This semiconducting gap of single-layer phosphorene corresponds to a large on-off current ratio of 10^5 , which is essential for any device applications. (3) The field-effect carrier (hole) mobility is found to be thickness dependent, and reported

to be as high as $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature. (3; 4) Further, the intrinsic band gap and mobility can be easily tuned by layer thickness (3; 4; 54) and external stress. (64) The intrinsic anisotropy in electronic, optical, thermal and mechanical properties make phosphorene an exciting material with promising applications in (opto) electronics, thermoelectronics, and spintronics. (3; 4; 15; 16; 67)

Inducing magnetism in otherwise non-magnetic 2D materials could potentially facilitate the application of these materials in spintronic devices and magnetic recording media. (27; 44; 276) The quest of inducing local magnetic moment is the obvious first step in this regard, followed by inducing magnetic ordering, and ability to control and tune it by gating, doping and functionalization. Transition metal (TM) doping is the conventional way to induce magnetism in such nonmagnetic 2D materials, and has been already deployed for graphene (44; 276) and phosphorene. (277–279) Interestingly, cobalt adsorbed pristine phosphorene is found to show magnetic ordering, which could be further manipulated by gating. (72) Moreover, room-temperature ferromagnetism is predicted in this system. The magnetic ordering in such metal doped 2D systems and the concurrent Curie temperature are dictated by the relative distance and orientation between the doped TMs. (280; 281) However, the magnetism may not be controllable in such systems due to very high TM diffusivity (resulting from their low activation barrier) on pristine 2D surface. (44; 276) Such high TM diffusivity will severely affect their spatial distribution on pristine 2D surface, resulting in uncontrolled magnetism. Therefore, it is desirable to decorate TMs at the intrinsic vacancy defects, which will anchor the TMs, and concurrently restrict their diffusion. (44; 282) With the recent experimental advent, such vacancy defects and defect-TM complexes can be created with atomic precision that has been demonstrated already for graphene. (283–285)

Here we report the electronic and magnetic properties of 3d TMs absorbed on

the pristine and defected single-layer phosphorene, and discuss our results in the context of spintronic applications. The present first-principles calculation is extensive; all the observed trends in electronic and magnetic properties are explained within microscopic models, and the important parameters for spintronic applications such as exchange-splitting and spin-flip energies are calculated. We argue that the TM doped pristine phosphorene is not suitable for any practical purpose due to very high TM diffusivity. In contrast, the TM-vacancy complexes are robust and exhibit a diverse electronic and magnetic properties.

6.2 Computational details

We use the spin-polarized density functional theory (DFT) (128; 129) within the projector augmented wave formalism (130) with a plane-wave cut-off of 500 eV. The exchange correlation is described with Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation, (83) if not explicitly specified. Few of the calculations are repeated with Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional. (85) All calculations are carried out using a 7×5 phosphorene supercell along the zigzag and armchair directions, respectively, and a vacuum layer of 15 Å is used. Reciprocal space integration is carried out using $4 \times 4 \times 1$ Monkhorst-Pack k-point sampling. All structures are optimized until all the forces on each atom are less than 0.01 eV/Å. Transition-metals are absorbed on the pristine, and defected single-layer phosphorene, and the present calculation refer to a very dilute limit of adatom (doping) concentration, 0.7%. The DFT is coupled with climbing-image nudged elastic band (CINEB) method (92) to calculate the activation barrier for TM diffusion. The integrity of the minimum energy path and thus of the first-order transition state is confirmed by one-and-only-one imaginary phonon frequency.

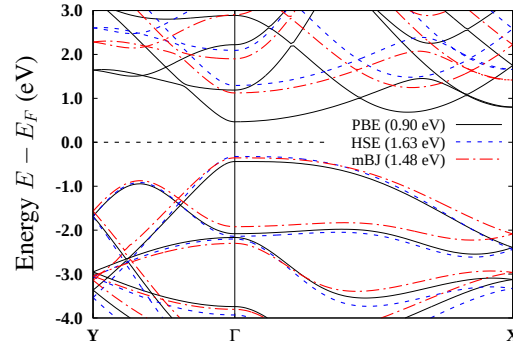


Figure 6.1: Band structure for single-layer pristine phosphorene within different exchange-correlation functionals, PBE, mBJ, and hybrid HSE06. The conventional PBE functional underestimates the gap. Note that both mBJ and hybrid HSE06 functionals have little effect on the valence band dispersion, but pushes the conduction band to higher energy, and thus widen the bandgap.

6.3 Results and Discussion

6.3.1 Pristine and defected single-layer phosphorene

We start our discussion with pristine single-layer phosphorene. The present discussion differs from the previous chapter since a different functional was used earlier. Phosphorus atoms are arranged in the puckered honeycomb lattice such that two half-layers are separated by 2.10 Å distance, and have two inequivalent P–P bonds, 2.22 (in-plane) and 2.26 Å (out-of-plane). The single layer phosphorene is found to have semiconductive nature with a direct band gap, which is calculated to be 0.90 and 1.48 eV within different treatment of exchange-correlation functionals, PBE and mBJ, respectively [Fig. 6.1]. This is in agreement with previous theoretical calculations. (54; 58; 277; 286; 287) In comparison, the spectroscopic measurements predict the gap to be 1.45–2.05 eV. (4; 60) It is well known fact that conventional DFT calculations tend to underestimate the gap, which could be improved via computationally expensive hybrid exchange-correlation functional or many-body perturbation (GW) approach. (4; 54; 58; 59) Indeed, the HSE06 hybrid

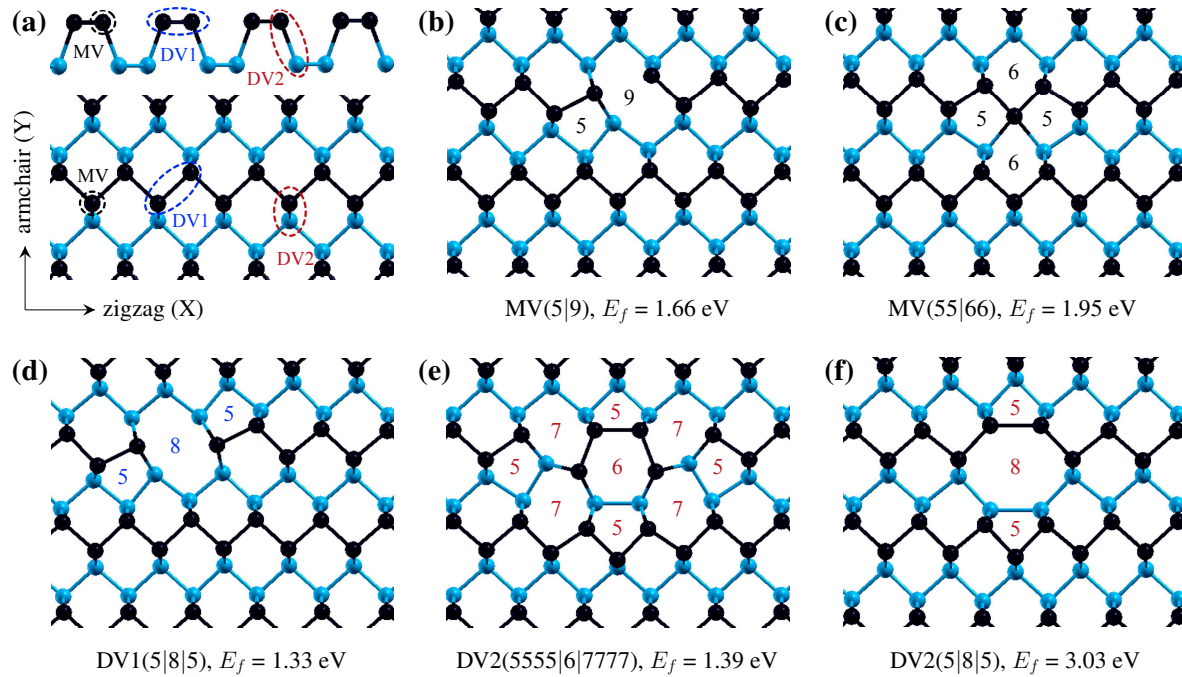


Figure 6.2: Point-defect structures in single-layer phosphorene and their formation energy. (a) Side and top view of pristine phosphorene. Two half-layers are indicated in black and light blue color. The atoms are highlighted, which are removed to create point defects. Note that the DV can be created by removing two neighbouring atoms from the same or different half-layers, DV1 and DV2, respectively. (b)-(c) The MV defect structures, with MV(5|9) as the ground state. (d)-(e) Different DV structures. The DV1(5|8|5) is the ground state, which is thermodynamically more stable than MV. Due to their very high formation energy, the other DV structures, DV2(5555|6|7777) and DV2(5|8|5) are much less probable.

functional improves the band gap to 1.63 eV [Fig. 6.1]. In the case of single and few-layer phosphorene, although the conventional PBE functional underestimates the gap, it is important to note that the electronic band dispersion is similar with hybrid functional or GW approach. (4; 54; 58; 59)

Next we consider the bare point-defects, mono- and di-vacancies. As-prepared 2D materials are prone to vacancy defects, (94; 287; 288) which can also be created with atomic precision, (283–285) and may alter the intrinsic electronic, magnetic and chemical properties. (94; 289–291) In the spintronic context, it would be interesting to address if the intrinsic semiconducting property is retained as

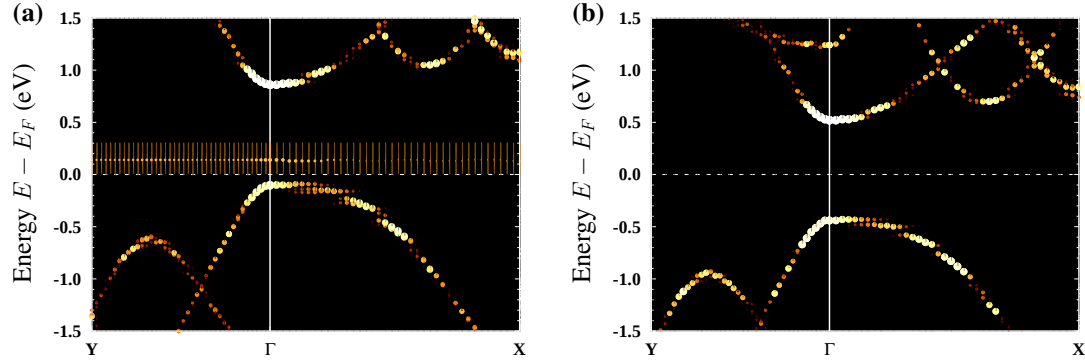


Figure 6.3: Band structure for (a) bare and (b) hydrogenated mono-vacancy in the MV(5|9) configuration calculated within PBE exchange-correlation functional. Due to unpassivated dangling bond, a mid-gap defect state appears, and thus the bandgap is lower, 0.21 eV. In contrast, while the dangling bond is passivated by hydrogen, the mid-gap state disappears and the defected phosphorene open-up the gap, 0.95 eV, which is equivalent to the pristine phosphorene.

the point-defects are introduced in single-layer phosphorene. Removing one P atom to create monovacancy (MV) in phosphorene [Fig. 6.2(a)] leaves one dangling bond each on three adjacent P-sites before lattice relaxation. Following this, there are two distinct relaxation paths, which lead to two distinct MV structures, MV(5|9) and MV(55|66), (153; 248; 287; 292; 293) shown in [Fig. 6.2(b)-(c)]. We find the Jahn-Teller distorted MV(5|9) [Fig. 6.2(b)] to be the most probable monovacancy structure with 1.66 eV formation energy, which is 0.29 eV lower than the hypervalent MV(55|66) structure [Fig. 6.2(c)]. The formation energy is calculated as $E_f = E_d - E_p + N\mu$, where E_d and E_p represent the energies of the fully relaxed system with and without the vacancy defect; N is the number of removed atoms, and μ is the chemical potential of P calculated from pristine phosphorene. Similar MV structures have been observed for flat graphene (98; 108; 110; 122) and slightly buckled silicene, (152; 291) but the formation energies in these cases are much higher, ~ 7.5 and 3 eV, respectively. (110; 152) Survival of one dangling bond in MV(5|9) induces a local magnetic moment of $1 \mu_B$ in phosphorene, and also generates a defect state 0.21 eV above the valence band maximum (VBM). Thus, bare

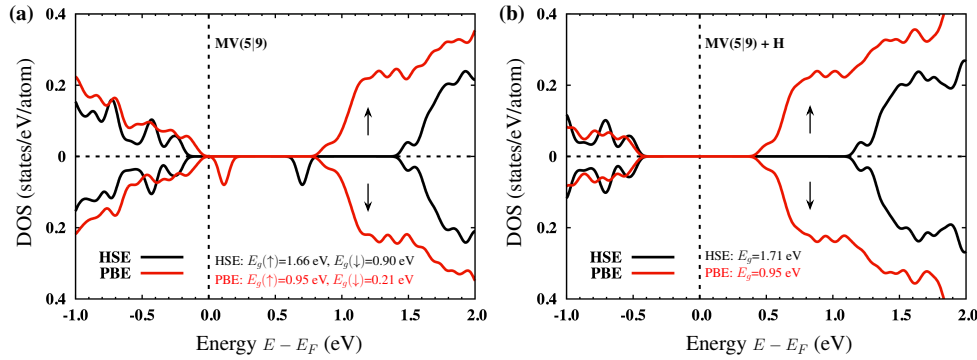


Figure 6.4: Calculated density of states for (a) bare and (b) hydrogenated mono-vacancy. Results from PBE and HSE06 functionals are compared. In the case of hybrid HSE06 functional, the conduction band is pushed higher in energy, and thus increases the bandgap.

MV(5|9) substantially reduces the intrinsic band gap of phosphorene.[Fig. 6.3(a)] However, once the dangling bond is passivated (with atomic H in the present case), both the local moment and defect state disappear, and the intrinsic semiconducting gap (0.95 eV) is recovered, which increases to 1.71 eV for hybrid HSE06 functional [Fig. 6.4(b)]. The complex supercell band structure is unfolded onto the primitive Brillouin zone. (88; 89)

Divacancy in phosphorene can be created in two different ways by removing two neighboring P-atoms from the same or different half-layers, which we classify as DV1 and DV2 type [Fig. 6.2(a)]. Similar to the situation in graphene, the concurrent relaxation and reconstruction via Stone-Wales (SW) bond rotation may lead to a plethora of divacancy structures. (153; 248; 292; 293) We find DV1(5|8|5), where the neighboring P-atoms are removed from the same half-plane, to be the most stable defect structure with 1.33 eV formation energy [Fig. 6.2(d)]. The other possibility of removing two neighboring atoms from two different half-layers relaxes to a different type of DV2(5|8|5) structure [Fig. 6.2(f)] with a much higher formation energy (3.03 eV). The other DV classes, DV(555|777), and DV(5555|6|7777) can be reconstructed from either of the DV(5|8|5) structures by SW bond rotations, which

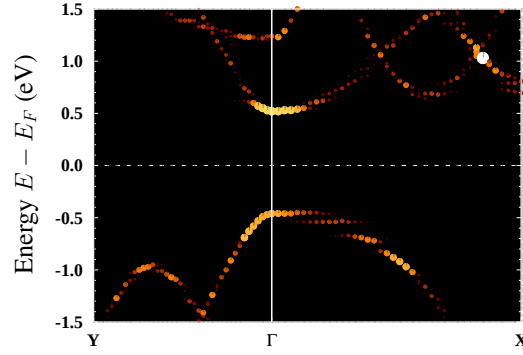


Figure 6.5: Band structure for divacancy DV1(5|8|5) calculated within PBE exchange-correlation functional for the 7×5 supercell.

is an activated process. The DV2(5555|6|7777) shown in [Fig. 6.2(e)] is found to be close in energy with DV1(5|8|5) ground state, with 1.39 eV formation energy. This structure is derived from DV2(5|8|5) by two successive SW rotations to minimise the strain energy. The DV(555|777) structures are found to be much higher in energy, (153; 292) and we did not consider them in the present study.

Due to the complete quenching of dangling bonds, DVs are found to be non-magnetic, and no mid-gap states are observed. Both DV defects DV1(5|8|5) and DV2(5555|6|7777) retain the intrinsic semiconducting nature of phosphorene with a band gap of 0.97 [Fig. 6.5] and 1 eV, respectively. The calculated PBE and HSE06 gaps [Fig. 6.6] for DV1(5|8|5) are close to the gaps for the pristine single-layer phosphorene within the same level of theory. Thus, the intrinsic semiconducting gap is robust against defects.

Similar DV structures have been found in graphene (94; 122) and silicene. (152) However, the qualitative stability of the DVs in these 2D materials is very different than the one predicted here for phosphorene. Moreover, similar to the case of MV, the DV formation energy in phosphorene is much smaller compared to graphene (~ 7.2 eV (153)) and silicene (2.84 eV (152)). This indicates that point-defect formation is comparatively easier in phosphorene. The reason behind smaller defect

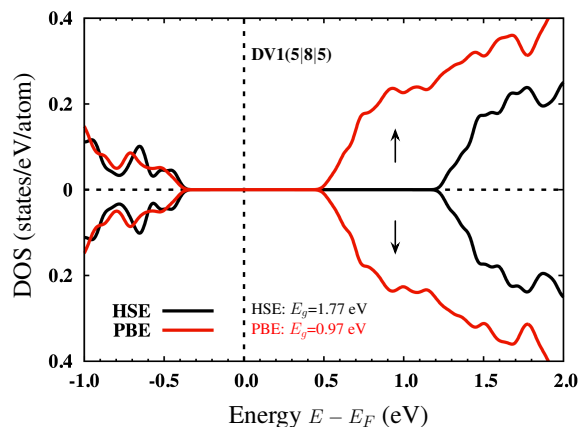


Figure 6.6: Calculated density of states for DV1(5|8|5) within PBE and hybrid HSE06 functionals.

formation energy is two fold. The P–P bond is less stronger than the C–C bond in graphene and Si–Si bond in silicene. Secondly, due to the inherent puckered structure of the phosphorene lattice, the local strain relaxation is much easier.

