Atomistic Insights into Electronic/Magnetic Properties of Transition-metal based Low Dimensional Systems for Spintronics Applications

Ph.D. Thesis

By

SOURABH KUMAR



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE MARCH 2020

Atomistic Insights into Electronic/Magnetic Properties of Transition-metal based Low Dimensional Systems for Spintronics Applications

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SOURABH KUMAR



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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled Atomistic Insights into Electronic/Magnetic Properties of Transition-metal based Low Dimensional Systems for Spintronics Applications in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from APRIL 2015 to August 2020 under the supervision of Dr. Biswarup Pathak, Associate Professor, Department of Chemistry, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Abstract

Spintronics involves the manipulation of electronic spin for futuristic applications in different areas such as magnetism, electronics, and photonics. Their interdependence is of great significance for revolutionizing spin-based technologies, such as spin-field effect transistors, spin-resonant tunneling diodes, spin-light emitting diodes, and many more. This intrinsic manipulation of electronic spin and its correlation with other relevant fields govern real-world device's functionalities. Hence, the origination and understanding of electronic spins in different architectures (materials) becomes crucial. Following the above challenges, we have decided to understand the various magnetic models and their association to properties such as electronic gap, Curie temperature, and conductivity. The dimensionality plays a crucial role in the alternation of electronic spins at the nanoscale. We are reducing the available degree of freedoms (possible spatial orientation) for the electronic spins on reducing the dimensions. Hence, the formation of nano-level architectures involving spintronics facilitates the development of multifunctional materials. Many materials with reduced dimensionality are already found to be promising for spintronics applications, such as two-dimensional (2D) metal chalcogenides and 2D metal-organic frameworks, and so.

Similarly, the type of chemical bonding involved in forming such materials is an essential parameter of concern. The understanding of chemical bonding tells about the favorable pathways involved in the electronic localization or delocalization. The extent of electron localization (or delocalization) in a system tells about the nature of magnetism. A further explanation is provided by employing the different magnetic exchange phenomenon. Collectively, all these parameters offer alternative pathways for tuning electronic and magnetic properties. Therefore, more efforts are needed to explore the low-dimensional materials and understand the chemistry behind such properties. In this context, computational simulations play a crucial role in understanding the atomic insights behind the evolution of magnetic and electronic properties in spintronics.

The contents of each chapter included in the thesis are briefly discussed as follows:

1.1 Introduction

This chapter is majorly categorized into three sections: magnetic models (Stoner, Hubbard, and Heisenberg) and magnetic-exchanges models (direct, super, and double-exchange). Then followed by a rapid discussion on spintronics and their applicability. Later, we have discussed the theory and computational methods involved in the present study.

Starting from the origination of magnetism, we have also discussed the contributions of several researchers in magnetism. Our goal majorly involves discussing the theory provided by Heisenberg, Stoner, and Hubbard in explaining magnetism. Later, we have also discussed the different magnetic exchange models such as direct-exchange, super-exchange, and double-exchange.

We have also discussed spintronics and their importance for futuristic applications.

The spin-polarized density functional calculations are used to investigate different types of electronic and magnetic properties. Hence, this chapter also includes a brief discussion on the Schrodinger equation and density functional theory. We have also discussed the basic theory involved in Ab initio molecular dynamics, Bader charge analysis, Crystal orbital Hamilton population analysis, and phonon dispersion.

1.2 An atomically thin ferromagnetic half-metallic pyrazine-fused Mn-porphyrin sheet: a slow spin relaxation system

In this chapter, we have studied the transition metal (TM = Cr, Mn, Fe, Co, Ni, Cu, and Zn) incorporated pyrazine fused porphyrin (TM-PP) systems for possible spintronics applications using the state-of-the-art density functional theory (DFT). Here, all the TM-PP systems are found to be energetically, mechanically, and thermally stable. The incorporation of transition metals results in the enhancement of

electronic and magnetic properties. All the TM-PP systems form a magnetic ground-state (except Ni and Zn) due to the TM²⁺ oxidation state under the square planer crystal field. Here, the maximum magnetic moment is localized on the transition metal centers sitting in the pores of the porphyrin sheet, whereas N atoms coordinating with the transition metal are antiferromagnetically coupled (except Cu). A semiconducting electronic picture is observed in all the TM-PP (except Mn-P). Here, the Mn-PP is found to be half-metallic with an electronic gap of 0.80 eV in one of the spin channels (up spin) under the PBE level of theory. The electronic picture of Mn-PP is further confirmed by the higher level of DFT functionals such as HSE06. The calculated Curie temperature for Mn-PP is found to be 269 K with the help of the Onsager equation $k_B T_C/J = 2.2691$. As the direct channel for electron-spin interaction is blocked in half-metallic ferromagnets. We have also studied the electronic picture of Mn-PP under applied strain. On applying the compressive strain up to 4 %, there is no change in the Mn-PP's halfmetallic electronic picture. However, under tensile strain, a spincrossover is observed from a low spin state (normal) to a high spin state (> 2 % strain). Here, the plausibility of mixing a high spin state with unquenched spin-orbit coupling provides a feasible way to achieve a higher MAE value. Our results suggest that a 2D TM-PP (Mn-PP) system acts as a possible candidate for spintronics applications due to magneto-mechanical control over electronic and magnetic properties.