The remarkable reduction in DV formation energy, compared to that of the two isolated MVs, indicates that DVs are thermodynamically more stable than isolated MVs. The isolated MVs will coalesce into DV via diffusion, which requires a rather small activation barrier as discussed in Chapter 5. Thus, DV is more important in the context of TM-vacancy complex, and for any practical purpose. However, these vacancy defects may appreciably alter the electronic structure of 2D materials by generating mid-gap states, which can act as sink for charge carrier and act as electron hole recombination centre. This may severely limit device performance in (opto)electronic applications. Unlike graphene and silicene, (94; 289–291) vacancy defects are found to be electronically inactive in phosphorene. We do not find any mid-gap states for hydrogenated MV and DV, and in both case the intrinsic semiconducting gap is retained. The semiconducting properties are also found to be very robust against extended defects such as dislocations, and grain boundaries. (287)

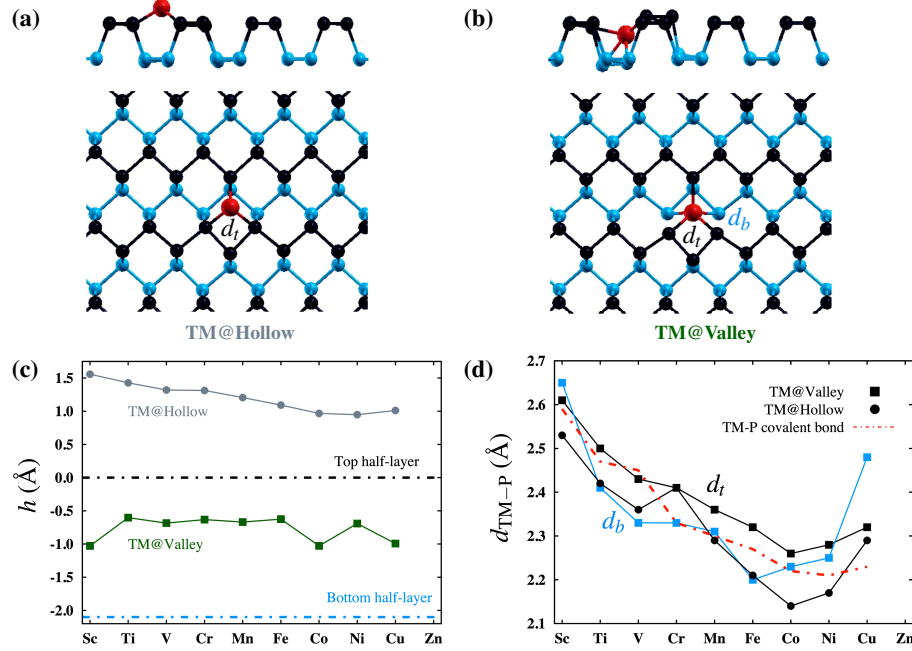


Figure 6.7: Transition-metal absorption on pristine phosphorene. Side and top view of (a) hollow and (b) valley site absorption. The TMs are absorbed at the valley site, between the top (black balls) and bottom (blue balls) half-layers. The valley site absorption is ~ 1 eV stronger than hollow site absorption. (c) Vertical height h of the absorbed TM with respect to the half-layers. Calculated TM-P bond lengths (d_{TM-P}) with the P-atoms from top (d_t) and bottom (d_b) half-layers, which are found to be covalent. The red dotted line refers to the corresponding TM-P covalent bond lengths. (294)

6.3.2 Inducing local moment: TM on pristine phosphorene

The conventional way to induce local magnetic moment in otherwise non-magnetic 2D materials is through absorption of TMs with localized d electrons. This has been attempted for graphene (276) and recently for phosphorene. (277; 279; 286) Following these recent reports, (277; 279; 286) it was earlier believed that TMs prefer the hollow site, where it is covalently bonded with three P atoms, all from the ‘top’ half-layer. [Figure 6.7(a)] Due to puckered structure, the TM atoms are relaxed away from the exact hollow site, resulting in two equivalent TM-P bonds with equal bond lengths, which is slightly smaller than the third bond. The height of the TM atoms above the phosphorene surface monotonically decreases along

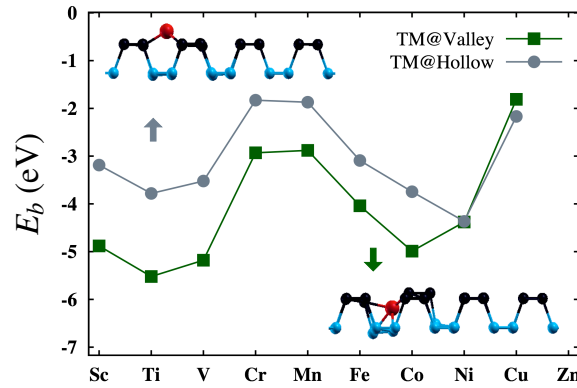


Figure 6.8: Absorption energy of 3d TM adatom on pristine phosphorene. Schematic illustration of adatom absorption at the hollow and valley sites are shown. For Sc–Co, a new absorption site TM@Valley is found to be thermodynamically more favourable than absorption at the hollow site, which has been proposed earlier. (277; 279; 286) The overall trends could be corroborated through crystal orbital Hamiltonian population (COHP) calculation as described in the main text.

the 3d series, which is commensurate with the corresponding TM covalent radius [Figure 6.7(c-d)].

In contrast, we predict a completely different absorption site with different bonding, electronic and magnetic properties. We find that TM prefers the valley site, where it is absorbed in between the two half-layers [Figure 6.7(b)] and forms five/seven TM–P bonds. The TM atoms are typically absorbed at depth between 0.5 to 1.0 Å measured from the top half-layer and their bonding is shorter than the TM–P single covalent bond.[Figure 6.7(c-d)] The TM binding energy at the valley site is substantially stronger (by -0.9 to -1.8 eV) compared to hollow site absorption (Figure 6.8). The binding (absorption) energy is calculated as $E_b = E_{\text{TM@P}} - E_{\text{P}} - \mu_{\text{TM}}$, where $E_{\text{TM@P}}$ and E_{P} is the energy of the system with and without the TM, μ_{TM} is the energy of a isolated TM. For Ni and Cu, both the absorption sites are found to be equally preferable. Due to closed-shell electronic configuration, Zn binds either very weakly (-0.15 eV at the hollow site) or does not bind at all (valley site). Incorporation of van der Waals interaction in the calculation does not improve the situation for Zn. Overall the metal atoms bind very

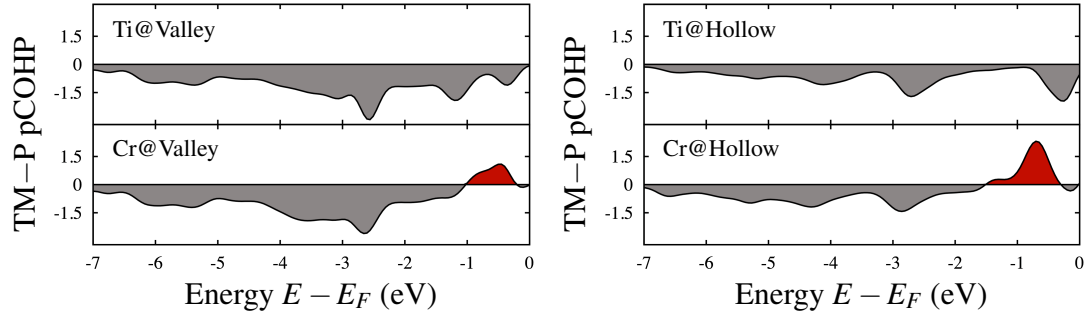


Figure 6.9: Partial TM-P COHP calculated for TMs absorbed on the pristine phosphorene at the valley and hollow sites. The negative (positive) pCOHP represents bonding (antibonding) states. The integrated pCOHP indicate the covalent TM-P bonds are relatively stronger for the valley site absorption than the absorption at the hollow site. This corroborate the stronger TM binding at the valley site.

strongly with phosphorene, and the binding energy ranges between -1.81 to -5.52 eV at the valley site (Figure 6.8). This is much stronger compared to the same on graphene, which is estimated in the range of -0.17 to -1.95 eV. (276) The stronger TM binding is due to the covalent TM-P bonding originated from the lone-pair electrons of P atoms.

To corroborate the overall trends in greater stability of valley site absorption and variation in binding energy along the $3d$ series, we have calculated the TM-P projected crystal orbital Hamiltonian population (pCOHP) (90; 91) as seen in [Figure. 6.9]. The integrated pCOHP, which is a measure of bonding, is found to be much higher for TM@Valley than the TM@Hollow configuration. For example, IpCOHP for Ti@Valley and Cr@Valley is much higher (-7.83 and -6.44 eV, respectively) than the corresponding absorption at the hollow site (-4.88 and -2.85 eV, respectively).

Now we turn our attention to the local moment induced by TM absorption. Calculated magnetic moments are shown in [Figure 6.10] for both TM@Valley and TM@Hollow absorption. Although the absorption at the hollow site is not preferred, calculated moments agree well with previous predictions. (277; 279; 286) The magnetic moment at the valley site is smaller than the hollow site absorption

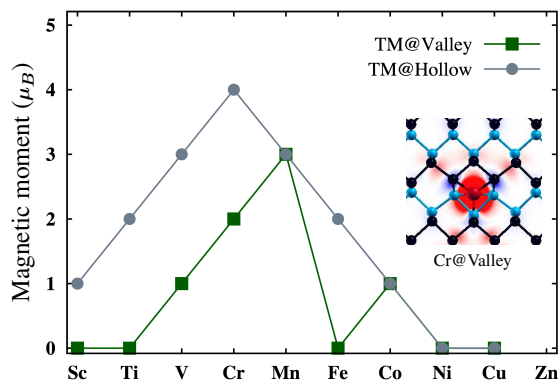


Figure 6.10: Local magnetic moment at the TM site for TM absorption on the pristine phosphorene. In general, the TM moment is smaller in case of TM@Valley absorption, which is found to be the favorable absorption site. The trend along the 3d series can be explained by simple electron counting. Representative magnetization density for the valley site absorption (Cr@Valley) is shown in the inset.

for Ti-Cr, while beyond Cr, both the absorption sites generate similar moments [Figure 6.10]. This observed trend in magnetic moment along the 3d series can be understood by simple electron counting. For TM@Hollow cases, two electrons take part in the bonding, and thus do not contribute to moment formation. The rest of the electrons are distributed in the four available *d*-orbitals such that a high-spin solution is favorable. For example, Mn@Hollow has five electrons that are distributed in four available non-bonding *d*-states, which give rise to a high-spin 3 μ_B moment. In contrast, four electrons take part in bonding for TM@Valley, which is evident from increased number of TM—P bonds. Rest of the *d*-electrons are distributed in three available *d*-orbitals such that a high-spin solution is favorable. For example, the Mn@Valley has three *d*-electrons that are to be distributed in three non-bonding *d*-orbitals, which consequently generates 3 μ_B moment (Figure 6.10). The low-spin solution is only 30 meV higher in energy in this case. The Fe@Valley is found to be the only exception to this simple model. The model predicts a 2 μ_B ground state, which we find to be almost 300 meV higher in energy than the non-magnetic ground state. The proximity polarization at the P atoms are found to be very small in these cases ($-0.04 \mu_B$ for Cr@Valley to $0.07 \mu_B$ for Mn@Valley).

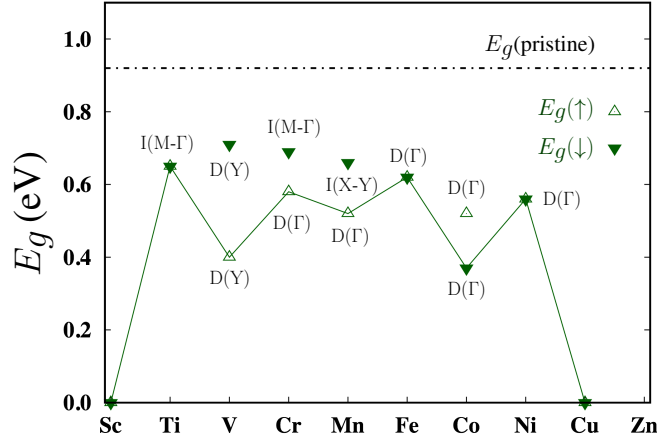


Figure 6.11: The magnitude and nature of spin resolved band gaps for TMs absorbed at the valley site on the single-layer phosphorene. The solid line is a guide to the lowest gaps along the $3d$ series. The nature of the gap is indicated by D (direct) and I (indirect) along with the k-points in the Brillouin zone. I(X-Y) indicates that the VBM is a X-point and CBM is at Y-point of the Brillouin zone.

Further, these TM@Phosphorene systems must have a semiconducting gap for any plausible spintronic application. Although the intrinsic gap decreases upon TM absorption, we find TM@Valley posses a formidable semiconducting gap in the range 0.4–0.65 eV, except for Sc and Cu [Figure. 6.11 and Table. 6.1]. The comparatively smaller gap is due to the appearance of hybridized $p - d$ states within the gap. It is also interesting to note that the anisotropic dispersion along the zigzag and armchair direction is not affected by the TM adatom absorption, which is intrinsic to single-layer phosphorene. Phosphorene becomes metallic due to Sc and Cu adatom adsorption [Figure. 6.11] as they dope electron. This is in agreement with the recent experimental observation, (295) and these systems could be used to lower the threshold voltage for n -type conduction.

Although TMs bind strongly on pristine phosphorene, induce local magnetic moment, and also hold semiconducting gap, such TM-phosphorene system may not be a good candidate material for any practical purpose due to very high TM diffusivity. The TM diffusion is an activated process, and on a 2D surface the diffusivity is defined as $D = \frac{1}{4}a_0^2\Gamma$, where a_0 is the jump distance, and Γ is the Arrhe-

Table 6.1: Calculated band gaps for TM absorbed at the valley site on pristine phosphorene. Nature of the gap is indicated by D (direct) and I (indirect), and the k-points are indicated in the parenthesis.

TM@Valley		
TM	$E_g(\uparrow)$ (eV)	$E_g(\downarrow)$ (eV)
Sc	–	–
Ti	I(M- Γ) = 0.65 D(M) = 0.66 D(Y) = 0.67 D(Γ) = 0.76	I(M- Γ) = 0.65 D(M) = 0.66 D(Y) = 0.67 D(Γ) = 0.76
V	D(Y) = 0.41 I(Γ -Y) = 0.41 D(Γ) = 0.43	D(Y) = 0.71 I(X-Y) = 0.80 D(Γ) = 0.83
Cr	D(Γ) = 0.59	I(M- Γ) = 0.69 D(Γ) = 0.81
Mn	D(Γ) = 0.52	I(X-Y) = 0.67 D(Γ) = 0.72
Fe	D(Γ) = 0.62	D(Γ) = 0.62
Co	D(Γ) = 0.53	D(Γ) = 0.38
Ni	D(Γ) = 0.57	D(Γ) = 0.57
Cu	–	–

nius jump rate, $\Gamma = \nu \exp(-E_a/k_B T)$ with ν being the prefactor related to atomic vibration, and E_a is the activation barrier. The activation barrier for valley to valley diffusion is calculated to be 0.69 eV for Co [Figure 6.12], which correspond to $D_{\text{Co}}(300 \text{ K}) = 2.61 \times 10^{-15} \text{ cm}^2/\text{s}$ assuming $\nu = 10^{13} \text{ Hz}$. Similarly, we calculate the activation barrier for Co diffusion between the metastable hollow sites to be 0.45 eV. The corresponding diffusivity in this case is $2.2 \times 10^{-9} \text{ cm}^2/\text{s}$, which is several

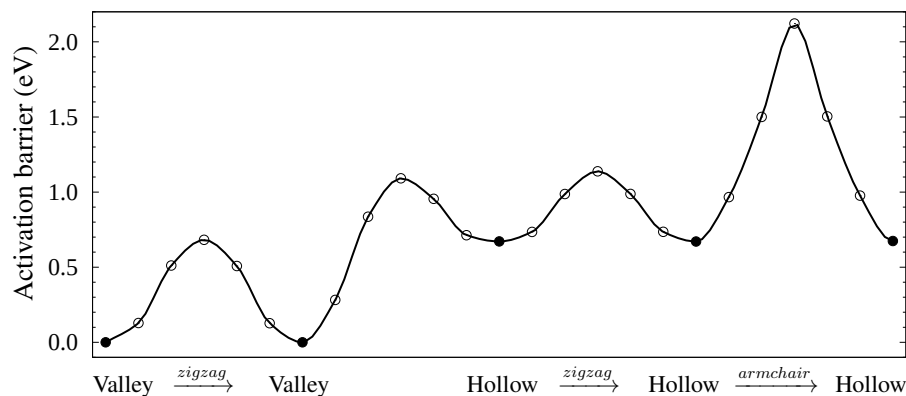


Figure 6.12: Activation barrier for Co adatom migration on pristine phosphorene. The low activation energy for valley-to-valley as well as hollow-to-hollow jumps result in a highly mobile Co atom at room temperature. The high migration energy along the armchair direction reflects the anisotropic character of phosphorene.

orders lower than the valley to valley diffusion. Thus, at 300 K, the Co atom will be very mobile. Our observation was later confirmed by the recent experiments on Co atom deposited on phosphorene surface. (71) The adatoms which were observed to be stable at 4 K showed high diffusivity at room temperature and resulted in three-fold reduction in Co areal density within ten minutes of room temperature annealing. Thus, due to very high diffusivity, TM induced magnetism on pristine phosphorene is not controllable due to time and temperature dependent spatial TM distribution. We also investigate the adatom jumps along the armchair direction [Figure 6.12]. A significantly high activation energy of 1.27 eV must be overcome by the adatom in order to diffuse in the armchair direction. As a result, the atom will preferentially move along the zigzag channel. Further, Co@Valley will retain its arrangement due to a 1.07 eV barrier to migrate to the hollow site. In contrast, the Co@Hollow site can migrate to valley site with ease due to a low barrier of 0.40 eV. From the above discussion, it is clear that TM migration barriers play an important role in determining the viability of the system towards spintronic applications. The high diffusivities for Co@Hollow and Co@Valley clearly demonstrate the operating range for TM–pristine phosphorene based spintronic

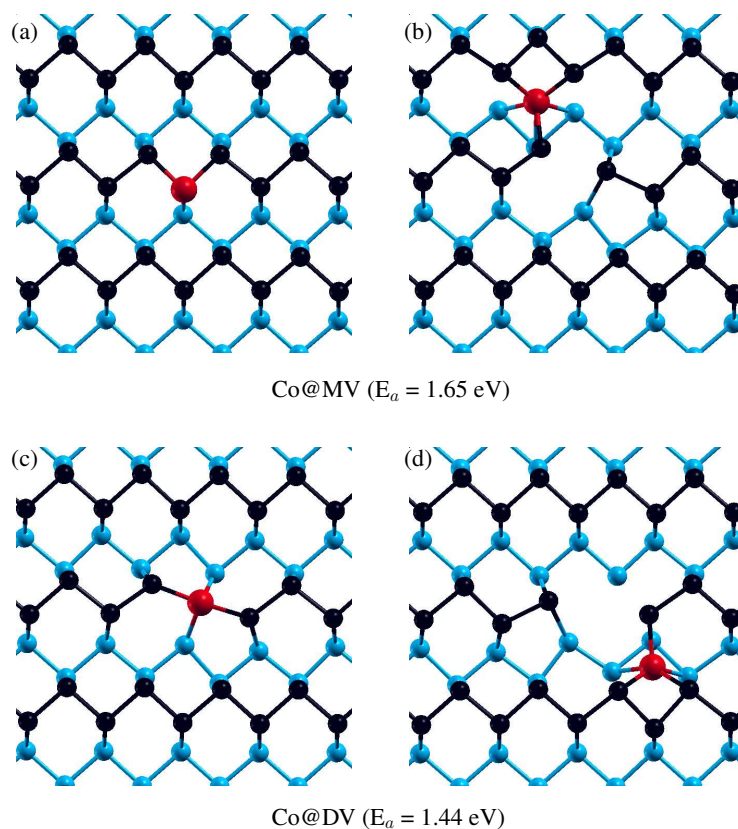


Figure 6.13: Migration of Co from vacancy complex to the nearest favorable site. (a-b) The activation energy for Co to break away from MV and migrate to next energetically favorable site is 1.65 eV. (c-d) Similarly, Co jumps from DV to the nearest metastable arrangement by overcoming an activation barrier of 1.44 eV. Compared to pristine phosphorene, the high migration barriers for Co in vacancy complexes will pin the TM atom at defect site at room temperature.

devices is below room temperature.

In contrast, vacancy defects could act as anchoring site, which substantially increases the activation barrier, and thus TM diffusivity is exponentially reduced. The calculated activation barrier for Co diffusion out of the vacancy defects are calculated to be 1.65 and 1.44 eV for Co@MV and Co@DV complexes, respectively [Figure 6.13] and their diffusivities at 300 K are several orders of magnitude lower than pristine phosphorene ($\sim 10^{-28} - 10^{-30}$ cm²/s). Such point-defects are present in the as-prepared samples or can be wishfully created on the phosphorene surface. Once absorbed at the defect site, the TM local moment is essentially pinned, and

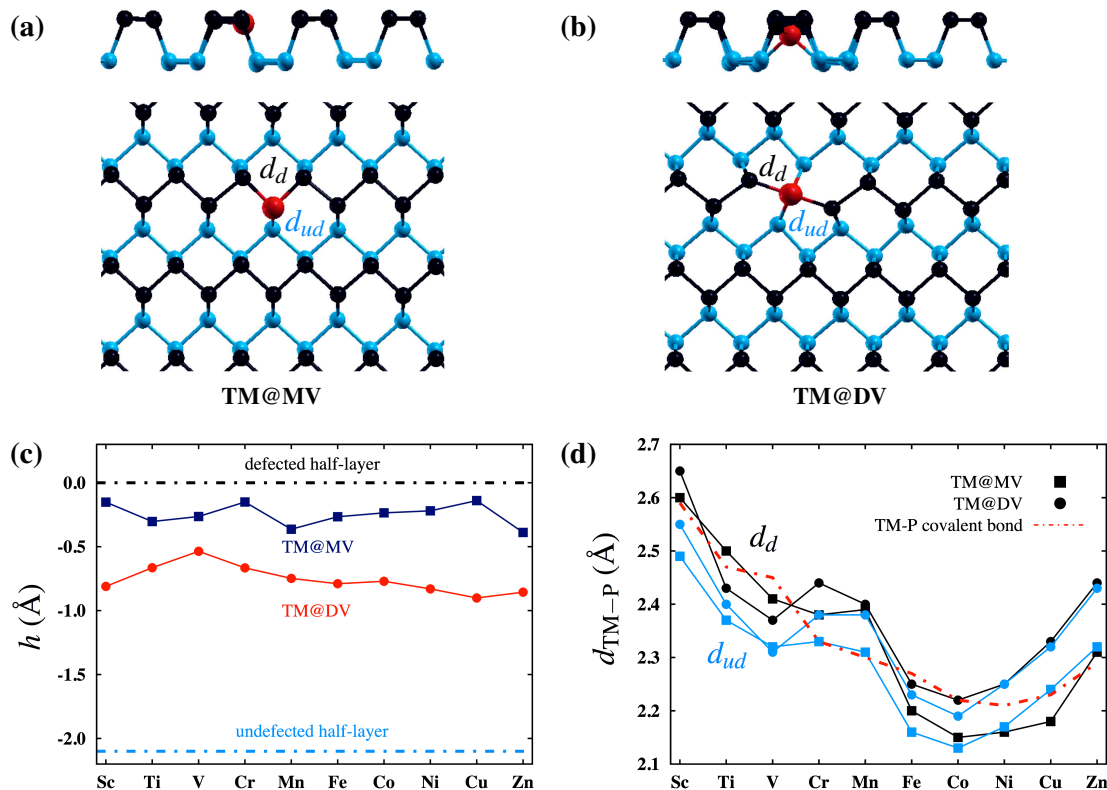


Figure 6.14: Transition-metal (red ball) absorption at the point-defects in their ground state. Side and top view of (a) TM@MV, and (b) TM@DV. The TMs are absorbed in the valley, between the defected (black) and undefected (blue) half-layers. (c) Non-monotonous variation of the depth h is observed along the 3d series. The TM in TM@DV complex, move further away from the defected layer compared to the TM@MV complex. (d) The TM-P bonds (d_{TM-P}), at the defected (d_d) and undefected (d_{ud}) layers, are found to be covalent. The TM-P covalent bond lengths are denoted by the red dotted line. (294)

thus the corresponding magnetism will be controllable. The TM@MV have been investigated recently, (278; 286) however, the microscopic picture is not clear yet. Moreover, as we have discussed earlier that the DV is thermodynamically more stable and thus abundant than the MV, which tend to coalesce and form DVs via vacancy diffusion. Therefore, the TM@DV complexes will be particularly more important for any practical purpose toward TM induced spintronics. Here we investigate both TM@MV and TM@DV complexes, and track their electronic and magnetic properties, and provide a microscopic picture.

6.3.3 Inducing local moment in TM-Vacancy complexes

The typical atomic configurations of TM@MV and TM@DV are shown in [Figures 6.14(a)-(b)]. Unlike graphene the TMs are accommodated inside the point-defects due to the intrinsic puckered structure of phosphorene. The TMs are absorbed between the two half-layers [Figure 6.14(c)], and thus the calculated vertical height h is negative. We find that all metals form two sets of chemical bonds with the under-coordinated P atoms from the defected and undefected half-layers, which we denote as d_d and d_{ud} , respectively [Figure 6.14(a)-(b)]. For TM@MV, metals form two d_d and one d_{ud} bonds. In contrast, two d_d and two d_{ud} bonds are created for TM@DV, and thus the metal atoms move further away from the defected half-layer [Figure 6.14(c)]. Both d_d and d_{ud} are comparable, and in cases, shorter than the corresponding TM-P covalent bondlengths, and follow similar qualitative trend for TM@MV and TM@DV [Figure 6.14(d)], which is correlated with the size of the metal ions. The bondlengths first decrease with increasing number of valence electrons for Sc-Co, and then increase for Co-Zn. It should be noted here that the slight deviation from this general trend for Cr, and Mn [Figure 6.14(d)] is due to their half-filled d shell, leading to weaker bonding.

We find that all the metals bind very strongly with the point defect [Figure 6.15(a)] with binding energy as strong (-7 to -4 eV) as in graphene, and also follow similar non-monotonic behavior. (44) To analyze the nature of electronic interaction between the defected phosphorene and the absorbed metal, we calculated the differential charge density $\Delta\rho(\mathbf{r})$, which is shown in the inset of Figure 6.15(a). The calculated $\Delta\rho(\mathbf{r})$ is typical of covalent bonding, which is reflected in strong TM-P bonding. This covalent bonding is also emulated in the respective TM-P bond lengths (Figure 6.14). The observed trend in binding can be explained by carefully looking into the TM-P bonding. The bare MV (DV) consists three (four) dangling

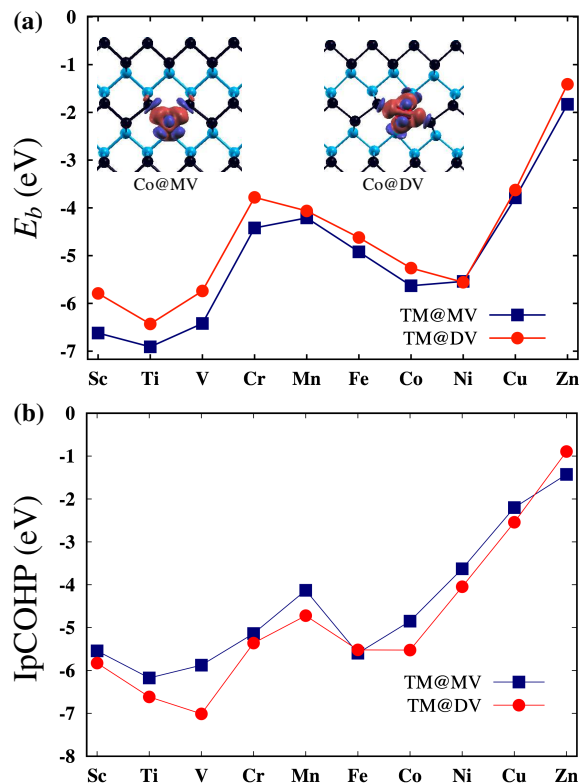


Figure 6.15: (a) Transition metal binding E_b for vacancy-TM complexes. The TM binding is little stronger in the case of TM@MV compared to TM@DV. The overall trend in E_b across the 3d series is similar to that of other two-dimensional materials. (44; 296) We argue that this trend could be understood completely by the covalent $p(\text{P})$ - $d(\text{TM})$ bonding. Representative differential charge densities $\Delta\rho(\mathbf{r})$ are shown in the inset for 0.03 $e/\text{\AA}^3$ isosurface, which indicate strong covalent bonding. The red (blue) color represents electron accumulation (depletion). (b) Calculated integrated partial COHP reveal that the qualitative trend in E_b along the 3d series shown in (a) is related to the trend in strong TM-P covalent bonding.

bonds, which are completely saturated by TM incorporation. The TM-defect binding is mainly derived by the hybridization between TM-3d and 3p orbitals of the under-coordinated P atoms. We find that the three bonding states are derived from P-3p and TM- d_{xy}/d_{z^2} orbitals for TM@MV. In contrast, the four bonding states for TM@DV are derived from TM- $d_{x^2-y^2}/d_{yz}$ and the neighbouring P-p orbitals.

The TM binding/absorption energy decreases for Ti-Cr, which in contrast increases as we move along Cr to Ni [Figure 6.15(a)]. The binding for Cu and Zn is comparatively much lower due to their filled atomic orbitals. Such evolution in

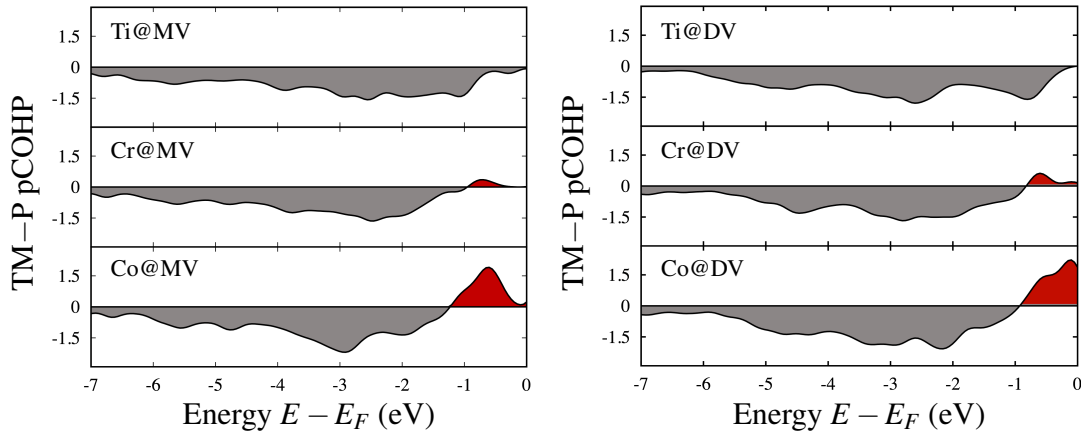


Figure 6.16: Partial COHP calculated for TM-P bonds for TM@defect complexes. The negative (positive) pCOHP represents bonding (antibonding) states. Large pCOHP values indicate strong TM-P covalent bonding. With increasing number of valence electrons along the $3d$ series, antibonding states appear near the Fermi level. Integrated pCOHP (in the range -7 eV to the Fermi level) indicate strong TM binding, and can explain the trend in absorption energy along the $3d$ series.

binding along the $3d$ series is generic to TM absorption on 2D materials but it still lacks a microscopic description. (44; 296) To corroborate the strong TM binding and the overall trend in [Figure 6.15(a)], we have calculated the TM-P projected COHP [Figure 6.16]. (90; 91) The bonding states are dominant in the valence band region indicating strong covalent TM-P interactions, which lead to strong metal binding. In order to quantify the TM-P covalent interaction, we have integrated the COHP up to the Fermi level, and summed over all the TM-P bonds [IpCOHP in Figure 6.15(b)]. The calculated IpCOHP and binding energy show similar qualitative evolution along the $3d$ series. This indicates that the differential covalent bonding is responsible for the observed trend in binding energy. For example, the Ti-P covalent bonding [$\text{IpCOHP}_{\text{Ti-P}} = -6.61$ eV] is much stronger than the Cr-P bonding [$\text{IpCOHP}_{\text{Cr-P}} = -5.36$ eV], which is reflected in their respective binding energies for DV complexes.

Now it would be interesting to investigate the effect of TM absorption at the defect site on the intrinsic semiconducting nature of phosphorene. The defect free

Table 6.2: Calculated band gaps for TM absorbed at the monovacancy.

TM@MV		
TM	$E_g(\uparrow)$ (eV)	$E_g(\downarrow)$ (eV)
Sc	$D(\Gamma) = 0.86$	$D(\Gamma) = 0.86$
Ti	$I(M-\Gamma) = 0.74$ $D(X) = 0.75$ $D(\Gamma) = 0.76$	$I(X-\Gamma) = 0.71$ $D(\Gamma) = 0.73$
V	$D(\Gamma) = 0.40$	$I(X-\Gamma) = 0.82$ $D(\Gamma) = 0.84$
Cr	$D(X) = 0.75$ $D(\Gamma) = 0.81$	$I(X-\Gamma) = 0.92$ $D(\Gamma) = 0.93$
Mn	$I(X-M) = 0.62$ $D(X) = 0.63$ $D(\Gamma) = 0.65$	$I(X-\Gamma) = 0.69$ $D(\Gamma) = 0.70$
Fe	$D(X) = 0.62$ $D(\Gamma) = 0.68$	$D(\Gamma) = 0.31$
Co	$D(X) = 0.55$ $I(X-\Gamma) = 0.60$ $D(\Gamma) = 0.61$	$D(X) = 0.55$ $I(X-\Gamma) = 0.60$ $D(\Gamma) = 0.61$
Ni	$I(X-M) = 0.47$ $D(X) = 0.51$ $D(\Gamma) = 0.53$	$I(X-M) = 0.33$ $D(X) = 0.33$ $D(\Gamma) = 0.38$
Cu	$I(X-Y) = 0.26$ $D(X) = 0.33$ $D(\Gamma) = 0.34$	$I(X-Y) = 0.26$ $D(X) = 0.33$ $D(\Gamma) = 0.34$
Zn	—	—

Table 6.3: Calculated band gaps for TM absorbed at the divacancy.

TM@DV		
TM	$E_g(\uparrow)$ (eV)	$E_g(\downarrow)$ (eV)
Sc	–	–
Ti	I(X–Y) = 0.49 D(X) = 0.52 D(Γ) = 0.53	I(X–Y) = 0.49 D(X) = 0.52 D(Γ) = 0.53
V	I(X–Y) = 0.13 I(X–Y) = 0.13 D(Γ) = 0.21	I(X–M) = 0.83 I(X–Y) = 0.83 D(Γ) = 0.84
Cr	I(Γ –M) = 0.55 D(Γ) = 0.60	–
Mn	D(X) = 0.60 D(Γ) = 0.61	D(Γ) = 0.73
Fe	I(X–M) = 0.09 I(X–Y) = 0.09 D(Γ) = 0.25	I(X–Y) = 0.28 I(X–M) = 0.28 D(Γ) = 0.35
Co	I(X–M) = 0.50 I(X–Y) = 0.50 D(Γ) = 0.57	–
Ni	I(X–M) = 0.20 I(X–Y) = 0.20 D(Γ) = 0.32	I(X–M) = 0.20 I(X–Y) = 0.20 D(Γ) = 0.32
Cu	–	–
Zn	D(X) = 0.14 D(Γ) = 0.15	D(X) = 0.14 D(Γ) = 0.15

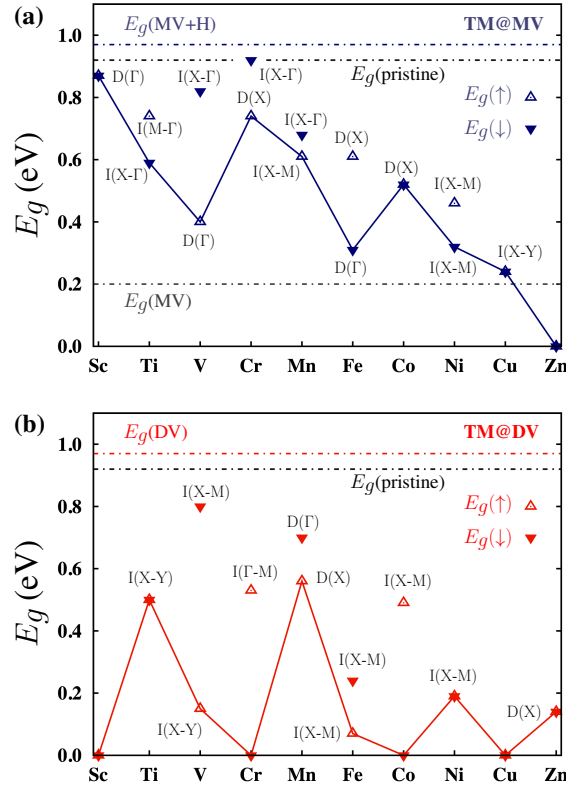


Figure 6.17: Spin-resolved band gaps for (a) TM@MV and (b) TM@DV complexes. The solid line is a guide to the lowest gap along the 3d series. The nature of the gap is indicated by D (direct) and I (indirect) along with the k-points in the Brillouin zone. I(X-Y) indicates that the VBM is at X-point and CBM is at Y-point in the first Brillouin zone. For TM@MV, the gap decreases as one moves along the 3d series. This trend is nonmonotonous with local structures. For all TM-doped cases the gap is calculated to be lower than the pristine or defected phosphorene. Moreover, Cr@DV and Co@DV show half-metallic behavior. The TM@DV complexes (V, Mn and Fe) show promise as spintronic materials with reasonable band gaps.

phosphorene is a direct gap semiconductor with 0.9 eV gap, which is found to be robust against the formation of point-defects as we have discussed earlier. Calculated spin-resolved band gaps are shown in [Figure 6.17] for both TM@MV and TM@DV complexes [individual gaps are reported in (Table. 6.2) and (Table. 6.3) listed at the end of the chapter]. The in-gap states appear due to metal absorption, which result in band gap that are smaller compared to the pristine and defected bare phosphorene. Further, the gap decreases along the 3d series for TM@MV complexes, however we observe this decrease to be nonmonotonous with local peaks

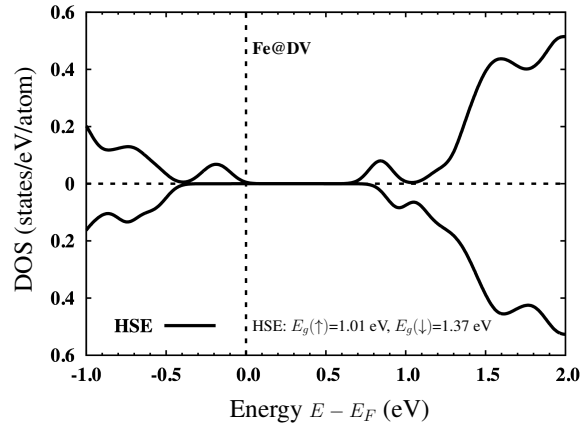


Figure 6.18: Calculated density of states for Fe@DV complex within hybrid HSE06 functional. The gap increases to 1.01 eV compared to 0.1 eV PBE gap, which makes it suitable for spintronic applications.

for (Cr/Mn/Co)@MV. In general, we find that CBM originates from TM-*d* orbitals, whereas the VBM is induced by either P-*p* or non-bonding TM-*d* orbitals. In contrast, while both VBM and CBM originate from TM-*d* orbitals, the calculated gaps are found to be much smaller.