1.3 Double-Exchange Magnetic Interactions in High-Temperature Ferromagnetic Iron Chalcogenide Monolayers

In this chapter, we have proposed a two-dimensional (2D) ironchalcogenide-based (Fe₃S₄) monolayer for room-temperature ferromagnetic applications. This 2D sheet can be exfoliated from a mineral having a lamellar structure known as Smythite, which is compositionally identical to Greigite. We have majorly focused on the charge-transfer process and complex magnetic ordering in the 2D Smythite lattice in this work. The proposed 2D sheet is found to be energetically, dynamically, and thermally stable. A small amount of

exfoliation energy (0.0134 eV/Å) for a 2D Smythite sheet suggests a weak interlayer interaction among the neighboring images. From Bader charge analysis, two different types of crystal fields are observed around the Fe centers $(Fe_2^{0.517e}Fe^{0.657e}S_2^{-0.571e}S_2^{-0.275e})$. The electronic and magnetic properties of the 2D Smythite sheet is confirmed with different DFT functionals such as GGA, GGA+U, B3LYP, HSE03, and HSE06. The GGA+U method is well known to describe electronic localization. Here, on employing the Hubbard $(U_{eff} = U - J; J = \text{effective on-site})$ exchange interactions) model, a magnetic transition is observed between the transition-metal centers. However, the maximum bandgap calculated with the DFT+U level of theory is 0.17 eV. This value is much less compared to the other hybrid functionals (~1.0 eV). However, the standard DFT predicts the electronic picture to be metallic and fails to describe the electron localization in the 2D Smythite lattice. After following the several DFT functionals, HSE06 functionals are used throughout the work. We have also investigated the magnetic interactions in 2D Smythite lattice by dividing the exchange mechanism models into two parts: in-lattice (molecular) and periodic approach with the nearest neighbors (NN) approach. Because of weak spin-orbit coupling (SOC), the non-collinear models cannot overcome Ligandfield and Jahn-Teller distortions. Three exchange mechanisms (Direct, Super, and Double-exchange) are found to be competing for the inlattice model. The presence of three magnetic centers diminishes the possibility of antiferromagnetic ordering. The in-lattice model confirms the ferromagnetic order in the 2D Smythite unit cell. To further confirm the nature of long-range ferromagnetic ordering in the 2D Smythite lattice, a 2×2 supercell is constructed with only two possible magnetic order (ferromagnetic and anti-ferromagnetic). The calculated value of Curie temperature (T_c) for 2D Smythite is 406 K. A strain model is employed $(\pm 2 \%)$ to understand the nature of ferromagnetic interactions. Out of possible magnetic exchange orderings (direct, super, and double), double-exchange ordering found to governing the ferromagnetic order. Also, a spin-orbit counterplot is constructed to confirm the in-plane Jahn-teller distortion. In conclusion, our study suggests that an in-lattice redox pair (Fe^{2+}/Fe^{3+}) in 2D systems can favor the ferromagnetic orderings.

1.4 Spin-Polarized Current in Ferromagnetic Half-Metallic Transition Metal Iodide Nanowire

After following up with intrinsic ferromagnetic ordering in the 2D systems, we discussed the possible magnetic orders in the 1D systems. The stabilization of magnetic orderings in the 1D system is very difficult. Due to the reduced number of nearest neighbors, the magnetic exchange interactions decrease, which results in the decrease of possible magnetic ordering. Many 1D systems are already known, which can be synthesized with atomic-scale tunability in the present time. We have considered a transition metal halide due to its intriguing magnetic applications and easy availability following such challenges. We have considered 3d transition-metal iodide (TMI₃) based nanowire with only two possible spatial orientations in the present work. They are categorized based on their spatial orientation, such as eclipsed (E) and staggered (S) types. Based on energetics (formation energy, E_f = $E_{NW} - 4 \times E_{TM} - 12 \times E_I$), we have excluded the E type nanowires from the current study. Also, FeI₃ and CoI₃ (S-type) nanowires are excluded due to their more positive values of formation energies compare to the early 3d TMIs nanowires. After that, we have performed the AIMD simulations to ensure the thermal stability of nanowires. All the remaining nanowires (ScI₃-MnI₃) are found to be thermally stable. We have calculated the electronic and magnetic properties of TMIs. Based on magnetic moment data and orbital hybridization, a "+3" oxidation state is suggested in the TMIs. All the nanowires are found to be semiconducting, except VI₃. The calculated electronic picture of VI₃ has a half-metallic ground-state, further confirmed with a higher level of DFT calculations, such as GW. A ferromagnetic ordering is proposed in the VI₃ nanowire, and the calculated value of Curie temperature (T_c) is 22.3 K. To analyze the nature of ferromagnetic interactions, COHP calculations, and strain vs. energy study is performed. Based on ICOHP

values, a metal-metal dimer model is proposed for inducing the magnetic interactions. This dimer interaction governs the magnetic and electronic properties in VI₃ nanowires. The same reason causes the TiI₃ nanowire to be non-magnetic by the pairing of available d^1 electrons. We have also analyzed the transport properties in the VI₃ nanowire by calculating an i - v characteristic graph. A large spin-polarized current is observed, which confirms the half-metallicity in the VI₃ nanowire. Moreover, the phonon dispersion calculation also confirmed the dynamic stability of the VI₃ nanowire. In conclusion, the ferromagnetic interactions in a low dimensional system can be stabilized, and 1D materials can be a promising candidate for spintronics applications.