In this regard, the case of metals absorbed at the divacancy is particularly interesting. Although, the band gaps are further reduced, the Ti, V, Mn, Fe, and Ni complexes retain gaps ranging between 0.1–0.6 eV. Reminding that the conventional generalized gradient approximation to the exchange-correlation functional underestimates the band gap, the true gaps should be larger than the PBE gaps reported in [Figure 6.17(b)]. Indeed while the PBE functional predicts a smaller gap of 0.1 eV for Fe@DV, the hybrid HSE06 functional estimates a much larger gap of 1.01 eV [Figure 6.18], which may be sufficient for spintronic devices. Moreover, metal doping at the divacancy could completely alter the intrinsic band structure from semiconducting phosphorene to half-metallic (Cr/Co)@DV or metallic (Sc/Cu)@DV complexes.

Now we turn our attention to the local moment created due to metal absorption at the point-defects. The calculated moments are shown in [Figure 6.19(a)], which

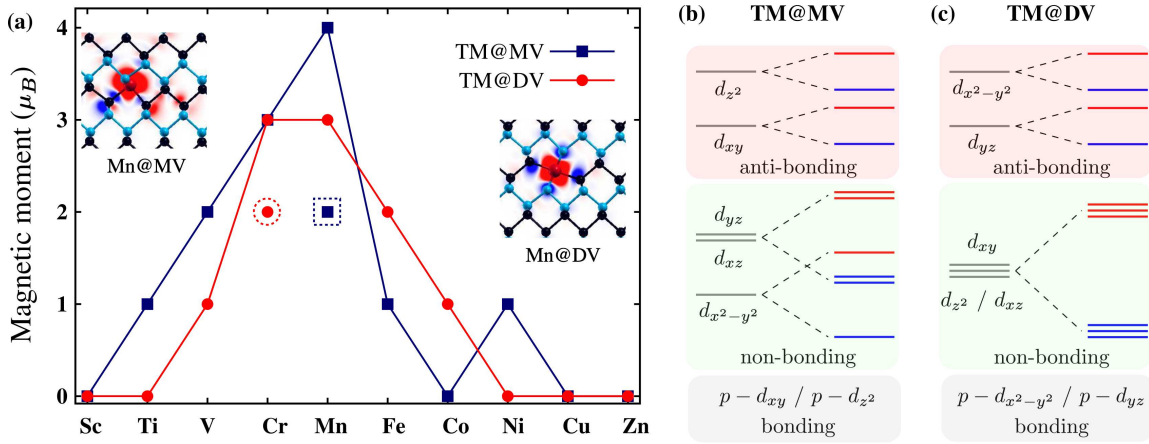


Figure 6.19: (a) Calculated magnetic moments of TM-vacancy complexes, with increasing valence electrons. For Mn@MV and Cr@DV, the solutions with $2\mu_B$ moments are very close in energy with their respective ground states (within 60 meV), which are also highlighted. Representative magnetization densities are shown in the inset. (b)-(c) Simple model to describe the observed trend in magnetic moment in (a) for TM@MV and TM@DV, respectively. In both the cases, the electrons are distributed in the non-bonding states such that it gives rise to high-spin solutions.

show a dome-shaped behavior for both TM@MV and TM@DV as the number of d -electrons increases. The density of states and magnetization density analyses [Figure 6.19(a)] point that the moment originates from the localized nonbonding d -orbitals, which also polarize the neighbouring P atoms. However, the proximity polarization of the P atoms are found to be small, -0.09 (Cr@MV) to $0.02 \mu_B$ (Mn@MV) for TMs absorbed at the monovacancy, and -0.07 (Mn@DV) to $0.07 \mu_B$ (Fe@DV) for TMs absorbed at the divacancy. The local moment at Ni ($0.50 \mu_B$) absorbed at the MV is found to be fragile with small exchange splitting and spin-flip energy.

By comparing the band structure and density of states of the TM-vacancy complexes to those with the defected phosphorene, we developed a simple model to explain the trends in magnetic moment [Figure 6.19(b)-(c)]. Removal of a single atom from phosphorene creates three dangling bonds, and thus, while a TM atom is placed at the MV, three of TM valence electrons form covalent TM-P bonds. We

find these to be two $d_{xy} - p(\text{P})$ and one $d_{z^2} - p(\text{P})$ covalent bonds [Figure 6.19(b)]. For example, three valence electrons of Sc completely saturates three MV dangling bonds, and thus Sc@MV does not produce any local moment. Next, for Ti-Co, rest of the TM electrons occupy the non-bonding d states, $d_{x^2-y^2}$, d_{xz} , and d_{yz} [Figure 6.19(b)], such that it always produces a high-spin solution. For example, Cr has six valence electrons, which give rise to $3 \mu_B$ moment. Once these non-bonding states are filled, the TM electrons occupy the anti-bonding d_{xy} and d_{z^2} states for Ni-Zn. The Mn@MV is found to be the only exception which does not follow this simple rule. However, the predicted $4 \mu_B$ solution is only 60 meV lower in energy than the $2 \mu_B$ solution, which is in accordance with the proposed model.

In contrast, four additional electrons are required to completely saturate the four dangling bonds in unrelaxed divacancy. Thus, for TM@DV, the TMs form four strong covalent bonds with the dangling P atoms. We find these to be two $d_{x^2-y^2} - p(\text{P})$ and two $d_{yz} - p(\text{P})$ covalent bonds. Thus, all the four valence electrons of Ti are consumed in TM-P covalent bonding, and Ti does not produce any local moment. For V-Ni, the rest of the d electrons occupy the non-bonding d_{xy} , d_{xz} and d_{z^2} orbitals [Figure 6.19(c)], such that it produces a high-spin solution. Next, the electrons in Cu and Zn are occupied in the anti-bonding d_{yz} and $d_{x^2-y^2}$ orbitals. The Cr@DV complex is the only exception to this model, which predicts a $2 \mu_B$ ground state. Instead, we find the $3 \mu_B$ solution to be 40 meV lower in energy.

The magnetic exchange splitting δE_{ex} between the majority and minority spin bands is the key to the magnetism. The calculated δE_{ex} for the systems with non-zero local moments [Figure. 6.19] are found to be quite large 0.40–2.50 eV [Table. 6.4], and is linearly correlated with the local moment. The spin imbalance owing to the exchange splitting produces the magnetic moment, and therefore the moment increases with exchange splitting. Further, the calculated exchange splitting is found to be larger in DV@TM than for MV@TM. Such large δE_{ex} is comparable to

Table 6.4: Calculated exchange splitting δE_{ex} and spin-flip δE_{sf} energies for metals absorbed on pristine and defected phosphorene.

TM	TM@Valley (eV)		TM@MV (eV)		TM@DV (eV)	
	δE_{ex}	δE_{sf}	δE_{ex}	δE_{sf}	δE_{ex}	δE_{sf}
Sc	–	–	–	–	–	–
Ti	–	–	0.64	0.64	–	–
V	0.79	0.70	1.20	0.70	1.05	1.05
Cr	1.00	0.92	2.00	1.30	1.80	1.80
Mn	1.49	0.72	1.15	0.65	2.40	2.40
Fe	–	–	0.76	0.76	2.48	1.49
Co	0.43	0.43	–	–	0.40	0.40
Ni	–	–	0.40	0.40	–	–

the corresponding magnetic TM bulk, and ultrathin TM films on nonmagnetic substrate. (297–300) For example, the calculated δE_{ex} for Fe@DV (2.48 eV) is substantially larger than epitaxial ML-Fe/Cu(100) [0.9–1.2 eV] and ML-Fe/Ag(100) [1.8 eV] that are measured via inverse photoelectron spectroscopy. (298) There could be some variation in δE_{ex} with momentum k , however, we do not observe any noticeable momentum variation due to dispersion less non-bonding d states. Another important quantity is the energy required for spin-flip transitions, which can either increase or decrease the local moment. We have calculated the moment diminishing spin-flip energies δE_{sf} [Figure. 6.19], which is related to the survival of the local moment. Similar to exchange splitting, the calculated δE_{sf} are also found to be quite large.

6.4 Summary

Here we investigate the electronic and magnetic properties of transition-metals absorbed on the pristine and defected single-layer phosphorene. Inducing local moment in otherwise non-magnetic semiconductor is the key first step toward plausi-

ble spintronic application. It was earlier believed that TMs are absorbed at the hollow site, however, we find that TMs favor the valley site, which is in between the two half-layers. Metals absorbed at this new site have completely different electronic and magnetic properties. Metals bind strongly on the pristine phosphorene, induce a local moment, and the semiconducting gap is retained. However, a very high metal diffusivity on the pristine phosphorene make them unfavorable for any practical purpose. Their high mobility leading to time-evolving spatial TM distribution makes the induced magnetism uncontrollable. Thus, one require the metals to be absorbed at the point-defects, which are present in as-prepared phosphorene or could be wishfully created. Moreover, the intrinsic semiconducting gap is found to be robust against the formation of such point-defects. These vacancy defects act as anchoring sites, where the metal atoms bind very strongly with phosphorene through strong covalent TM-P interaction. The evolution of metal absorption energy along the $3d$ series follow a generic trend as observed for other 2D materials, which we have qualitatively explained via detailed COHP calculations.

We propose that due to much higher thermodynamic stability of the bare divacancy defects over monovacancy, the TM@DV complexes are better proposition for spintronic applications. Although the calculated gaps for TM@DV complexes are relatively lower than the gaps for pristine and defected bare phosphorene, some of these complexes retain a formidable gap (1.01 eV for Fe@DV) along with a local moment that may be useful for spintronic application. The $3d$ evolution in local moment for TM-defect complexes has been explained within a simple model. Moreover, the magnetism in these TM-defect complexes are stable with large exchange splitting and spin-flip energy together. Thus, we argue that V, Mn, and Fe absorbed at the divacancy defect to be good candidates for spintronic device applications. We also note that metal absorption could completely alter the intrinsic semiconducting nature of the single-layer phosphorene and give rise to half-

metallic [(Cr/Co)@DV] or metallic [(Sc/Cu)@DV] composite system. Although the present study indicate the TM@DV complexes to be encouraging candidates for spintronic device application, further theoretical and experimental efforts are necessary concerning long-range magnetic ordering, and corresponding transition temperature. We hope the present study will encourage such investigations in future.

CHAPTER 7

HIGH-TEMPERATURE KONDO SCREENING IN Cr-DOPED PHOSPHORENE

Correlated interaction between dilute localized impurity electrons with the itinerant host conduction electrons in metals gives rise to the conventional many-body Kondo effect below sufficiently low temperature. In sharp contrast to these conventional Kondo systems, we report an intrinsic, robust and high-temperature Kondo state in two-dimensional semiconducting phosphorene. While absorbed at a thermodynamically stable lattice defect, Cr impurity triggers an electronic phase transition in phosphorene to provide conduction electrons, which strongly interact with the localized moment generated at the Cr site. These manifests into intrinsic Kondo state, where the impurity moment is quenched at multi-stage and at temperatures in the 40–200 K range. Further, along with a much smaller extension of Kondo cloud, the predicted Kondo state is shown to be robust under uniaxial strain and layer thickness, which greatly simplifies its future experimental realization. We predict the present study will open up new avenues in Kondo physics and trigger further theoretical and experimental studies. The above findings have been published in *Physical Review B* 97, 045132 (2018).

7.1 Introduction

Kondo effect observed in non-magnetic metals with dilute magnetic impurities was an early manifestation of the strongly correlated electron system, where the electrical resistance and magnetic properties are severely altered at low temperature. (301–303) Rather than saturation, the resistivity increases as the temperature is lowered below a critical temperature known as Kondo temperature T_K . Further, the impurity magnetic moment is screened below T_K by the formation of a many-body singlet state with the itinerant conduction electrons of the metal host. This serves as scattering centre for conduction electrons resulting in anomalous temperature dependence in resistance.

Beyond the traditional metal-impurity systems, a wide range of artificial Kondo systems have been realized with the advent in nano-fabrication. Composite systems including single molecules, (304–306) carbon nanotubes (307; 308) and quantum dots (309; 310) attached with metallic electrodes/tunnel-junctions are found to exhibit Kondo resonance. In contrast to these three-dimensional systems, two dimensional confinement of conduction electrons in layered materials featuring distinct electronic structure may lead to unusual Kondo screening at high temperature. In this context, the Fermi level in graphene could easily be tuned relative to the Dirac point to provide the required conduction electrons. Thus, graphene is expected to manifest Kondo screening, and indeed has been observed in defected or transition-metal doped graphene. (76; 77; 311; 312) In contrast, the two-dimensional semiconductors cannot naturally host Kondo state due to the lack of conduction electrons, and thus it would be fascinating to design Kondo screening by tuning chemical potential. This will open up a possibility to investigate many-body Kondo physics in reduced dimension including the quantum phase transition between unscreened and screened impurity moment.

Here, we predict a new class of Kondo system in two-dimensional semiconducting phosphorene, which is intrinsic and robust, that are markedly different from the artificial Kondo systems.^(304–310) Since the recent exfoliation of single and few-layer phosphorene, it has attracted enormous attention due to anisotropic electronic properties,^(3; 4; 313) and investigated in the context of many-body physics apart from a plethora of plausible technological applications.^(4; 313) A topologically insulating and Dirac semimetal states have been predicted or realized in few-layer phosphorene under external electric field or adatom adsorption.^(73; 75; 314)

We engineer two-dimensional semiconducting phosphorene such that it becomes susceptible to many-body Kondo screening. As discussed in Chapter 6, Sc and Cu impurities absorbed on single-layer phosphorene (SLP) triggers semiconductor to metal transition without impurity moment formation,^(226; 315) while the V, Mn, and Fe impurities generate unscreened moments as the systems remain semiconducting.⁽²²⁶⁾ In sharp contrast, while absorbed at the thermodynamically most stable divacancy defect, Cr impurity retains a localized moment, and also alters the electronic structure of phosphorene such that it becomes susceptible to Kondo screening. Here, we particularly investigate the non-trivial questions that are essential for the appearance of Kondo effect – Impurity absorption site and the concurrent electronic phase transition, impurity spin state, and the interaction between the moment generating impurity state with the host conduction electrons. Strong interaction between the impurity and conduction electrons, which are delocalized along the armchair direction, results into high temperature Kondo state. The impurity moment is quenched at different temperatures in the range 40–200 K. Further, the proposed Kondo state is predicted to be robust against layer thickness and moderate strain, which may be induced by the substrate. We also provide an insight about the Kondo cloud, which has remained experimentally elusive. This is largely due to the fact that the extension of Kondo cloud in conventional

metal-impurity system is $\sim 1 \mu\text{m}$ and is much larger than the dimension of current quantum devices. (316–318) In contrast, the Kondo cloud extension in the present system is predicted to be orders of magnitude smaller and could possibly be detected.

7.2 Computational details

Calculations are based on spin-polarized density functional theory (DFT) within the projector augmented wave formalism with an energy cutoff of 500 eV. (128–130) The exchange-correlation energy is described by Perdew-Burke-Ernzerhof functional (PBE). To estimate the robustness of the first-principles predictions, selected calculations are repeated with Heyd-Scuseria-Ernzerhof hybrid functional (HSE06). (194) Hubbard like on-site Coulomb interaction was considered within rotationally invariant approach (DFT+ U_{Cr}). (86) Single layer and bilayer phosphorene were modelled with 7(zigzag) $\times$ 5(armchair) and 6(zigzag) $\times$ 4(armchair) supercells, respectively. A vacuum layer of 15 Å are used, and the structures were optimized until all the force components are below 0.01 eV/Å threshold. Reciprocal space integration was carried out using 4 $\times$ 4 $\times$ 1 Monkhorst-Pack $\mathbf{k}$ -point grid. We addressed the inter-layer interaction in bilayer phosphorene (BLP) with non-local van der Waals functional (optB88-vdW) of Langreth and Lundqvist. (242)

7.3 Results and Discussion

The pristine SLP is a semiconductor, and the intrinsic point defects are electronically inactive that does not perturb the transport gap. (56; 226; 287) The divacancy (DV) with 5-8-5 ring structure is the thermodynamically most stable point defect in SLP. A divacancy (DV) in puckered phosphorene lattice can be created by removing two adjacent atoms from the same or different half-layers. The DV of the first

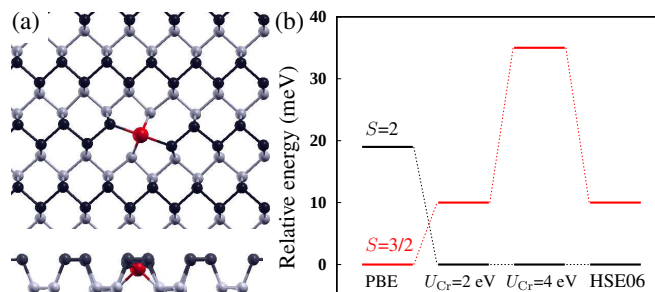


Figure 7.1: (a) Top and side view of Cr absorption at the DV(5|8|5) on SLP. The Cr impurity (red ball) is absorbed in-between the two half-layers indicated in black and white balls, at the valley site. (b) The Cr impurity is found to have competing spin-3/2 and spin-2 states. While the conventional PBE exchange-correlation predicts a spin-3/2 ground state, inclusion of on-site Coulomb interaction and hybrid exchange-correlation anticipate the spin-2 state as the ground state.

kind is known to be thermodynamically most stable with DV(5|8|5) configuration with 1.33 eV formation energy. While there are many other possible DV configurations, their formation energies are found to be higher, which has been discussed in literature in great details including Chapter 6. (153; 226; 287; 292) A distinct divacancy configuration (5|7|5|7) was reported, (319) however, we find this structure to be 113 meV higher in energy. While the conventional PBE functional underestimates the DV-SLP gap to 0.97 eV, the hybrid HSE06 functional (1.77 eV) improves the result.

7.3.1 Kondo state in Cr@DV-SLP

The Cr impurity is absorbed at the thermodynamically favored DV(5|8|5) configuration between the two half-layers such that Cr binds with P atoms from both defected and un-defected half-layers. [Figure 7.1(a)] As the Cr impurity is absorbed at the valley site (between the half-layers), it forms strong covalent bonds through hybridization between the P- p_x/p_y and Cr- $d_{x^2-y^2}/d_{yz}$ orbitals. The half-filled electronic shell results in two competing spin states $S = 3/2$ (Cr^{3+}) and $S = 2$ (Cr^{2+}) within different theoretical hierarchy, which are also the most common oxidation

Table 7.1: Structural details of Cr absorption, which is influenced by supplemented Coulomb interaction for Cr impurity, U_{Cr} for their respective ground state configurations. The depth is measured from the defected half-layer. In response to an increasing Coulomb interaction, the Cr-P bonds are elongated.

Coulomb interaction	Cr-P (Å) bonds	Depth (Å)
PBE	2.38–2.44	0.66
$U_{\text{Cr}} = 2 \text{ eV}$	2.47–2.48	0.58
$U_{\text{Cr}} = 4 \text{ eV}$	2.51–2.54	0.52

states for Cr. The Cr^{3+} ($S = 3/2$) state is found to be most stable within conventional PBE exchange-correlation functional. The competing Cr^{2+} ($S = 2$) state is 20 meV higher in energy [Figure 7.1(b)]. For on-site Hubbard-like Coulomb interaction at the Cr-impurity, the later was found to be the ground state, which is also the case for hybrid HSE06 functional. The preferred oxidation state of Cr depends on the Cr-P distances. The spin-2 solution is obtained for on-site Hubbard-like Coulomb interaction due to increasing $\langle \text{Cr} - \text{P} \rangle$ distances. Subsequently, Cr moves closer to the defected half-layer (Table 7.1).

Cr impurity absorbed at the DV triggers an electronic phase transition, and Cr@DV-SLP becomes half-metallic within PBE exchange correlation functional [Figure 7.2(a)]. However, it is necessary to confirm the intrinsic nature of such electronic phase transition and rule out any artefact arising from the conventional exchange-correlation description. Therefore, we have recalculated using the on-site Coulomb interaction U_{Cr} , and expensive hybrid HSE06 exchange-correlation functional, which improves the description of $p - d$ interaction. Indeed, the electronic half-metallic phase along with Cr impurity moment are found to be robust within the adopted theoretical hierarchy [Figure 7.2(b-c) and Figure 7.3(a)]. This indicates the semiconductor to half-metal transition is robust and not an artefact

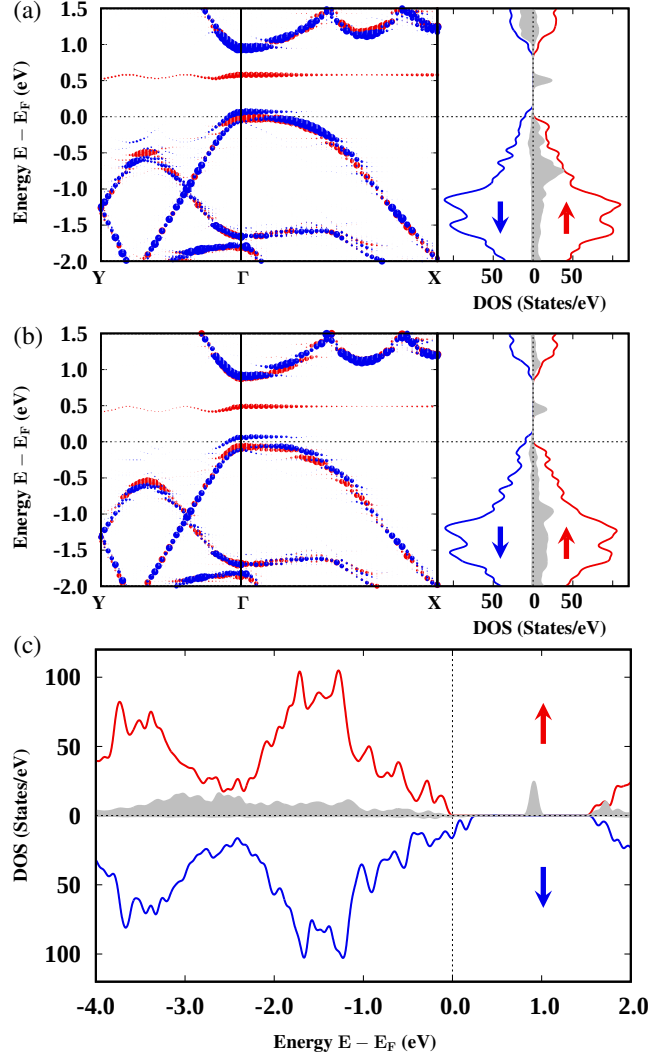


Figure 7.2: Unfolded band structure and the corresponding density of states of Cr@DV-SLP with very small $\sim 0.7\%$ Cr-impurity concentration, calculated with (a) PBE exchange-correlation functional, (b) On-site Coulomb interaction $U_{\text{Cr}} = 2$ eV, and (c) Density of states of Cr@DV-SLP calculated with HSE06 hybrid exchange-correlation functional. All calculations are performed for $S = 2$ spin ground state. The half-metallic character is consistent within all the considered theoretical hierarchy. Red (blue) color represents the majority (minority) channel. The electronic band structures for the supercells are calculated using the band unfolding technique implemented in the BandUP code (88; 89).

of underlying theoretical approximations.

With increasing U_{Cr} (0–4 eV), the $p - d$ hybridization decreases, and is reflected through increasing $\langle P - \text{Cr} \rangle$ distances. A careful study of the partial density of states suggests that the bonding is derived through $p - d_{yz}$ hybridization, which

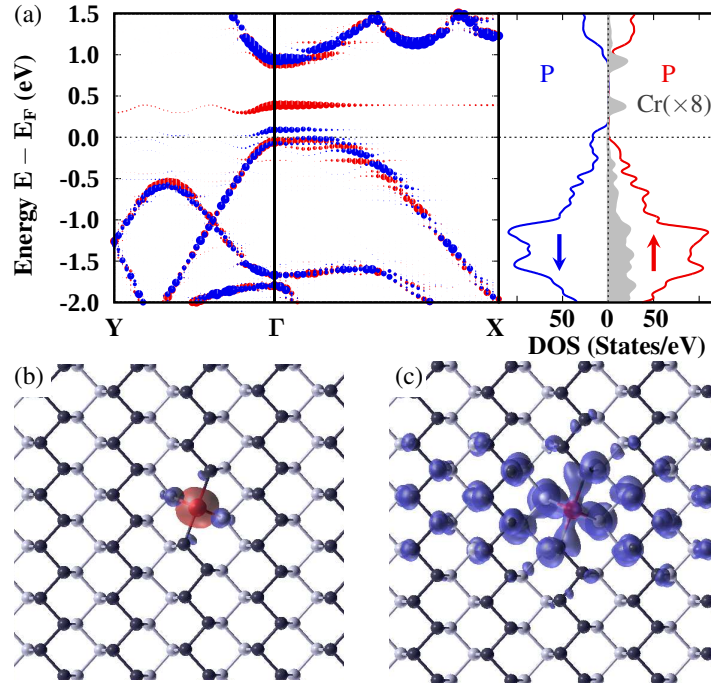


Figure 7.3: (a) Unfolded band structure and the corresponding density of states (DOS) of Cr@DV-SLP calculated with DFT + U_{Cr} formalism for $U_{Cr}=4$ eV. While the anisotropic dispersion along the armchair and zigzag directions is retained, the defected Cr@DV-SLP becomes half-metallic. Further, the conduction electrons are of P- p character. (b) The magnetization density indicates that the Cr magnetic moment is mainly localized at the impurity site. (c) The corresponding charge density indicates that the conduction electrons are delocalized along the armchair direction and over the entire supercell (~ 23 Å).

dictates $S=2$ spin state localized at the impurity [Figure 7.3(b)]. This state is 10, 35 and 10 meV lower in energy than the competing $S = 3/2$ state, for $U_{Cr} = 2, 4$ eV, and HSE06, respectively [Figure 7.1(b)]. Regardless of the impurity spin state, the Cr@DV-SLP is found to be half-metallic, where the gap is closed in the minority spin channel. The unreconstructed DV in SLP generates four dangling bonds, which are incompletely filled by Cr absorption and produces Cr^{2+}/Cr^{3+} solutions. Therefore, defected SLP becomes hole-doped and consequently the Fermi level shifts lower in energy resulting in gap closing. The partial density of states corroborates this picture, where the E_F lies within the band that is arising from the P- p electrons [Figure 7.3(a)]. Further, the charge density corresponding

to the conduction electrons near the E_F indicates that these conduction electrons are delocalized over the entire supercell (~ 23 Å), along the armchair direction [Figure 7.3(c)] with very high carrier mobility. We note that the electronic phase transition is of Lifshitz type, (320) and a hole-pocket emerges at the Γ -point [Figure 7.3(a)]. Such Lifshitz transition triggers interesting electronic responses. (321–323) Although Lifshitz transition has been reported for single and few-layer phosphorene, (73; 314; 321; 322) in majority of these cases the Fermi surface topology changes due to neck formation. In the present case for Cr@DV-SLP, the Lifshitz transition arises due to pocket formation, and precedes Kondo screening.

The corresponding impurity moment is localized on the absorbed Cr, as evident from the magnetization density [Figure 7.3(b)]. The high-spin $S=2$ ground state, within supplemented electron correlation and hybrid exchange-correlation functional approaches [Figure 7.1(b)], arises from half-filled d_{z^2} , d_{xy} , $d_{x^2-y^2}$ and d_{xz} orbitals, which are non-degenerate due to the lack of symmetry around Cr-impurity. In contrast, the competing $S = 3/2$ impurity state arises from the d_{z^2} , d_{xy} , and d_{xz} orbitals. The presence of such localized Cr moment along with P- p conduction electrons indicates the possibility of Kondo state (Figure 7.3). However, for the occurrence of Kondo resonance, the magnetic impurity levels must have sizeable electronic coupling with the host conduction electrons, and must not behave as free moment.

In this context, we consider the crystal orbital Hamilton population (COHP) scheme for identifying the bonding interaction between Cr- d and P- p states. (90; 91) Here, the wave function calculated using plane-wave method is utilized to evaluate the density and Hamiltonian matrix elements, which are then projected over local orbitals. The resultant picture can distinguish between bonding, non-bonding, and anti-bonding interactions between atoms. In case of Cr@DV-SLP, the partial crystal orbital Hamilton population (pCOHP) indicate substantial hy-

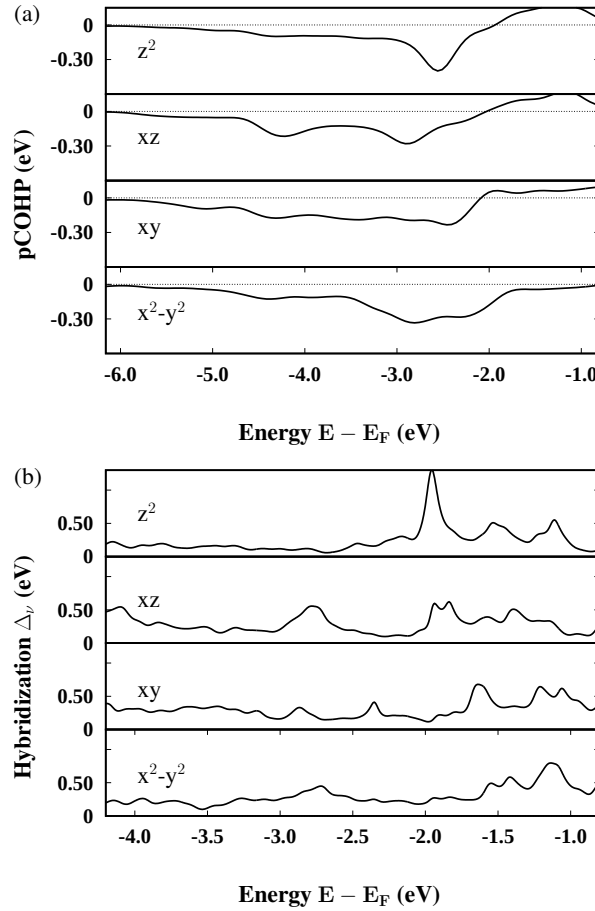


Figure 7.4: (a) Projected crystal orbital Hamilton population (pCOHP) between Cr- d and P- p electrons is evaluated for $U_{Cr} = 4$ eV. The negative (positive) pCOHP values refer to bonding (anti-bonding) nature of interaction between Cr- d and P- p electrons. The presence of bonding interaction for all magnetic d orbitals with the P- p electrons favors screening of all moments during Kondo state formation. (b) Hybridization Δ_ν evaluated using the Kramers-Kronig relation for Cr- d orbitals in case of $U_{Cr} = 4$ eV.

bridization between the moment generating Cr- d orbitals and host conduction P- p electrons. We observe bonding states in the vicinity of the band centers of each d orbital contributing to the impurity moment. The presence of such hybridized states supports strong interaction between Cr- d and P- p states [Figure 7.4 (a)].

Further, the hybridization Δ_ν between the unpaired Cr- d orbitals with the P- p conduction electrons is quantified from the partial density of states (pDOS) ρ_ν

using a Kramers-Kronig relation, (324)

$$\Delta_\nu(\epsilon) = -\text{Im} \left[\int d\epsilon' \frac{\rho_\nu(\epsilon')}{\epsilon - \epsilon' - i0} \right]^{-1}.$$

The calculated $\Delta_\nu(\epsilon)$ shows strong interaction between the localized d -orbital with the conduction electron as shown in [Figure 7.4 (b)]. The hybridization values are useful for estimating the Kondo temperature T_K as discussed in the below section.

7.3.2 Nature of Kondo state

Thus, the Cr@DV-SLP system has all the ingredients required to form Kondo state at low temperature: local Cr impurity moment, host conduction electrons, and a sizeable coupling between them. However, the nature of Kondo state and a correct model are very difficult to predict and non-trivial. For the classic case of Fe impurities in gold and silver, the correct model description has only been determined very recently, (325) which was first observed in 1930s. (301; 303) Although, the spin-orbit coupling is not considered in the present calculations, it may be expected to be negligible as in the case of Co-absorbed graphene. (311) Such scenario is expected to generate conventional spin-only SU(2) Kondo state. Further, as all the half-filled impurity d -states interact strongly with the conduction electrons, the impurity moment will be completely screened, and a four-channel spin-2 Kondo state is expected. However, the competing spin-3/2 impurity state is only 10-30 meV higher in energy depending on theoretical hierarchy. Thus, one may not completely rule out a spin-3/2 three-channel Kondo state. Further, we estimate the Kondo temperature T_K for the screening of each half-filled Cr- d orbitals corresponding to the spin-2 state ($U_{\text{Cr}}=4$ eV) by using, (326)

$$k_B T_K \simeq \sqrt{2\Delta_\nu \frac{U_\nu}{\pi}} \exp \left[-\frac{\pi}{2\Delta_\nu} \left(\frac{1}{|\epsilon_\nu|} + \frac{1}{|\epsilon_\nu + U_\nu|} \right)^{-1} \right],$$

Table 7.2: Band centres ϵ_ν and Coulomb repulsion energies $\mathcal{U}_\nu$ are calculated from the partial density of states for $S = 2$ spin ground state with $U_{\text{Cr}} = 4$ eV. The hybridization Δ_ν is evaluated using the Kramers-Kronig relation at the band center. The orbital Kondo temperatures are calculated using these parameters. The non-degenerate d -orbitals at Cr impurity are quenched at different temperatures.

Orbital ν	ν -band center ϵ_ν (eV)	Coulomb repulsion $\mathcal{U}_\nu$ (eV)	Hybridization Δ_ν (eV)	T_K (K)
z^2	-2.21	3.15	-0.276	202
xz	-2.20	2.53	-0.120	119
xy	-2.27	3.22	-0.204	43
$x^2 - y^2$	-2.16	3.12	-0.227	78

where ϵ_ν is the energy of the d -level (~ 2.2 eV), $\mathcal{U}_\nu$ is the Coulomb interaction energy that are calculated from pDOS ρ_ν , and Δ_ν ranges between 0.10–0.30 eV (Table 7.2).

T_K denotes the temperature below which Kondo resonance is anticipated for the concerned d orbital. Here, we calculate the relevant quantities from the projected density of states. The estimated T_K is found to be high between 40–200 K, where the non-degenerate d -orbitals form Kondo singlet at different temperatures, and the impurity moment is completely quenched at multi-stage. We anticipate ellipsoidal Kondo cloud elongated along the armchair direction. The ellipsoidal nature arises from the prominent delocalization of conduction electrons in the armchair direction. The coherence length and consequently the Kondo cloud dimension will be significantly greater along armchair direction. We estimate the coherence length $\xi_K = \hbar v_F / k_B T_K \sim 20\text{--}4$ nm, where Fermi velocity $v_F \sim 10^5$ m/s and $T_K \sim 40\text{--}200$ K, which is orders of magnitude smaller than a typical $\xi_K \sim 1$ μm in conventional metal-impurity systems. Thus, it could be finally possible to experimentally detect the Kondo cloud in the present system, which remains elusive

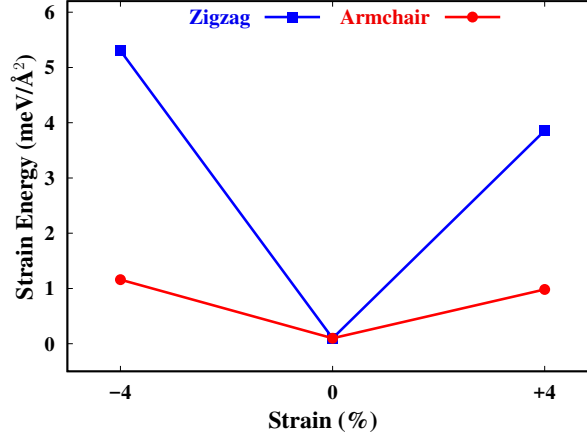


Figure 7.5: Strain energy of pristine SLP under uniaxial strain applied along armchair and zigzag directions. Straining the phosphorene lattice along the armchair direction is easier compared to the zigzag direction.

till today. (318; 327; 328)

7.3.3 Kondo state in uniaxially strained Cr@DV-SLP

Having discussed the strategy to design intrinsic Kondo state in free-standing semiconducting SLP, we next discuss its robustness on a substrate and with increasing layer thickness. The substrate effect is incorporated via induced strain in SLP, while the plausible effect of substrate on the intrinsic electronic structure of SLP has not been considered, and is beyond the scope of this study. Although pristine SLP is known to withstand an uniaxial tensile strain up to 30% due to its puckered structure, the electronic structure is found to be amenable. (218; 243; 329) Further, ripples and corrugations in large area SLP could lead to strained regions. (330) Thus, it is prudent to investigate the robustness of Kondo state in strained SLP. We have considered a moderate $\epsilon_{a/z} = \pm 4\%$ uniaxial strain along both armchair and zigzag directions.