1.5 Evidence of Spin Hall Effect in Two-Dimensional Global Minimum Fe-P Monolayer

Following the search of spintronics materials, the thought of proposing a new two-dimensional material came to our attention, which can be experimentally synthesized and may have the potential capabilities for spintronics applications. In this work, our search was motivated by the recent reports on Fe-based systems, such as Fe₃GeTe₃ and Fe₃P. Here, the magnetism is driven by the intrinsic ferromagnetism of Fe. Phosphorus is chosen as a counter pair of Fe due to its excellent tendency of catenation. Fe-P systems are known to form many metastable phases with different types of magnetic ordering. Several Fe-P (Fe_xP_y) based compositions are considered from a Fe rich ($5 \ge x \ge y$) to P rich ($5 \ge x \ge y$) $y \ge x$) phase. Global optimization tools carefully examine each composition. After that, their energetics is compared with some preexisting 2D materials such as Fe₂P and Fe₃P. Our proposed structures are found to be energetically more favorable. Then, we have analyzed the thermal and dynamic stabilities for all the $Fe_x P_y$ compositions. Among them, FeP₂ monolayer is found to be energetically, thermally, and dynamically stable. The presence of electronic instability is confirmed with different chemical bonding analysis tools, such as COHP methods. FeP₂ is found to be non-magnetic with high electronic density at the Fermi level. The mechanical strain can tune the electronic

instability present in the FeP₂ monolayer. In the strain vs. energy study, the non-magnetic ground-state is found to be robust under compressive strain. However, with applied tensile stress, a small amount of magnetic moments rises in the FeP₂ monolayer. The magnetic moment reaches up to 0.357 μ_B per unit cell for 2% of biaxial tensile strain. A Zeeman-type band splitting is observed with a spin-splitting (Δ_z) gap of 260 meV at the Γ -point. Such a large band-splitting can give rise to long-range ferromagnetic interactions. The calculated Curie temperature ($T_c = 471$ K) confirms the presence of ferromagnetic ordering in the FeP₂ monolayer. This ferromagnetic state is free from any dopants and defects. Finally, we have investigated the transport properties of the FeP₂ monolayer. The calculated spin-hall conductivity value $(34 \hbar)$ $e \ \Omega \text{cm}^{-1}$) suggest that the intrinsic spin-hall properties in FeP₂ monolayer (Figure 4). This value is further tuned by the mechanical strain (80 $\hbar/e \ \Omega \text{cm}^{-1}$). In conclusion, a new 2D FeP₂ monolayer is proposed with intriguing magnetic and transport properties. In such materials, the electronic spins can be tuned by electric current.

2. Conclusion

In this thesis, we have explored several low-dimensional materials for futuristic spintronics applications. Several computational techniques and mechanistic studies are used to describe the electronic and magnetic properties. Collectively, they are useful for the development of spintronics devices. The findings of the thesis are outlined as follows:

- Transition-metal based porphyrins sheet can be a potential candidate for spintronics applications with flexible electronic and magnetic properties tuned by the intrinsic spin-crossover mechanisms.
- Lamellar structures of pre-existing minerals (Smythite) with mixed hybridization of transition-metals can provide an alternative route to reach strong ferromagnetism in nanoscale devices such as 2D Smythite lattice.
- iii) In 1D systems, the long-range magnetic interactions are absent or rarely present. The magnetic interactions can be

stabilized in 1D systems, which are further supported by the metal-metal dimer formations. The electronic properties are also tuned by such factors, which also give rise to intriguing transport properties.

iv) A spin-hall state is observed on theoretically proposed 2D
 FeP₂ global monolayer. The presence of intrinsic spin-orbit coupling, high fermion density, and lack of structural asymmetry gives rise to the spin-hall conductivity in such a system.

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Acronyms

DFT	Density functional theory
LDA	Local density approximation
LSDA	Local spin-density approximation
GGA	Generalized Gradient Approximation
PBE	Perdew-Burke-Ernzerhof
HSE	Heyd-Scuseria-Ernzerhof
AIMD	Ab initio molecular dynamics
COHP	Crystal orbital Hamilton populations
2D	Two-dimensional
PP	Porphyrin-based
1D	One-dimensional
SDD	Spin-density difference
SOC	Spin-orbit coupling
MAE	Magnetic anisotropy energy
ESP	Electrostatic potential
PR	Poisson's ratio
DOS	Density of states
PDOS	Partial density of states
TM	Transition-metal
СТ	Charge transfer
DE	Double-exchange
LDOS	Local density of states
FM	Ferromagnetic
AFM	Anti-ferromagnetic
JT	Jahn-teller
BZ	Brillouin zone



Introduction

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Chapter 1

Introduction

Here, we will discuss the different schemes combines to explore the magnetism and electronic structure in low-dimensional materials. Starting from itinerant electron theory (Stoner) to localized-moment description (Heisenberg), the following mechanisms are described by a generalized multiorbital Hubbard model. The end of the chapter will be concluded with a focus on density functional theory and other valuable computational techniques.

1.1 History

The main idea of magnetism involving the Heisenberg model originates from the Heitler-London method, based on the chemical bond [1]. The lowering of energy in the Heitler-London model is described by the exchange of electrons between two H atoms (forming the H₂ molecule). An anti-parallel spin alignment during the formation of a chemical bond favors the formation of a chemical bond by enhancing the extent of orbital overlap. Heisenberg adopts the same idea to describe the total atomic moment (S_i) located on atomic site "i" to describe the extent of exchange between the two neighbor sites by the following formula:

$$V_{ij} = -2J_{ij}\dot{S}_i.\dot{S}_j \tag{1.1}$$

Here, the sign of " J_{ij} " describes the order of spin alignment. The positive value of J_{ij} represents the ferromagnetic interactions, whereas negative represents the anti-ferromagnetism. Whereas the Bloch-Wigner approach motivates the Stoner model [2]. The formation of the momentum sphere describes the magnetism in the Block-Wigner-Slater model. The momentum sphere model, also known as the Fermi sphere, represents a momentum state's double occupancies due to up-spin and down-spin electrons. From Bloch's point of view, the magnetization is controlled by minimizing total kinetic energy and exchange interactions. An exchange interaction favors the alignment of spins in the conduction electrons in the same momentum states. On the contrary, Pauli's

exclusion principle disfavors the alignment in the same momentum states, which in-turns favor the migration of electrons to higher momentum states by increasing the system's kinetic energy [3]. A competitive nature describes whether the ferromagnetism survives or not. Here, the exchange interactions are known to originate from the electrostatic Coulomb repulsion between the same spin electrons. Bloch has not considered the electrostatic Coulomb interactions between the anti-parallel spins. Wigner first pointed out in 1934 [4] and describes the lack of correlation effects in the Bloch model of ferromagnetism. Slater has corrected the itinerant exchange (represented by the Bloch) with the exchange interactions of intra-atomic origin [5-6]. In this model, the electron with a S_z spin axis flits from one atom to a nearby atom and keeping its spin polarization axis the same as the initial position. This mechanism extends over the whole lattice in a similar manner, which leads to the spin alignment and ferromagnetism. A similar spin configuration after the hopping describes the minimum energy state. Hence, such hopping of electrons from one site to others by keeping their spin axis favors ferromagnetism.