First, we discuss the strained SLP under moderate uniaxial strains $\epsilon_{a/z} = \pm 4\%$ along the armchair and zigzag directions. We have calculated the strain energy

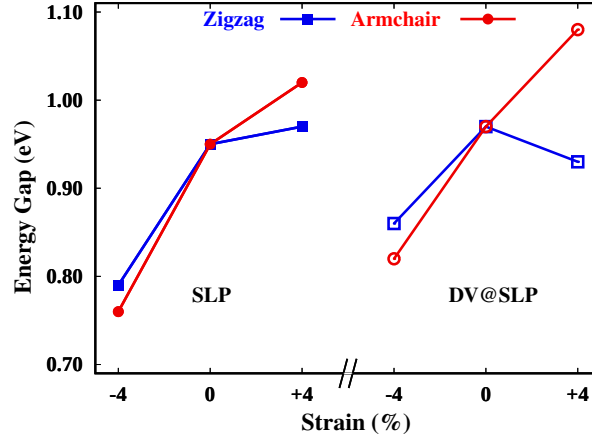


Figure 7.6: Calculated energy gaps for pristine SLP (left) and DV-SLP (right) under uniaxial strain applied along armchair and zigzag directions using the conventional PBE functional.

while relaxing the lattice in the transverse direction, and the corresponding strain energy is calculated as,

$$E_S = \frac{E_{\text{strained}} - E_{\text{pristine}}}{A_{\text{pristine}}},$$

where E_{strained} and E_{pristine} are the total energy of uniaxially strained and pristine supercell, while A_{pristine} is the cross-section of pristine supercell. Calculated strain energy is shown in [Figure 7.5]. We find that the applied strain could easily be accommodated along the armchair direction due to puckering than the zigzag direction. This is reflected from the higher strain energy along the zigzag direction compared to the armchair direction. The anisotropic response is attributed to weaker bonding between P atoms along the armchair direction and thus it is energetically less expensive to distort the structure along this direction. The lattice relaxation in the transverse direction in response to the uniaxial strain is found to be distinct for both cases. For $\varepsilon_a = 4\%$ tensile (compressive) strain the distance between the half-layers decreases (increases) by 1%, and thus decrease (increase) puckering. In contrast, when a strain is applied along zigzag direction $\varepsilon_z = 4\%$, lattice along the armchair direction relaxes in proportionate fashion ($\sim 3\%$), while

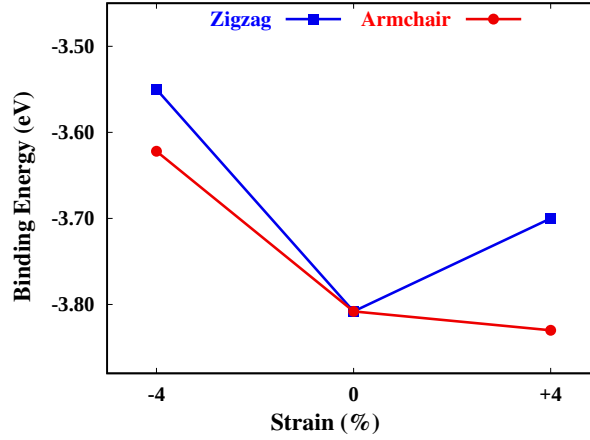


Figure 7.7: Binding energy for Cr@DV-SLP. The applied strain does not affect the binding energy significantly, which remains in the 3.80–3.50 eV range.

the distance between the half-layers are mostly unaffected ($< 0.5\%$). Therefore, strain in the lattice is expected to modify the intrinsic electronic structure of SLP.

Generally for pristine SLP with $-4\% \leq \varepsilon_{a/z} \leq 4\%$, the band gap increases with uniaxial tensile strain, while a compressive strain reduces the gap [Figure 7.6]. The band gaps lie between 0.75–1.05 eV within the applied strain range, and the results are in agreement with previous reports. (218) Further, the DV-SLP remains semiconducting under applied strain with 0.8–1.0 eV gap. We observe that the compressive (tensile) strain leads to decrease (increase) in band gap for pristine SLP. Further, the band gaps are found to be direct in nature for all cases except for $\varepsilon_z = -4\%$. Most importantly, the intrinsic semiconducting nature remains intact for DV-SLP for considered strain range [Figure 7.6]. Although the DV-SLP behave in qualitatively similar fashion as the pristine SLP, the calculated gap for $\varepsilon_z = 4\%$ is found to be lower than its unstrained counterpart, which is in agreement with the previous report. (230)

It would be interesting to investigate how strain affects the absorption energy of Cr-impurity at the DV. The absorption site of Cr-impurity at the valley site remains unchanged in strained DV-SLP. While the Cr absorption energy is found to

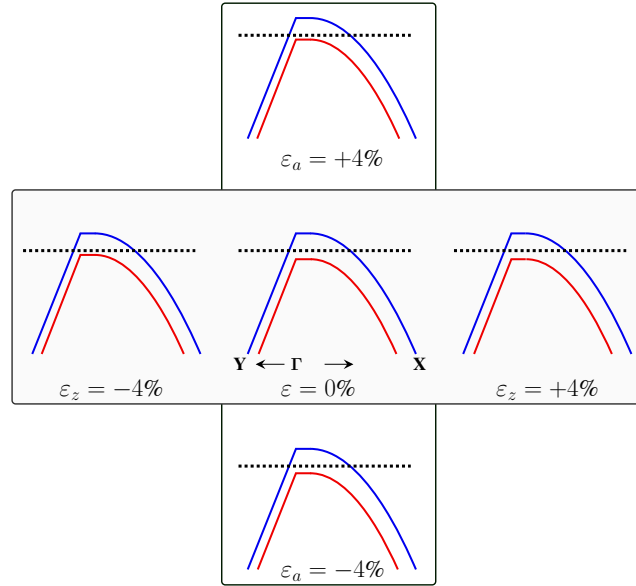


Figure 7.8: Schematic band structure of Cr@DV-SLP under moderate uniaxial tensile and compressive strains along armchair $\varepsilon_a = \pm 4\%$ and zigzag $\varepsilon_z = \pm 4\%$ directions. Similar to the unstrained Cr@DV-SLP, the electronic structure remains half-metallic under uniaxial strains, and the conduction electrons are delocalized along the armchair directions. Further, the conventional PBE functional and supplemented on-site Coulomb interaction of $U_{\text{Cr}} = 2$ and 4 eV indicate qualitatively similar trend.

be ~ 3.8 eV in the absence of strain, applied strain does not significantly affect the binding energy, and remains in the 3.8–3.5 eV range for the $\varepsilon_{a/z} = \pm 4\%$ strain range (Figure 7.7). In general, the absorption energy decreases with increasing strain except for $\varepsilon_a = 4\%$ which almost remains unaltered.

Further, the magnetic and electronic structures of strained Cr@DV-SLP are strikingly similar with the unstrained counterpart. The overall magnetic structure of absorbed Cr impurity remains unaffected in the strained DV-SLP. The relative stability of competing spin-3/2 and spin-2 impurity states is similar to the earlier discussed case of unstrained SLP. For the entire $-4\% \leq \varepsilon_{a/z} \leq 4\%$ range, the spin-2 impurity state is found to be the ground state with $U_{\text{Cr}} \geq 2$ eV, where the d_{z^2} , d_{xy} , d_{xz} and $d_{x^2-y^2}$ orbitals generate the impurity moment. The Cr@DV-SLP remains half-metallic under the uniaxial strain (Figure 7.8), and the conduction electrons re-

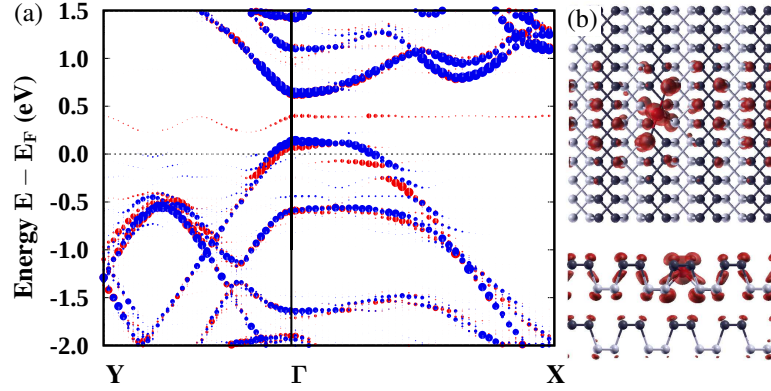


Figure 7.9: (a) The defected DV-BLP is semiconducting whereas the Cr-impurity absorption at DV transforms the electronic structure to metallic. (b) The P-*p* conduction electrons are delocalized along the armchair direction in the defected layer, and over the entire supercell considered. Although the above results are shown for $U_{\text{Cr}}=4$ eV, the PBE and $U_{\text{Cr}}=2$ eV provide qualitatively similar results.

tain their delocalized behavior along the armchair direction. The COHP and $\Delta_v(\epsilon)$ calculations indicate a sizeable coupling between the moment generating Cr-*d* orbitals with the host P-*p* conduction electrons. Thus, Cr@DV-SLP under moderate strain survives with all the features required for the appearance of Kondo state.

7.3.4 Kondo state in bilayer Cr@DV-BLP

The experimental fabrication of SLP might be a challenging task compared to a few-layer phosphorene. Thus, we investigate the effect of layer thickness on the Kondo state. In this regard, we have investigated BLP with energetically preferable AB stacking, which is a natural order in black phosphorus. Calculated lattice parameters, 3.33 and 4.52 Å along the zigzag and armchair directions respectively; and the interlayer separation of 3.20 Å are in good agreement with the previous results. (54; 331) The band gap decreases in pristine BLP (0.55 eV within the PBE exchange-correlation functional), in agreement with earlier results. (54; 73; 215) Similar to SLP, the DV defect is also electronically inactive in BLP with 0.57 eV gap. Given that the band gap decreases with increasing layer thickness, such reduction

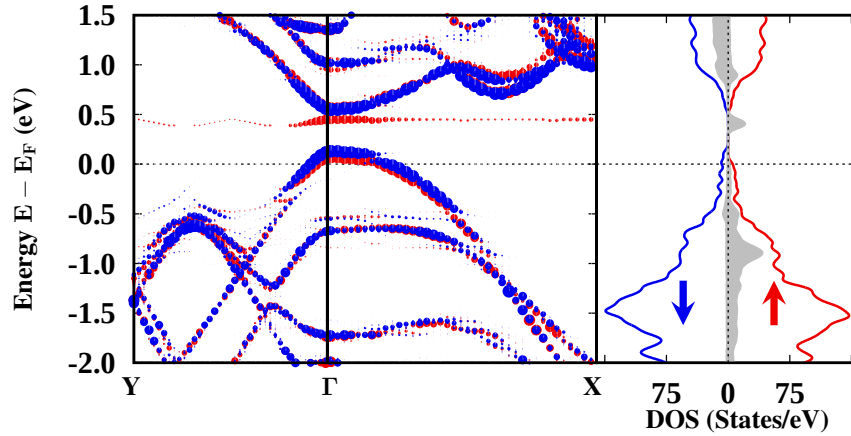


Figure 7.10: (a) Unfolded band structure and the corresponding density of states of Cr@DV-BLP calculated with PBE exchange-correlation functional. Unlike the half-metallic nature of Cr@DV-SLP, the Cr impurity absorption in DV-BLP leads to a metallic solution.

might help the semiconductor to metal electronic crossover while Cr is absorbed at DV-BLP. Indeed, Cr@DV-BLP is found to be metallic [Figure 7.9(a)]. The Cr impurity is absorbed at the valley site [Figure 7.9(b)], with strong binding energy of -3.10 eV ($S = 2$ with $U_{\text{Cr}} = 4$ eV). Moreover, the intrinsic electronic structure of DV-BLP is completely altered and the Cr@DV-BLP becomes metallic in both spin channels regardless of the on-site Coulomb interaction strength [Figure 7.9(a) and Figure 7.10], with delocalized conduction electrons along the armchair direction [Figure 7.9(b)]. Further, the absorbed Cr-impurity generates a localized impurity moment. The energy difference between the competing $S=3/2$ and $S=2$ spin states is found to be -44 , -21 and 2 meV for $U_{\text{Cr}} = 0$, 2 , and 4 eV, respectively. For both the spin solutions the moment generating Cr- d states have strong hybridization with the conduction electrons. In this case, the non-degenerate d -moments are quenched at temperatures in the range $18 - 80$ K. Therefore, we infer that increasing layer thickness will not hinder the possibility of Kondo state in bilayer and few-layer phosphorene.

7.4 Summary

In summary, within the first-principles calculations, we rigorously report the evidences of intrinsic, robust and high-temperature Kondo screening in Cr absorbed at a thermodynamically stable defect site in semiconducting phosphorene. The semiconductor to (half) metal phase transition is induced by Cr impurity. In addition, a competing spin-3/2 or spin-2 localized state is generated at the Cr impurity. Further, the conduction electrons are delocalized along the armchair direction, and strongly interact with the moment generating Cr- d orbitals at the impurity site. We infer these picture leads to a spin-only SU(2) Kondo state. A multi-channel screening is predicted, and the moments at the non-degenerate d -orbitals are quenched at different temperatures in the range 40 – 200 K. Further we show that such Kondo state is robust under layer thickness, and moderate strain, which could be induced by substrate. Such robustness will simplify its experimental realization. While the present investigation addresses the magnetic screening with vanishingly small impurity concentration, it would be interesting to study the competition and crossover between screening and RKKY-induced magnetic order with increasing impurity concentration. We hope the present results will trigger further theoretical and experimental studies.

CHAPTER 8

SUMMARY AND FUTURE OUTLOOK

The field of 2D materials has come a long way from its wunderkind days and has become one of the most active areas of research within condensed matter physics. Our work addresses a few outstanding queries on 2D materials and defects within such materials: *How defects form and migrate in 2D materials, and whether such defects can introduce magnetism and many-body states in 2D materials?* We have focused on two distinct candidates which span the breadth of 2D materials: graphene and phosphorene. While graphene is flat and highly symmetric, phosphorene is puckered and anisotropic. Moreover, graphene is a semi-metal with high chemical stability whereas phosphorene is a semiconductor and prone to degradation. From a fundamental perspective, a thorough understanding of defect formation and migration mechanism of these two materials will be instructive in understanding prospective 2D materials. For example, the orthorhombic crystal structure of phosphorene is important as a class of low-symmetry materials consisting of monoelemental group V or bielemental group IV–VI atoms can be derived from phosphorene.

The microscopic mechanism of vacancy migration in graphene and various experimental scenarios including Jahn-Teller distortion, hydrogen functionalization, charge transfer between graphene and TEM grid, the role of adjacent defects were discussed in Chapter 3. We showed that the lattice relaxation perpendicular to the graphene sheet along with an extended in-plane strain relaxation is crucial to arrive at the correct migration mechanism. The absence of out-of-plane relaxation in few-layer graphene result in a high activation energy. Above mechanism can be

experimentally inferred from high-resolution atomic force microscopy or geometric phase analysis. Our predictions of vacancy concentration, charge-dependent as well as strain-dependent migration barriers in graphene can be confirmed through temperature or gate-voltage controlled experiments. We are also very curious to understand the effect of space travel on graphene, (332) where defects and charge doping will play a decisive role in the viability of graphene under extreme conditions.

Our study on ferromagnetism in nitrogen-doped graphene (Chapter 4) outlined the contribution of various nitrogen doped complexes that are either substitutional or occupy vacancy defects in graphene, towards inducing magnetism in graphene. While the individual defects result in local moment formation, the ferromagnetic ordering emerges for the high concentration of graphitic and triazinic complexes. We show that the amount of graphitic complexes in graphene can be increased by healing vacancy defects with N adatoms at high temperatures. Experimental efforts to incorporate N atoms in above fashion are necessary for robust ferromagnetism in nitrogen-doped graphene. Magnetotransport and spin polarized STM measurements will assist in understanding the local electronic structure and transport in such samples. Further studies to identify additional defect complex arrangements that result in ferromagnetism can include multiple species such as sulfur, phosphorus, fluorine over a wide range of concentration.

We provided a detailed understanding of how defects migrate and initiate degradation in phosphorene in Chapter 5. Experimental investigations on defects in phosphorene and the effect of temperature on these defects are necessary to improve the theoretical models of degradation. The contrasting vacancy diffusion between phosphorene and graphene highlight the flexible and weak P-P bonding. Phosphorene offers an advantage over graphene in terms of accessible defect activity at relatively low temperatures. Alternatively, the puckered structure of

phosphorene increases the complexity of defect structures, and their experimental identification is an additional challenge. Successful strategies to avoid degradation in phosphorene can be replicated elsewhere, including upcoming 2D materials that are highly reactive.

The absorption of $3d$ transition-metal (TM) atom on phosphorene led to local moment formation in phosphorene (Chapter 6). The TM absorbed on pristine surface will lead to uncontrolled magnetism since these are highly mobile at room temperature. Instead, defect complexes were shown to be strong anchoring sites for TM atoms. We identified V/Fe/Mn absorbed at the divacancy defect as suitable candidates for spintronics applications. Further, the TM–vacancy complexes mostly retained an energy gap and induced a local moment with large exchange splitting and spin–flip energies. Generating a local moment is the first step towards spintronic functionality in phosphorene. A robust magnetic order must develop between the adjacent moments, and the embedded moments must remain both thermodynamically and kinetically stable to realize practical applications. Typically, a fraction of the TM atoms that are deposited on phosphorene will embed in vacancy defects while the remainder will be weakly absorbed on pristine surface. The attractive interaction between defect complex and the adjacent TM atom can be thermally accelerated to form TM–vacancy defect complexes, for which the activation energies for TM diffusion in the vicinity of defects must be evaluated. Further investigation into the long-range magnetic ordering for TM atoms is necessary to determine the ordering temperature. It would be interesting to study the role of anisotropy of the underlying phosphorene electrons on the magnetic ordering of TM atoms.

Finally, we showed that the semiconducting 2D phosphorene could be tailored to host a many-body Kondo state by tuning its chemical potential (Chapter 7). Cr impurity doped at the divacancy defect in phosphorene results in an

electronic phase transition such that, first a Lifshitz transition occurs, followed by Kondo screening. The experimental feasibility is addressed by discussing the Kondo screening temperatures and Kondo cloud dimensions, as well as the robustness of the system under strain and layer thickness. Similar investigations in other 2D materials should open new avenues for Kondo physics beyond graphene. Cr-doped phosphorene is an interesting playground to probe the conduction and correlated electrons at the edge of Kondo cloud. Further, at slightly higher impurity concentration, we predict the competition between Kondo screening and RKKY interaction can be controlled by gate doping.