In the Heisenberg model, the magnetism is induced by the moments localized on the atomic sites. This picture of electron localization is perfectly valid for magnetic insulators. However, the same model cannot be used to describe magnetism in metals, where charge carriers govern the magnetic effects, such as in 3*d* transition-metals. Based on the above expression for J_{ij} (exchange interaction), the Hamiltonian for the Heisenberg model can be written as

$$H = -J\Sigma_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j \tag{1.2}$$

Here, we have only considered a single exchange parameter (J) for describing the magnetic interactions. In real systems, several values of J's can be present. The positive sign of J value represents the ferromagnetism. However, from chemical bond theory, the pairing of the electron is favorable (anti-parallel spin alignment), representing the negative values for exchange parameter J. These two pictures are
contradictory to each other; a positive J requires ferromagnetism, and a negative J describes the chemical bond formation. To support his conclusion, Heisenberg concluded that the larger principal quantum number is needed for the ferromagnetism. But failed to prove the absence of ferromagnetism in few 3d transition metals. This was partially cleared by the Slater curve, in which the values of J change with interatomic distances. Hence, both models are insufficient to explain ferromagnetism in the broad class of materials. The extent of electron localization further depends upon factors such as d-bands, crystal-fields, and many more. Here, we will consider the Hubbard model in terms of electron localization limit to explain the ferromagnetism by correlating both the models (Stoner and Heisenberg).

1.2 Stoner, Hubbard, and Heisenberg

For describing the exact nature of ferromagnetism in high-temperature magnets, it is essential to understand the itinerant nature of electrons in pure metals and their compounds (Figure 1.1).

	Stoner	Heisenberg	Hubbard	
T = 0	^ ^ ^ ^ 	^ ^ ^ ^ 	^ ^ ^ ^ 	
$T < T_c$	<u> </u>	*****	14177	
$T > T_c$	0 0 0 0 0	14-245	** 1 * >	

Figure 1.1: Different types of magnetic models at 0 K, below the Curie temperature (T_c) and above the T_c .

It has been universally accepted that the *d*-electrons in metals such as Mn, Fe, Co, etc., are itinerant types in nature [7]. But they do not fall in the perfect Stoner model of magnetism. As the prediction of Curie temperature by single-flip excitation methods is well overestimated. Hence, the transition metals with 3d valence electrons can be considered within the Stoner and Heisenberg model (Hubbard case). At such point, the self-consistent solution for the disordered itinerant electronic states

(above T_c) have lower energy (more negative) compare to the nonmagnetic state (Stoner case). These itinerant electronic states present on the atoms can rotate from a perfectly ordered state to a disordered state.

In the most straightforward formulation, the Hubbard Hamiltonian [8] can be written as $H_h = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_i U n_{i\uparrow} n_{j\downarrow}$ (1.3)

where U represents the characteristic Hubbard coulomb interaction, trepresents the hopping parameter, $c_{i\sigma}^{\dagger}$ (and $c_{j\sigma}$) represents the electron creation (and annihilation) operator, and $n_{i\uparrow}$ (and $n_{j\downarrow}$) represents the spin-density operator. The Hubbard model describes the interplay between kinetic energy and Coulomb interactions. There are two limiting cases in the Hubbard model: the non-interacting limit (bandlimit) when $t \gg U$ and atomic-limit (no hopping) when $U \gg t$. In bandlimit, there are no interactions available, and only hopping terms survive. In such cases, energy levels form bands, and the system behaves as metals. In the opposite case, the electrons will be distributed over atomic sites to minimize the Coulomb energy. In a non-degenerate and half-filled system, this results in the exact filling of every possible site available. This configuration is the lowest energy configuration, where hopping will only increase the energy (double occupied site). Thus, the system behaves as an insulator in the atomic limits. It is well known that at the half-filling and in the atomic limit, the Hubbard model becomes a nearest-neighbor Heisenberg antiferromagnet:

$$H = \Sigma_{\langle i,j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j \tag{1.4}$$

Here, the exchange parameter $J_{ij} = \frac{4t_{ij}t_{ji}}{U}$ and electron spin operator S_i is defined as $S_i = \frac{1}{2}c_{i\alpha}^{\dagger}\sigma_{\alpha\beta}c_{i\beta}$ (1.5)

where σ 's are the Pauli spin matrices. Here, the kinetic exchange interaction parameter (J_{ij}) is of the order of Neel (magnetic) transition temperature. This model correctly describes the magnetism in localized 4f-electrons materials. However, this model is not appropriate for transition metals due to the longitudinal and transverse magnetic fluctuations. Hence, the most suitable model is the Hubbard Hamiltonian, fitted to Heisenberg or Stoner model based on electroncorrelation limits.