Beyond the single layer investigations, heterostructure studies of the above materials are equally promising. It is possible to induce magnetism as well as quantum anomalous Hall effect in graphene with close proximity to a 2D ferromagnetic insulator. (333) Similarly, graphene–phosphorene heterostructures not only prevent phosphorene from chemical degradation but also tune the optoelectronic properties of phosphorene. (334) The recent discovery of Mott insulator and superconductivity in ‘magic angle’ bilayer graphene has paved the way for twistronics and straintronics, (335; 336) where the role of defects remain unknown. It is truly an exciting time to study 2D materials.

BIBLIOGRAPHY

- [1] K. S. Novoselov *et al.*, Science **306**, 666 (2004).
- [2] K. F. Mak *et al.*, Phys. Rev. Lett. **105**, 136805 (2010).
- [3] L. Li *et al.*, Nat. Nanotechnol **9**, 372 (2014).
- [4] H. Liu *et al.*, ACS Nano **8**, 4033 (2014).
- [5] S. Lebègue *et al.*, Phys. Rev. X **3**, 031002 (2013).
- [6] M. Ashton, J. Paul, S. B. Sinnott, and R. G. Hennig, Phys. Rev. Lett. **118**, 106101 (2017).
- [7] N. Mounet *et al.*, Nat. Nanotechnol. **13**, 246 (2018).
- [8] F. Schwierz, Nat. Nano. **5**, 487 (2010).
- [9] S. V. Morozov *et al.*, Phys. Rev. Lett. **100**, 016602 (2008).
- [10] A. S. Mayorov *et al.*, Nano Lett. **11**, 2396 (2011).
- [11] B. Radisavljevic *et al.*, Nat. Nano. **6**, 147 (2011).
- [12] D. Xiao *et al.*, Phys. Rev. Lett. **108**, 196802 (2012).
- [13] K. F. Mak, K. He, J. Shan, and T. F. Heinz, Nat. Nanotechnol. **7**, 494 (2012).
- [14] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, Nat. Phys. **10**, 343 (2014), review Article.
- [15] T. Low *et al.*, Phys. Rev. Lett. **113**, 106802 (2014).

- [16] R. Fei *et al.*, Nano Lett. **14**, 6393 (2014).
- [17] Y. Lin, T. V. Williams, and J. W. Connell, J. Phys. Chem. Lett. **1**, 277 (2010).
- [18] C. R. Dean *et al.*, Nat. Nanotechnol. **5**, 722 (2010).
- [19] F. Xia, H. Wang, and Y. Jia, Nat. Commun. **5**, 4458 (2014).
- [20] T. T. Tran *et al.*, Nat. Nanotechnol. **11**, 37 (2015).
- [21] G. R. Bhimanapati *et al.*, ACS Nano **9**, 11509 (2015).
- [22] Y. Wang, N. Xu, D. Li, and J. Zhu, Adv. Funct. Mater **27**, 1604134 .
- [23] D. Deng *et al.*, Nat. Nanotechnol. **11**, 218 (2016), review Article.
- [24] D. Akinwande *et al.*, Extreme Mech. Lett. **13**, 42 (2017).
- [25] Q. Fu and X. Bao, Chem. Soc. Rev. **46**, 1842 (2017).
- [26] I. Žutić, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. **76**, 323 (2004).
- [27] W. Han, R. K. Kawakami, M. Gmitra, and J. Fabian, Nat. Nano. **9**, 794 (2014).
- [28] B. Náfrádi, M. Choucair, and L. Forró, Adv. Funct. Mater **27**, 1604040 .
- [29] Y. P. Feng *et al.*, Wiley Interdiscip. Rev. Comput. Mol. Sci **7**, e1313 .
- [30] F. Liu, P. Ming, and J. Li, Phys. Rev. B **76**, 064120 (2007).
- [31] A. H. Castro Neto *et al.*, Rev. Mod. Phys. **81**, 109 (2009).
- [32] M. Sepioni *et al.*, Phys. Rev. Lett. **105**, 207205 (2010).
- [33] E. H. Lieb, Phys. Rev. Lett. **62**, 1201 (1989).
- [34] S. Sorella and E. Tosatti, EPL (Europhysics Letters) **19**, 699 (1992).
- [35] H. J. Queisser and E. E. Haller, Science **281**, 945 (1998).

- [36] H. Terrones, R. Lv, M. Terrones, and M. S. Dresselhaus, *Rep. Prog. Phys* **75**, 062501 (2012).
- [37] R. R. Nair *et al.*, *Nat. Commun.* **4**, 2010 (2013).
- [38] A. W. Robertson *et al.*, *ACS Nano* **7**, 4495 (2013).
- [39] H. González-Herrero *et al.*, *Science* **352**, 437 (2016).
- [40] R. R. Nair *et al.*, *Nature Commun.* **4**, 2010 (2013).
- [41] K. M. McCreary *et al.*, *Phys. Rev. Lett.* **109**, 186604 (2012).
- [42] O. V. Yazyev and L. Helm, *Phys. Rev. B* **75**, 125408 (2007).
- [43] J. Červenka, M. I. Katsnelson, and C. F. J. Flipse, *Nat. Phys.* **5**, 840 (2009).
- [44] A. V. Krasheninnikov *et al.*, *Phys. Rev. Lett.* **102**, 126807 (2009).
- [45] T. Eelbo *et al.*, *Phys. Rev. Lett.* **110**, 136804 (2013).
- [46] Y. Tison *et al.*, *ACS Nano* **9**, 670 (2015).
- [47] D. Usachov *et al.*, *Nano Lett.* **11**, 5401 (2011).
- [48] H. Wang, T. Maiyalagan, and X. Wang, *ACS Catal.* **2**, 781 (2012).
- [49] P. Blonski *et al.*, *J. Am. Chem. Soc.* **139**, 3171 (2017).
- [50] Y. Liu *et al.*, *Nat. Commun.* **7**, 10921 (2016).
- [51] Q. Miao *et al.*, *Sci. Rep.* **6**, 21832 (2016).
- [52] J. Li *et al.*, *Carbon* **84**, 460 (2015).
- [53] W. Han *et al.*, *Phys. Rev. Lett.* **105**, 167202 (2010).
- [54] J. Qiao *et al.*, *Nature Commun.* **5**, 4475 (2014).

- [55] J. Pei *et al.*, Nat. Commun. **7**, 10450 (2016).
- [56] X. Wang *et al.*, Nat. Nano. **10**, 517 (2015).
- [57] A. Brown and S. Rundqvist, Acta Cryst. **19**, 684 (1965).
- [58] V. Wang, Y. Kawazoe, and W. T. Geng, Phys. Rev. B **91**, 045433 (2015).
- [59] A. N. Rudenko and M. I. Katsnelson, Phys. Rev. B **89**, 201408 (2014).
- [60] L. Liang *et al.*, Nano Lett. **14**, 6400 (2014).
- [61] R. W. Keyes, Phys. Rev. **92**, 580 (1953).
- [62] D. Warschauer, J. App. Phys. **34**, 1853 (1963).
- [63] Y. Maruyama, S. Suzuki, K. Kobayashi, and S. Tanuma, Physica B+C **105**, 99 (1981).
- [64] A. S. Rodin, A. Carvalho, and A. H. Castro Neto, Phys. Rev. Lett. **112**, 176801 (2014).
- [65] R. A. Doganov *et al.*, Nat. Commun. **6**, 6647 (2015).
- [66] X. Liu *et al.*, J. Phys. Chem. Lett. **6**, 773 (2015).
- [67] M. Engel, M. Steiner, and P. Avouris, Nano Lett. **14**, 6414 (2014).
- [68] Y. Huang *et al.*, Chem. Mater **28**, 8330 (2016).
- [69] G. Abellán *et al.*, J. Am. Chem. Soc. **139**, 10432 (2017).
- [70] A. Ziletti *et al.*, Phys. Rev. Lett. **114**, 046801 (2015).
- [71] B. Kiraly *et al.*, Nat. Commun. **9**, 3904 (2018).
- [72] L. Seixas, A. Carvalho, and A. H. Castro Neto, Phys. Rev. B **91**, 155138 (2015).

- [73] J. Kim *et al.*, Science **349**, 723 (2015).
- [74] Y. Li, S. Yang, and J. Li, J. Phys. Chem. C **118**, 23970 (2014).
- [75] Q. Liu *et al.*, Nano Lett. **15**, 1222 (2015).
- [76] J. Ren *et al.*, Nano Lett. **14**, 4011 (2014).
- [77] J.-H. Chen *et al.*, Nature Phys. **7**, 535 (2011).
- [78] A. Rich, N. R. Davidson, and L. Pauling, *Structural chemistry and molecular biology* (W. H. Freeman, San Francisco, 1968).
- [79] M. Born and R. Oppenheimer, Annalen der Physik **389**, 457 (1927).
- [80] D. R. Hartree, Mathematical Proceedings of the Cambridge Philosophical Society **24**, 89–110 (1928).
- [81] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [82] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [83] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [84] J. Sun, A. Ruzsinszky, and J. P. Perdew, Phys. Rev. Lett. **115**, 036402 (2015).
- [85] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
- [86] S. L. Dudarev *et al.*, Phys. Rev. B **57**, 1505 (1998).
- [87] V. Popescu and A. Zunger, Phys. Rev. B **85**, 085201 (2012).
- [88] P. V. C. Medeiros, S. Stafström, and J. Björk, Phys. Rev. B **89**, 041407 (2014).
- [89] P. V. C. Medeiros, S. S. Tsirkin, S. Stafström, and J. Björk, Phys. Rev. B **91**, 041116 (2015).

- [90] R. Dronskowski and P. E. Bloechl, *J. Phys. Chem.* **97**, 8617 (1993).
- [91] V. L. Deringer, A. L. Tchougréeff, and R. Dronskowski, *J. Phys. Chem. A* **115**, 5461 (2011).
- [92] G. Henkelman, B. P. Uberuaga, and H. Jónsson, *J. Chem. Phys.* **113**, 9901 (2000).
- [93] L. Vicarelli, S. J. Heerema, C. Dekker, and H. W. Zandbergen, *ACS Nano* **9**, 3428 (2015).
- [94] F. Banhart, J. Kotakoski, and A. V. Krashenninnikov, *ACS Nano* **5**, 26 (2011).
- [95] G. M. Rutter *et al.*, *Science* **317**, 219 (2007).
- [96] J.-H. Chen *et al.*, *Phys. Rev. Lett.* **102**, 236805 (2009).
- [97] O. V. Yazyev and S. G. Louie, *Nat. Mater.* **9**, 806 (2010).
- [98] A. Hashimoto *et al.*, *Nature* **430**, 870 (2004).
- [99] K. Kim *et al.*, *Nano Lett.* **8**, 3092 (2008).
- [100] J. C. Meyer *et al.*, *Nano Lett.* **8**, 3582 (2008).
- [101] L. Tapasztó *et al.*, *Phys. Rev. B* **78**, 233407 (2008).
- [102] D. Teweldebrhan and A. A. Balandin, *Appl. Phys. Lett.* **94**, 013101 (2009).
- [103] M. M. Ugeda, I. Brihuega, F. Guinea, and J. M. Gómez-Rodríguez, *Phys. Rev. Lett.* **104**, 096804 (2010).
- [104] P. Y. Huang *et al.*, *Nature* **469**, 389 (2011).
- [105] T. Niu *et al.*, *J. Am. Chem. Soc.* **135**, 8409 (2013).
- [106] J. C. Meyer *et al.*, *Nature* **446**, 60 (2007).

- [107] J. Kotakoski, A. V. Krasheninnikov, U. Kaiser, and J. C. Meyer, Phys. Rev. Lett. **106**, 105505 (2011).
- [108] A. W. Robertson *et al.*, ACS Nano. **7**, 4495 (2013).
- [109] O. Lehtinen *et al.*, Nanoscale **6**, 6569 (2014).
- [110] A. A. El-Barbary *et al.*, Phys. Rev. B **68**, 144107 (2003).
- [111] R. R. Nair *et al.*, Nat. Phys. **8**, 199 (2012).
- [112] J. J. Palacios and F. Ynduráin, Phys. Rev. B **85**, 245443 (2012).
- [113] J. Jobst and H. B. Weber, Nat. Phys. **8**, 352 (2012).
- [114] J.-H. Chen *et al.*, Nat. Phys. **8**, 353 (2012).
- [115] J. H. Warner *et al.*, Nat. Nano. **4**, 500 (2009).
- [116] O. Lehtinen, S. Kurasch, A. V. Krasheninnikov, and U. Kaiser, Nat. Commun. **4**, 2098 (2013).
- [117] B. W. Jeong, J. Ihm, and G.-D. Lee, Phys. Rev. B **78**, 165403 (2008).
- [118] Ç. Ö. Girit *et al.*, Science **323**, 1705 (2009).
- [119] A. Santana, A. M. Popov, and E. Bichoutskaia, Chem. Phys. Lett. **557**, 80 (2013).
- [120] H. Du, Y. Jia, Q. Sun, and Z. Guo, Phys. Lett. A **379**, 1270 (2015).
- [121] J. I. Paredes, P. Solís-Fernández, A. Martínez-Alonso, and J. M. D. Tascón, J. Phys. Chem. C **113**, 10249 (2009).
- [122] G.-D. Lee *et al.*, Phys. Rev. Lett. **95**, 205501 (2005).

- [123] A. Krashennnikov, P. Lehtinen, A. Foster, and R. Nieminen, Chem. Phys. Lett. **418**, 132 (2006).
- [124] H. Zhang *et al.*, Diam. Relat. Mater. **19**, 1240 (2010).
- [125] T. Trevethan *et al.*, Nanoscale **6**, 2978 (2014).
- [126] A. T. Lee, B. Ryu, I.-H. Lee, and K. J. Chang, J. Phys.: Cond. Mat. **26**, 115303 (2014).
- [127] A. Das *et al.*, Nat. Nano. **3**, 210 (2008).
- [128] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- [129] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
- [130] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- [131] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- [132] H. Padmanabhan and B. R. K. Nanda, Phys. Rev. B **93**, 165403 (2016).
- [133] A. V. Krashennnikov and R. M. Nieminen, Theor. Chem. Acc. **129**, 625 (2011).
- [134] M. R. C. Hunt and S. J. Clark, Phys. Rev. Lett. **109**, 265502 (2012).
- [135] J. Kotakoski, F. R. Eder, and J. C. Meyer, Phys. Rev. B **89**, 201406 (2014).
- [136] L. Rodrigo, P. Pou, and R. Pérez, Carbon **103**, 200 (2016).
- [137] J. Ma, D. Alfè, A. Michaelides, and E. Wang, Phys. Rev. B **80**, 033407 (2009).
- [138] J. H. Warner *et al.*, Science **337**, 209 (2012).
- [139] A. Lherbier *et al.*, Phys. Rev. B **86**, 075402 (2012).

- [140] J. D. Wadey *et al.*, Chem. Phys. Lett. **648**, 161 (2016).
- [141] Z. Hou and K. Terakura, J. Phys. Chem. C **119**, 4922 (2015).
- [142] M. Yang *et al.*, AIP Adv. **1**, 032111 (2011).
- [143] V. A. Borodin, T. T. Vehviläinen, M. G. Ganchenkova, and R. M. Nieminen, Phys. Rev. B **84**, 075486 (2011).
- [144] T. O. Wehling, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. B **80**, 085428 (2009).
- [145] M. Ziatdinov *et al.*, Phys. Rev. B **89**, 155405 (2014).
- [146] M. Casartelli, S. Casolo, G. F. Tantardini, and R. Martinazzo, Carbon **77**, 165 (2014).
- [147] M. Riccò *et al.*, Nano Lett. **11**, 4919 (2011).
- [148] E. Asari, M. Kitajima, K. G. Nakamura, and T. Kawabe, Phys. Rev. B **47**, 11143 (1993).
- [149] C. Gong *et al.*, Nanoscale **9**, 13725 (2017).
- [150] G. Teobaldi, K. Tanimura, and A. L. Shluger, Phys. Rev. B **82**, 174104 (2010).
- [151] A. Zobelli, C. P. Ewels, A. Gloter, and G. Seifert, Phys. Rev. B **75**, 094104 (2007).
- [152] J. Gao *et al.*, Nanoscale **5**, 9785 (2013).
- [153] T. Hu and J. Dong, Nanotech. **26**, 065705 (2015).
- [154] Y. Zhang *et al.*, Phys. Rev. Lett. **117**, 166801 (2016).
- [155] G. H. Vineyard, J. Phys. and Chem. Solid. **3**, 121 (1957).

- [156] M. Kabir, S. Mukherjee, and T. Saha-Dasgupta, Phys. Rev. B **84**, 205404 (2011).
- [157] E. Wigner, Trans. Faraday Soc. **34**, 29 (1938).
- [158] G. Henkelman, A. Arnaldsson, and H. Jónsson, J. Chem. Phys. **124**, 044706 (2006).
- [159] J. Tucek *et al.*, Chem. Soc. Rev. **47**, 3899 (2018).
- [160] D. W. Boukhvalov, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. B **77**, 035427 (2008).
- [161] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **54**, 17954 (1996).
- [162] J. Fernández-Rossier and J. J. Palacios, Phys. Rev. Lett. **99**, 177204 (2007).
- [163] O. V. Yazyev and M. I. Katsnelson, Phys. Rev. Lett. **100**, 047209 (2008).
- [164] M. Kabir and T. Saha-Dasgupta, Phys. Rev. B **90**, 035403 (2014).
- [165] G. Z. Magda *et al.*, Nature **514**, 608 (2014).
- [166] S. Ganguly, M. Kabir, and T. Saha-Dasgupta, Phys. Rev. B **95**, 174419 (2017).
- [167] M. Slota *et al.*, Nature **557**, 691 (2018).
- [168] A. G. Swartz *et al.*, ACS Nano **6**, 10063 (2012).
- [169] Z. Wang *et al.*, Phys. Rev. Lett. **114**, 016603 (2015).
- [170] J. C. Leutenantsmeyer, A. A. Kaverzin, M. Wojtaszek, and B. J. van Wees, 2D Mater. **4**, 014001 (2017).
- [171] P. Esquinazi *et al.*, Phys. Rev. Lett. **91**, 227201 (2003).