1.3 Magnetic Exchange Models

The magnetism in the insulators is well described and comparably understood in the literature. Here, we will discuss the different types of magnetic exchange models in crystalline materials. From Bloch-Wilson's theory on electronic band-structure, the band formed in crystalline materials with filled bands or empty bands leads to the materials insulating behavior. This electronic theory of bands has some significant drawbacks, which Mott later addresses. According to Mott, the electron-electron interactions can be somewhat significant in governing such properties. Despite having the odd number of electrons in the unit cell of NiO, the system is found to be insulating. This observation is entirely contradictory to the band theory of Wilson-Bloch. The Mott provides the expression for this energy gap as

$$E_{gap} = U - 2zt \tag{1.6}$$

where $U \gg t$, for a solid to be insulator (Mott insulators). In NiO, Ni is in a +2 state (8 valence electrons). Due to strong electron-correlation in the narrow *d* bands of Ni, the hopping of electrons is prohibited from one site to another. This results in an insulating state in the NiO [9-10]. The localization of electrons also induces magnetizations. The insulating magnetic behavior mainly arises from various exchange interactions such as Direct-exchange, Super-exchange, and Doubleexchange. The direct-exchange model is based on the Heisenberg model of magnetism, where the spin flipping happens between the two nearby spins (Figure 1.2). The first example of the direct-exchange interaction is observed in MnF₂, where the exchange integral (*J*) found to be negative and leads to the anti-ferromagnetism with a $T_N \cong 10$ K.



Figure 1.2: Schematic presentation showing competition between direct-exchange mechanism and Pauli principle.

However, this method is not the most common one observed in the insulators or metals. The most common model followed in the insulators is the super-exchange mechanism. This model is first pointed out by the Kramers (1934) [11] and later expanded by several scientists such as Anderson [12]. We will discuss the super-exchange model by considering the example of the MnO unit-cell (Figure 1.3). In MnO, O atoms share *p*-orbitals between two Mn atoms. This results in the two possible spin configurations in the Mn-O-Mn. First state defined by the configuration, $Mn_1^{\uparrow} - O^{\uparrow\downarrow} - Mn_2^{\downarrow}$ (antiparallel) and the second state as $Mn_1^{\uparrow} - O^{\uparrow\downarrow} - Mn_2^{\uparrow}$ (parallel). If there is no interaction between the two Mn ions, these states will degenerate and result in a ground-state.



Figure 1.3: Schematic representation for super-exchange mechanism in MnO and double-exchange mechanism in $La_{1-x}A_xMnO_3$.

From here, an excited state involves the transfer of an electron from oxygen anion to any Mn cation $(Mn_1^{\uparrow\uparrow} - O^{\downarrow} - Mn_2^{\downarrow})$. The coupling of excited state with ground state results in a hybrid wavefunction with even lower energy (more stability) from quantum mechanical resonance

theory. John B. Goodenough and Junjiro Kanamori developed a set of semi-empirical rules (also known as Goodenough-Kanamuri rules) in the 1950s for explaining the magnetic exchange interactions in such compounds [13-15]. They are found to be phenomenally successful in rationalizing the magnetic properties in many compounds. They are based on electron occupancies and symmetry relations of occupying atomic orbitals. Two magnetic ions (with half-occupied orbitals) coupled through non-magnetic ions result in the antiferromagnetic from the Pauli exclusion principle. At the same time, the coupling between a magnetic ion (with half-filled orbitals) and a magnetic ion (with full filled orbitals) is ferromagnetic. A magnetic ion with completely or halffilled orbitals can interact ferromagnetically or antiferromagnetically with an ion having vacant orbitals. However, ferromagnetic interactions are dominating in such cases. When multiple types of interactions are simultaneously operating, the antiferromagnetic interactions are found to be dominating. Such interactions are independent of the intra-atomic exchange term. There are certain limitations to the Goodenough-Kanamori rules and mainly arise when 1) direct-exchange interaction competes with the super-exchange interactions, 2) cation-anion-cation deviates from 180°, 3) presence of non-static electron occupancies 4) in the existence of strong spin-orbit coupling. A Double-exchange mechanism is also a type of super-exchange interactions, mainly present in the systems with mixed hybridizations [16]. An example of a doubleexchange mechanism is observed in the $La_{1-x}A_xMnO_3$. Both Mn^{3+} and Mn⁴⁺ states co-exist in the crystal of LaMnO₃. Here, the valency of the anion (O atom) remains constant, but the valencies of Mn varies between $Mn_1^{3+} - O_2 - Mn_2^{4+}$. Here, the exchange interactions are facilitated by the electron transfer between Mn_1 to 0 and then followed by the 0 – Mn_2 . Formation of two resonating structure $(Mn_1^{3+} - O_2 - Mn_2^{4+})$ and $Mn_1^{4+} - O_2 - Mn_2^{4+}$) lowers the energy during the exchange interactions (Figure 1.3). Here, spin multiplicity remains to conserve during the exchange. Hence, the ferromagnetic interactions are stabilized in the LaMnO₃.

1.4 Spintronics

Spintronics is one of the most emerging technologies which has the potential to replace the present world electronics if it can provide the solutions in terms of reduced cost, area, power consumption, speed, etc. The central area of focus in spintronics comes from spintronics' engagement with the present world's need. On a financial scale, semiconductor technology's revenue is over more than 30 times compared to spintronics. However, spintronics has several areas to be evolved in the context of technological advancement. The technology involves in spintronics is more energy-efficient compared to semiconductors technology. The spin memory is non-volatile as it doesn't affect by the loss in charge/current. Compared to the semiconductor's world, the field of spintronics can offer increased information transfer speed, high integration densities for devices, low power consumptions, and non-volatility. For electronic transport, the electrical resistivity is exceptionally low for magnetic materials (10^{-7}) - 10^{-8} $\Omega.m$) compare to semiconducting $(10^{-5}-10^8 \Omega.m)$. Spin polarization and doping density control the electron transport and resistivity (and spin diffusion length) in materials. In spintronics, spin polarization is the critical factor that defines the efficiency of spincurrent per unit energy introduced or the spin-transport. The spintronics field allows the control of electronic spin and its fundamental charge, which influences magnetic anisotropy, exchange energy, spin diffusion length, etc., by direct/indirect pathways. Theoretically, the spin polarization (P_n) is related to the spin density (n) by the given relation: [17-19]

$$P_n = (n_{\uparrow} - n_{\downarrow})/(n_{\uparrow} + n_{\downarrow}) \tag{1.7}$$