- [172] B. Sanyal, O. Eriksson, U. Jansson, and H. Grennberg, *Phys. Rev. B* **79**, 113409 (2009).
- [173] S. Haldar *et al.*, *Phys. Rev. B* **89**, 205411 (2014).
- [174] M. A. Akhukov, A. Fasolino, Y. N. Gornostyrev, and M. I. Katsnelson, *Phys. Rev. B* **85**, 115407 (2012).
- [175] Y. Wang *et al.*, *Nano Lett.* **9**, 220 (2009).
- [176] H. S. S. R. Matte, K. S. Subrahmanyam, and C. N. R. Rao, *J. Phys. Chem. C* **113**, 9982 (2009).
- [177] A. Ney *et al.*, *Appl. Phys. Lett.* **99**, 102504 (2011).
- [178] D. Nafday, M. Kabir, and T. Saha-Dasgupta, *Phys. Rev. B* **93**, 045433 (2016).
- [179] D. M. Edwards and M. I. Katsnelson, *J. Phys.: Condens. Matt.* **18**, 7209 (2006).
- [180] X. Hong, S.-H. Cheng, C. Herding, and J. Zhu, *Phys. Rev. B* **83**, 085410 (2011).
- [181] H.-J. Kim and J.-H. Cho, *Phys. Rev. B* **87**, 174435 (2013).
- [182] Y. Ito *et al.*, *J. Am. Chem. Soc.* **137**, 7678 (2015).
- [183] G. Khurana *et al.*, *Nanoscale* **5**, 3346 (2013).
- [184] L. Zhao *et al.*, *Science* **333**, 999 (2011).
- [185] R. Lv *et al.*, *Sci. Rep.* **2**, 586 (2012).
- [186] A. Zabet-Khosousi *et al.*, *J. Am. Chem. Soc.* **136**, 1391 (2014).
- [187] Y. Tison *et al.*, *ACS Nano* **9**, 670 (2015).
- [188] Y. Fujimoto and S. Saito, *Phys. Rev. B* **84**, 245446 (2011).

- [189] A. Lherbier, A. R. Botello-Méndez, and J.-C. Charlier, *Nano Lett.* **13**, 1446 (2013).
- [190] D. Deng *et al.*, *Chem. Mater.* **23**, 1188 (2011).
- [191] R. Mandal *et al.*, *J. Magn. Magn. Mater.* **479**, 67 (2019).
- [192] C. Ronchi *et al.*, *J. Phys. Chem. C* **121**, 8653 (2017).
- [193] A. M. Valencia and M. J. Caldas, *Phys. Rev. B* **96**, 125431 (2017).
- [194] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003).
- [195] J. Sun *et al.*, *Nat. Chem.* **8**, 831 (2016).
- [196] E. B. Isaacs and C. Wolverton, *Phys. Rev. Mater.* **2**, 063801 (2018).
- [197] M. V. Ulybyshev and M. I. Katsnelson, *Phys. Rev. Lett.* **114**, 246801 (2015).
- [198] A. Das *et al.*, *Nat. Nano.* **3**, 210 (2008).
- [199] R. Babar and M. Kabir, *Phys. Rev. B* **98**, 075439 (2018).
- [200] F. Yndurain, *Phys. Rev. B* **90**, 245420 (2014).
- [201] P. O. Lehtinen *et al.*, *Phys. Rev. Lett.* **91**, 017202 (2003).
- [202] Z. Hou and K. Terakura, *J. Phys. Chem. C* **119**, 4922 (2015).
- [203] R. Zan, Q. M. Ramasse, U. Bangert, and K. S. Novoselov, *Nano Lett.* **12**, 3936 (2012).
- [204] T. Ohta *et al.*, *Science* **313**, 951 (2006).
- [205] G. Giovannetti *et al.*, *Phys. Rev. B* **76**, 073103 (2007).
- [206] S. Y. Zhou *et al.*, *Nat. Mater.* **7**, 259 (2008).

- [207] H. Park, A. Wadehra, J. W. Wilkins, and A. H. Castro Neto, Phys. Rev. B **87**, 085441 (2013).
- [208] T. Kondo *et al.*, Phys. Rev. B **86**, 035436 (2012).
- [209] W. Scopel, W. S. Paz, and J. C. Freitas, Solid State Commun. **240**, 5 (2016).
- [210] S. Saremi, Phys. Rev. B **76**, 184430 (2007).
- [211] L. Brey, H. A. Fertig, and S. Das Sarma, Phys. Rev. Lett. **99**, 116802 (2007).
- [212] Y.-F. Lu *et al.*, ACS Nano **7**, 6522 (2013).
- [213] S. Zhang *et al.*, ACS Nano **8**, 9590 (2014).
- [214] Z. Luo *et al.*, Nat. Commun. **6**, 8572 (2015).
- [215] V. Tran, R. Soklaski, Y. Liang, and L. Yang, Phys. Rev. B **89**, 235319 (2014).
- [216] S. Das, M. Demarteau, and A. Roelofs, ACS Nano **8**, 11730 (2014).
- [217] X. Wang *et al.*, Nat. Nanotechnol. **10**, 517 (2015).
- [218] X. Peng, Q. Wei, and A. Copple, Phys. Rev. B **90**, 085402 (2014).
- [219] J. Yuan *et al.*, ACS Nano **9**, 555 (2015).
- [220] S. Muduli *et al.*, Angew. Chem. **57**, 7682 (2018).
- [221] U. Diebold, Surface Science Reports **48**, 53 (2003).
- [222] A. Janotti and C. G. Van de Walle, Phys. Rev. B **76**, 165202 (2007).
- [223] S. H. Song *et al.*, Nat. Commun. **8**, 2121 (2017).
- [224] B. Kiraly *et al.*, Nano Lett. **17**, 3607 (2017).
- [225] J. V. Riffle *et al.*, J. Appl. Phys. **123**, 044301 (2018).

- [226] R. Babar and M. Kabir, J. Phys. Chem. C **120**, 14991 (2016).
- [227] Y. Cai *et al.*, J. Am. Chem. Soc. **138**, 10199 (2016).
- [228] Z. Qiu *et al.*, Nano Lett. **17**, 6935 (2017).
- [229] Z.-D. Sha, Q.-X. Pei, Y.-Y. Zhang, and Y.-W. Zhang, Nanotechnology **27**, 315704 (2016).
- [230] F. Hao and X. Chen, J. Appl. Phys. **120**, 165104 (2016).
- [231] Z.-D. Sha, Q.-X. Pei, Q. Wan, and Z.-S. Liu, J. Phys. Chem. C **121**, 4708 (2017).
- [232] S. T. Skowron, I. V. Lebedeva, A. M. Popov, and E. Bichoutskaia, Chem. Soc. Rev. **44**, 3143 (2015).
- [233] S. J. Yoo, H. Kim, J.-H. Lee, and J.-G. Kim, Nanotechnology **29**, 065702 (2018).
- [234] A. Castellanos-Gomez *et al.*, 2D Materials **1**, 025001 (2014).
- [235] A. Favron *et al.*, Nat. Mater. **14**, 826 (2015), article.
- [236] T. Zhang *et al.*, J. Am. Chem. Soc. **140**, 7561 (2018).
- [237] K. L. Kuntz *et al.*, ACS Appl. Mater. Interfaces **9**, 9126 (2017).
- [238] T. Yang *et al.*, Phys. Rev. B **92**, 125412 (2015).
- [239] H. Zehua *et al.*, Angew. Chem. **56**, 9131 (2017).
- [240] Z. Qionghua, C. Qian, T. Yilong, and W. Jinlan, Angew. Chem. **55**, 11437 (2016).
- [241] A. A. Kistanov *et al.*, 2D Materials **4**, 015010 (2017).
- [242] M. Dion *et al.*, Phys. Rev. Lett. **92**, 246401 (2004).

- [243] Q. Wei and X. Peng, *Appl. Phys. Lett.* **104**, 251915 (2014).
- [244] E. J. G. Santos, S. Riikonen, D. Sánchez-Portal, and A. Ayuela, *J. Phys. Chem. C* **116**, 7602 (2012).
- [245] S. Haldar *et al.*, *Phys. Rev. B* **92**, 235408 (2015).
- [246] P. Śpiewak and K. J. Kurzydłowski, *Phys. Rev. B* **88**, 195204 (2013).
- [247] J. R. Weber, A. Janotti, and C. G. Van de Walle, *Phys. Rev. B* **87**, 035203 (2013).
- [248] Y. Guo and J. Robertson, *Sci. Rep.* **5**, 14165 (2015).
- [249] X. Li *et al.*, *Nanoscale* **8**, 17801 (2016).
- [250] J. Carrasco, N. Lopez, F. Illas, and H.-J. Freund, *J. Chem. Phys.* **125**, 074711 (2006).
- [251] P. Krüger *et al.*, *Phys. Rev. Lett.* **100**, 055501 (2008).
- [252] I. Beinik *et al.*, *Nat. Commun.* **6**, 8845 (2015).
- [253] H. Cheng and A. Selloni, *Phys. Rev. B* **79**, 092101 (2009).
- [254] T. Trevethan *et al.*, *Phys. Rev. B* **90**, 174108 (2014).
- [255] R. H. Telling, C. P. Ewels, A. A. El-Barbary, and M. I. Heggie, *Nat. Mater.* **2**, 333 (2003).
- [256] L. Liu *et al.*, *Nanoscale* **6**, 5729 (2014).
- [257] L. Wu *et al.*, *J. Phys. Chem. C* **117**, 17066 (2013).
- [258] M. Fortin-Deschênes, P. L. Levesque, R. Martel, and O. Moutanabbir, *J. Phys. Chem. Lett.* **7**, 1667 (2016).
- [259] M. T. Lusk and L. D. Carr, *Phys. Rev. Lett.* **100**, 175503 (2008).

- [260] Z. Dai *et al.*, Phys. Rev. Materials **1**, 074003 (2017).
- [261] A. K. Geim and K. S. Novoselov, Nat. Mater. **6**, 183 (2007).
- [262] K. S. Novoselov *et al.*, Nature **490**, 192 (2012).
- [263] R. Mas-Balleste, C. Gomez-Navarro, J. Gomez-Herrero, and F. Zamora, Nanoscale **3**, 20 (2011).
- [264] S. Z. Butler *et al.*, ACS Nano **7**, 2898 (2013).
- [265] A. K. Geim and I. V. Grigorieva, Nature **499**, 419 (2013).
- [266] M. Xu, T. Liang, M. Shi, and H. Chen, Chem. Rev. **113**, 3766 (2013).
- [267] P. R. Wallace, Phys. Rev. **71**, 622 (1947).
- [268] Y.-W. Son, M. L. Cohen, and S. G. Louie, Phys. Rev. Lett. **97**, 216803 (2006).
- [269] S. Y. Zhou *et al.*, Nat. Mater. **6**, 770 (2007).
- [270] R. Balog *et al.*, Nat. Mater. **9**, 315 (2010).
- [271] K. F. Mak, C. H. Lui, J. Shan, and T. F. Heinz, Phys. Rev. Lett. **102**, 256405 (2009).
- [272] S.-M. Choi, S.-H. Jhi, and Y.-W. Son, Phys. Rev. B **81**, 081407 (2010).
- [273] Q. H. Wang *et al.*, Nat. Nano. **7**, 699 (2012).
- [274] M. Osada and T. Sasaki, Adv. Mater. **24**, 210 (2012).
- [275] D. J. Late *et al.*, Adv. Mater. **24**, 3549 (2012).
- [276] H. Sevincli, M. Topsakal, E. Durgun, and S. Ciraci, Phys. Rev. B **77**, 195434 (2008).

- [277] T. Hu and J. Hong, J. Phys. Chem. C **119**, 8199 (2015).
- [278] A. Hashmi and J. Hong, J. Phys. Chem. C **119**, 9198 (2015).
- [279] X. Sui *et al.*, J. Phys. Chem. C **119**, 10059 (2015).
- [280] S. Lisenkov, A. N. Andriotis, and M. Menon, Phys. Rev. Lett. **108**, 187208 (2012).
- [281] C. B. Crook *et al.*, Sci. Rep. **5**, 12322 (2015).
- [282] Y. Gan, L. Sun, and F. Banhart, Small **4**, 587 (2008).
- [283] A. V. Krasheninnikov and F. Banhart, Nat. Mater. **6**, 723 (2007).
- [284] K. K. Gomes *et al.*, Nature **483**, 306 (2012).
- [285] H. Wang *et al.*, Nano Lett. **12**, 141 (2012).
- [286] P. Srivastava *et al.*, J. Phys. Chem. C **119**, 6530 (2015).
- [287] Y. Liu *et al.*, Nano Lett. **14**, 6782 (2014).
- [288] H.-P. Komsa *et al.*, Phys. Rev. Lett. **109**, 035503 (2012).
- [289] J. J. Palacios, J. Fernández-Rossier, and L. Brey, Phys. Rev. B **77**, 195428 (2008).
- [290] C. Attacalite *et al.*, Phys. Rev. B **83**, 144115 (2011).
- [291] R. Li *et al.*, Phys. Rev. B **90**, 045425 (2014).
- [292] W. Hu and J. Yang, J. Phys. Chem. C **119**, 20474 (2015).
- [293] M. Umar Farooq, A. Hashmi, and J. Hong, Sci. Rep. **5**, 12482 (2015).
- [294] P. Pyykkö and M. Atsumi, Chem. Eur. J. **15**, 186 (2009).
- [295] S. P. Koenig *et al.*, Nano Lett. **16**, 2145 (2016).

-
- [296] X. Sun *et al.*, Appl. Phys. Lett. **106**, 222401 (2015).
- [297] F. J. Himpsel, J. E. Ortega, G. J. Mankey, and R. F. Willis, Advances in Physics **47**, 511 (1998).
- [298] F. J. Himpsel, Phys. Rev. Lett. **67**, 2363 (1991).
- [299] J. E. Ortega and F. J. Himpsel, Phys. Rev. B **47**, 16441 (1993).
- [300] U. Alkemper *et al.*, Phys. Rev. B **50**, 17496 (1994).
- [301] J. Kondo, Prog. Theor. Phys. **32**, 37 (1964).
- [302] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, London, 1993).
- [303] W. de Haas, J. de Boer, and G. van den Berg, Physica **1**, 1115 (1934).
- [304] J. Park *et al.*, Nature **417**, 722 (2002).
- [305] W. Liang *et al.*, Nature **417**, 725 (2002).
- [306] A. Zhao *et al.*, Science **309**, 1542 (2005).
- [307] J. Nygard, D. H. Cobden, and P. E. Lindelof, Nature **408**, 342 (2000).
- [308] P. Jarillo-Herrero *et al.*, Nature **434**, 484 (2005).
- [309] D. Goldhaber-Gordon *et al.*, Nature **391**, 156 (1998).
- [310] S. M. Cronenwett, T. H. Oosterkamp, and L. P. Kouwenhoven, Science **281**, 540 (1998).
- [311] T. O. Wehling *et al.*, Phys. Rev. B **81**, 115427 (2010).
- [312] L. Fritz and M. Vojta, Rep. Prog. Phys. **76**, 032501 (2013).

- [313] A. Carvalho *et al.*, Nature Rev. Mater. **1**, 16061 (2016).
- [314] J. Kim *et al.*, Phys. Rev. Lett. **119**, 226801 (2017).
- [315] S. P. Koenig *et al.*, Nano Lett. **16**, 2145 (2016).
- [316] I. Affleck and P. Simon, Phys. Rev. Lett. **86**, 2854 (2001).
- [317] C. A. Büsser *et al.*, Phys. Rev. B **81**, 045111 (2010).
- [318] J. Park, S.-S. B. Lee, Y. Oreg, and H.-S. Sim, Phys. Rev. Lett. **110**, 246603 (2013).
- [319] Y. Cai *et al.*, J. Am. Chem. Soc. **138**, 10199 (2016).
- [320] I. M. Lifshitz, Sov. Phys. JETP **11**, 1130 (1960).
- [321] A. Ziletti, S. M. Huang, D. F. Coker, and H. Lin, Phys. Rev. B **92**, 085423 (2015).
- [322] Z. J. Xiang *et al.*, Phys. Rev. Lett. **115**, 186403 (2015).
- [323] S. Slizovskiy, A. V. Chubukov, and J. J. Betouras, Phys. Rev. Lett. **114**, 066403 (2015).
- [324] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).
- [325] T. A. Costi *et al.*, Phys. Rev. Lett. **102**, 056802 (2009).
- [326] M. Ternes, A. J. Heinrich, and W.-D. Schneider, J. Phys. Condens. Matter **21**, 053001 (2009).
- [327] H. C. Manoharan, C. P. Lutz, and D. M. Eigler, Nature **403**, 512 (2000).
- [328] L. Borda, Phys. Rev. B **75**, 041307 (2007).
- [329] D. Çakır, H. Sahin, and F. M. Peeters, Phys. Rev. B **90**, 205421 (2014).

- [330] G. Wang, G. C. Loh, R. Pandey, and S. P. Karna, *Nanotechnology* **27**, 055701 (2016).
- [331] J. Dai and X. C. Zeng, *J. Phys. Chem. Lett.* **5**, 1289 (2014).
- [332] <http://news.nus.edu.sg/press-releases/graphene-enters-stratosphere>.
- [333] J. Zhang *et al.*, *Phys. Rev. B* **97**, 085401 (2018).
- [334] Y. Cai, G. Zhang, and Y.-W. Zhang, *J. Phys. Chem. C* **119**, 13929 (2015).
- [335] Y. Cao *et al.*, *Nature* **556**, 80 (2018).
- [336] Y. Cao *et al.*, *Nature* **556**, 43 (2018).

LIST OF PUBLICATIONS

Publications included in this thesis

1. *Transition metal and vacancy defect complexes in phosphorene: A spintronic perspective*

Rohit Babar and Mukul Kabir

The Journal of Physical Chemistry C 120, 14991 (2016)

2. *Gate-dependent vacancy diffusion in graphene*

Rohit Babar and Mukul Kabir

Physical Review B 98, 075439 (2018)

3. *Engineering the Kondo state in two-dimensional semiconducting phosphorene*

Rohit Babar and Mukul Kabir

Physical Review B 97, 045132 (2018)

4. *Ferromagnetism in nitrogen-doped graphene*

Rohit Babar and Mukul Kabir

Physical Review B 99, 115442 (2019)

5. *Defect-driven degradation in phosphorene*

Rohit Babar and Mukul Kabir

Manuscript in preparation

Publications not included in this thesis

6. *Photocatalytic activity of phosphorene derivatives: coverage, electronic, optical and excitonic properties*

S. Arra, K. R. Ramya, **Rohit Babar** and Mukul Kabir

The Journal of Physical Chemistry C 122, 7194 (2018)

7. *Photoluminescence quenching in self assembled CsPbBr₃ quantum dots on few layer black phosphorous sheets*
S. Muduli, P. Pandey, G. Devatha, **Rohit Babar**, D. C. Kothari, M. Kabir, P. Pillai, S. Ogale
Angewandte Chemie 57, 7682 (2018)
8. *F-doped carbon nano-onion film as scaffold for highly efficient and stable Li metal anode: A novel laser direct-write process*
D. Puthusseri, M. Wahid, A. Basu, **Rohit Babar**, M. Kabir, S. Ogale
Nanoscale 10, 7630 (2018)
9. *Nature of magnetism and transport in B_xC_yN_z thin films: The intriguing role of nitrogen defects in the electronic structure*
R. Mandal, **Rohit Babar**, M. Tripathi, S. Datta, R. J. Choudhary, M. Kabir, and S. Ogale
Journal of Magnetism and Magnetic Materials 479, 67 (2019)
10. *Exciton in phosphorene: Strain, impurity, thickness and heterostructure*
S. Arra*, **Rohit Babar*** and Mukul Kabir (* equal contribution)
Physical Review B 99, 045432 (2019)