Here, n_{\downarrow} and n_{\uparrow} represents the down and up spin electron density in the system. The value of $P_n = 1$ represents a novel electronic structure in ferromagnetic systems, known as Half-metals. Spin-polarized electrons are essential for spin-transport properties and readily available in ferromagnetic metals. But spin-polarized electrons can form in non-

magnetic systems by spin injection. Ferromagnetic metals (Fe, Co) and half-metallic ferromagnets can introduce the spin polarization in nonmagnetic systems. Other ways to introduce the spin polarizations are electric field, magnetic field, thermal gradient, and many more. The former method (spin injection by FM) has its own advantages while considering the spin polarization [20]. Apart from spin polarization, the spin-diffusion length, magnetic anisotropy energy, Curie temperature are other significant factors that needed concerns. With the decrease in device size, the spin-orbit effects also decrease, ensuring magnetic components stability against the temperature. To encounter such factors, low-dimensional materials with perpendicular anisotropy are of important concern. Similarly, the number of exchange interaction parameters are decreased due to the reduced number of neighbors, which influences the Curie temperature. On the contrary, the spin diffusion length follows a different path. Spin diffusion length defines an electrons tendency to carry the spin memory over a particular length (or distance). Materials with high spin-orbit coupling have spin diffusion length from few nanometers to tens of nanometers, whereas nonmagnetic materials with weak spin-orbit effects have thousands of nanometers. Concerning all such aspects, we have explored materials with reduced dimensionality to deal with such key parameters in spintronics applications.

1.5 Schrödinger Equation

For a non-relativistic case, one can write the total energy (kinetic plus potential) for a system with the help of position-space representations. In the present scenario, the expression for the Kinetic energy for a collection of M nuclei can be written as

$$E_{kin} = \Sigma_{k=1}^{M} \left(\frac{P_k^2}{2M_k} \right) + \Sigma_{i=1}^{N} \left(\frac{p_i^2}{2m_e} \right)$$
(1.8)

Here, each nucleus is position at $\overrightarrow{R_k}$ vector with (labeled as k) a charge of $Z_k e$. M_k (and m_k) denote the mass of the nuclei of k^{th} nuclei (and

electron), whereas P_i (and p_i) denotes the momentum of nuclei (and electrons). The classical potential energy for this system is written as

$$E_{pot} = \frac{1}{2} \sum_{k_1 \neq k_2 = 1}^{M} \frac{1}{4\pi\epsilon_0} \frac{Z_{k_1} Z_{k_2} e^2}{|\vec{k}_{k_1} - \vec{k}_{k_2}|} + \frac{1}{2} \sum_{k_1 \neq k_2 = 1}^{N} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_{i_1} - \vec{r}_{i_2}|} - \sum_{k=1}^{M} \sum_{i=1}^{N} \frac{1}{4\pi\epsilon_0} \frac{Z_k e^2}{|\vec{k}_{k_1} - \vec{r}_{i_1}|}$$
(1.9)

The first and second term represents the nucleus-nucleus and electronelectron interactions, whereas the third term represents nucleus-electron interactions. The momentum p_i for a particle having the mass m can be replaced by the operator $\frac{\hbar}{i} \vec{\nabla}$. The modified Hamilton for the above system is written as

$$\widehat{H} = \sum_{k=1}^{M} \frac{\hbar^2}{2M_k} \overrightarrow{\nabla}_{\vec{R}_k}^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m_e} \overrightarrow{\nabla}_{\vec{r}_i}^2 + \frac{1}{2} \sum_{k_1 \neq k_2 = 1}^{M} \frac{1}{4\pi\epsilon_0} \frac{Z_{k_1} Z_{k_2} e^2}{|\vec{R}_{k_1} - \vec{R}_{k_2}|} + \frac{1}{2} \sum_{k_1 \neq k_2 = 1}^{N} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_{i_1} - \vec{r}_{i_2}|} - \sum_{k=1}^{M} \sum_{i=1}^{N} \frac{1}{4\pi\epsilon_0} \frac{Z_k e^2}{|\vec{R}_{k_1} - \vec{r}_{i_1}|}$$
(1.10)

The solution for the time-independent Schrodinger equation is written as $\hat{H}\psi = E\psi$ (1.11)

where ψ depends upon the spin- and position-coordinates of all nuclei (\vec{X}) and all electrons (\vec{x}) . Accordingly, the Schrodinger equation takes the form

$$\begin{aligned} \hat{H}\psi &= (\hat{H}_{k,n} + \hat{H}_{k,e} + \hat{H}_{p,n-n} + \hat{H}_{p,e-e} + \hat{H}_{p,n-e}\psi(\vec{x},\vec{X}) \\ &= \vec{E}.\psi(\vec{x},\vec{X}) \end{aligned}$$
(1.12)

Now, we will introduce the Born-Oppenheimer approximation in the Schrodinger equation. The main idea behind this is that the movement of electrons is much faster than the nuclei. Hence, for a given set of positions for the nuclei, electron position changes much rapidly. The solution for this condition is to transform the wavefunction as a product of two wavefunctions.

$$\psi(\vec{X}, \vec{x}) = \psi_n(\vec{X}) \cdot \psi_e(\vec{X}, \vec{x}) \tag{1.13}$$

Inserting the above values into the Schrodinger equation (1.12) results in the following equation

$$(\hat{H}_{k,n} + \hat{H}_{k,e} + \hat{H}_{p,n-n} + \hat{H}_{p,e-e} + \hat{H}_{p,n-e})\psi_n(\vec{X}).\psi_e(\vec{X},\vec{x}) = \psi_n(\vec{X}).\psi_e(\vec{X},\vec{x})$$
(1.14)

With more variables, the equation becomes more complicated to be solved for the multi-nuclei system. Hence, several approximations are needed to only the Schrodinger equation. Due to $M_K >> m_i$, the kinetic energy part for nuclei is exceedingly small and can be neglected. Subsequently, the above equation further simplified to the following expression

$$\frac{(\hat{H}_{k,n} + \hat{H}_{p,n-n})\psi_n(\vec{x})}{\psi_n(\vec{x})} + \frac{(\hat{H}_{k,e} + \hat{H}_{p,e-e} + \hat{H}_{p,n-e})\psi_e(\vec{x},\vec{x})}{\psi_e(\vec{x},\vec{x})} = E$$
(1.15a)

Or

$$\frac{(\hat{H}_{k,e} + \hat{H}_{p,e-e} + \hat{H}_{p,n-e})\psi_e(\vec{x},\vec{x})}{\psi_e(\vec{x},\vec{x})} = E - \frac{(\hat{H}_{k,n} + \hat{H}_{p,n-n})\psi_n(\vec{x})}{\psi_n(\vec{x})}$$
(1.15b)

The right-hand side of the above equation (1.15b) does not depend upon the electron coordinates \vec{x} . Hence, the left-hand side of the above equation can be solved independently

$$\frac{(\hat{H}_{k,e} + \hat{H}_{p,e-e} + \hat{H}_{p,n-e})\psi_e(\vec{X},\vec{x})}{\psi_e(\vec{X},\vec{x})} = E_e(\vec{X})$$
(1.16)

By neglecting the kinetic energy of the nuclei, the total energy expression reduces to

$$E = \frac{1}{2} \sum_{k_1 \neq k_2 = 1}^{M} \frac{1}{4\pi\epsilon_0} \frac{Z_{k_1} Z_{k_2} e^2}{|\vec{R}_{k_1} - \vec{R}_{k_2}|} + E_e(\vec{X})$$
(1.17)

In Hartree approximations, one seeks for an approximate solution of the electronic Schrodinger equation. The reconstruction of the electronic wavefunction is performed, in which a system of N electrons considered as N electrons occupying the N different orbitals. Each orbital has one vacant seat to accommodate only one electron in the energetically lowest configuration. Here, the electronic wavefunction (ψ_e) is represented by the symbol ϕ and wavefunction is given by the following expression:

$$\phi(\vec{x}_1, \vec{x}_2, \vec{x}_3 - -, \vec{x}_N) = \phi_1(\vec{x}_1), \phi_2(\vec{x}_2), \phi_3(\vec{x}_3) - -, \phi_N(\vec{x}_N) \quad (1.18)$$

To provide an approximate solution for the above wavefunction in Hartree approximation, we will introduce the variational method for solving the time-independent Schrodinger equation.

For a general eigenvalue problem, the corresponding equation is given by the relation $\hat{A}f_n = a_n f_n$ (1.19)

where A is Hermitian and a linear operator, f_n is an eigenfunction and a_n is an eigenvalue. In quantum theory, the expectation value of experimental observables in each state for a given system is calculated as matrix elements of eigenfunctions. The general expression followed

as
$$\frac{\langle f_n | \hat{0} | f_n \rangle}{\langle f_n | f_n \rangle} = \frac{\langle f_n | \hat{A} | f_n \rangle}{\langle f_n | f_n \rangle}$$
 (1.20)

where \hat{A} and \hat{O} are related to each other by a condition, in which at n = 0 ($f_n = f_0$) and the corresponding eigenvalue is a_0 .

At
$$n = 0$$
, $\frac{\langle f_0 | \hat{A} | f_0 \rangle}{\langle f_0 | f_0 \rangle} = \frac{a_0 \langle f_0 | f_0 \rangle}{\langle f_0 | f_0 \rangle} = a_0$ (1.21)

But if we thought that the above expression is an ideal case for the value of $f_{n=0}$. The representation of the same expression for the Schrodinger equation will be different as the $f_0 \cong \phi$.

Now, the presentation for the minimization of the expectation value of the electronic Schrodinger equation is as follows:

$$F = \langle \phi | \hat{H}_e | \phi \rangle - \Sigma_{i,j} \lambda_{ij} [\langle \phi_i | \phi_j \rangle - \delta_{i,j}]$$
(1.22)

where λ_{ij} is a Lagrange multiplier and $\langle \phi_i | \phi_j \rangle = \delta_{i,j}$ represents the condition of orthonormality. Now, the minimization of the wavefunction is related to $\delta F = 0$;

$$\phi_k(\vec{x}) \to \phi_k(\vec{x}) + \delta \phi_k(\vec{x}) \tag{1.23}$$

when $\delta \phi_k(\vec{x})$ is small. This approximation helps in determining the ϕ_i for each orbital for the electronic Schrodinger equation [21-22]. However, there are severe problems present in the present solution. This expression does not consider the electrons to be indistinguishable. Over the past decades, researchers have devoted their attention to solving the Schrödinger equation with several approximations and improvements, such as the Hartree-Fock method (antisymmetry conditions), Hartree-Fock-Roothaan method (fixed basis functions), and many-more [23-26].

1.6 Density Functional Theory

Hohenberg and Kohn introduce density functional theory (DFT) in 1964 [27-28]. They have considered a case non-degenerate ground state while describing the DFT in their work and represented the Hamiltonian as

$$H = T + U + V \tag{1.24}$$

where T is the kinetic energy operator and U is the electron-electron interaction operator, with

$$V = \int v(r)\psi^*(r)\psi(r)dr \quad (v(r) = \text{external potential})$$
(1.25)

The electron-electron interactions and kinetic energies are summed as a universal functional of charge density, as ground state Ψ is a functional of electronic density $(n(r) \equiv [\Psi, \psi^*(r)\psi(r)])$, which itself is functional of v(r). With the help of the above statements, they have defined a new universal functional

$$F[n(r)] \equiv (\Psi, (T+U)\Psi) \tag{1.26}$$

Then, they have provided an energy functional for a given potential (v(r)) by using this universal functional as:

$$E_{\nu}[n] = \int v(r)n(r)dr + F[n]$$
(1.27)

From this, they have established that this unique functional reaches its minimum for the correct ground state density n(r), if the total number of particles kept constant.

$$N[n] = \int n(r)dr = N \tag{1.28}$$

These above developments led to the famous Hohenberg and Kohn theory or more commonly named density functional theory. In 1965, Kohn and Sham [28] introduced the local density approximation, which is later modified to this energy functional by several authors (LDA) as [29-30]

$$E = \int v(r) n(r) dr + \frac{1}{2} \iint \frac{n(r)n(r')}{|r-r'|} dr dr' + T_s[n] + E_{xc}[n]$$
(1.29)

where $T_s[n]$ = kinetic energy for non-interacting electrons and $E_{xc}[n]$ = exchange-correlation energy of interacting electrons with the same density. For slowly varying densities, they have obtained the expression for E_{xc} in terms of exchange-correlation per electron.

$$E_{xc}[n] = \int n(r)\epsilon_{xc}(n(r))dr$$
(1.30)

where ϵ_{xc} = per electron exchange and correlation energy of a uniform electron gas whose density is n[r]. The next step was taken by the Kohn-Sham in deriving from the stationary property of equation by a straightforward equation or also known as the Kohn-Sham equation

$$\left\{-\frac{1}{2}\nabla^{2} + \left[v(r) + \int \frac{n(r')}{|r-r'|} dr' + \mu_{xc}(n(r))\right]\right\}\psi_{i}(r) = \epsilon_{i}\psi_{i}(r) \quad (1.31)$$

where charge density is calculated using the wavefunctions of occupied states as

$$n(r) = \sum_{i=1}^{N} |\psi(r)|^2$$
(1.32)

The equation formulated by the Kohn-Sham have some key features to underscore the following points: (a) The number of particles must be kept constant, and (b) The outcomes of electronic structure calculation performed with the DFT (or LDA) potentials to represent the assets of DFT or LDA; either the ground state density of the system must be known ("correct") or reached its absolute minima if not appropriately defined (as in former case) [30]. After that, several modifications were performed over the decades to encounter the flaws in DFT (or LDA), such as "the bandgap problem" in the semiconductors and insulators. Later, local spin-density approximation (LSDA) is introduced to account for the electron spin in LDA, [31-32]

$$E_{xc}^{LDA}[n_{\uparrow}, n_{\downarrow}] = \int \epsilon_{xc}(n_{\uparrow}, n_{\downarrow})n(\vec{r}) d^{3}r \qquad (1.33)$$

But, LSDA has severe flaws in determining the magnetic properties of the metal oxide insulators. Due to the overestimation of the exchange-correlation energy caused by the similar electron density within the LSDA. The correction is provided by representing the density in terms of the gradient of the density and later referred to as generalized gradient approximations (GGA), [33-35]

$$E_{xc}^{LDA}[n_{\uparrow}, n_{\downarrow}] = \int \epsilon_{xc} (n_{\uparrow}, n_{\downarrow}, \vec{\nabla}_{n_{\uparrow}}, \vec{\nabla}_{n_{\downarrow}}) n(\vec{r}) d^{3}r$$
(1.34)

Both the methods are failed to describe the strong correlation between the partially filled d and f orbitals. To encounter such flaws, Hubbard "U" potential based methods are introduced in the DFT picture to fill the electron correlation part [36-43]. DFT+U based methods have been found to provide the ground-state properties and excited-state properties in the magnetic systems. However, the semiempirical nature of Hubbard parameters makes the results less reliable in the absence of experimental data. As the electronic picture (bandgap) of a system is strongly influenced by the U value (Mott Transition). Later, hybrid functionals are introduced to deal with the systems with a strong electron correlation. In the present time, several DFT functionals are available to fill the voids in density functional theory, such as HSE06, PBE0, B3LYP, and many more [44-48]. Collectively, density functional based methods have seen an enormous advancement in their applicability and governing a vast range of properties.

1.7 Other Computational Tools

1.7.1 Ab initio Molecular Dynamics (AIMD)

Ab initio molecular dynamics simulation is mainly used to investigate temperature-dependent dynamical effects in solid-state materials and solution models. Compare to classical molecular dynamics, the temperature-induced forces are calculated within the DFT framework. Due to the development in computational sciences, now it is possible to perform AIMD based calculations from hundreds to few thousands of atoms. In the doctoral thesis, the AIMD calculations are carried out using NVT and NPT canonical ensembles with a range of time profiles. The thermostat is either based on a Nose-Hoover or Langevin model. In the Nose-Hoover model [49-52], an extra degree of freedom is introduced into the Hamiltonian, and in Lagrangian of the system, the heat bath is present as an integral part with a fictitious coordinate s;

$$\mathcal{L} = \sum_{i=1}^{N} \frac{m_i}{2} s^2 \dot{r_i^2} - U(r) + \frac{Q}{2} \dot{s}^2 - g k_B T \ln s$$
(1.35)

where, first two terms in the above equation represent the kinetic and potential energy of the system, whereas the third and fourth term represents the kinetic and potential energy of the coordinate *s*. Here, m_i and k_B represents the mass of ion "*i*" and Boltzmann constant, *g* represents the number of degrees of freedoms provided, and *Q* represents the effective mass of "*s*". In Langevin thermostat [53-55], the temperature is introduced by the modification in Newton's equation of motion:

$$\dot{r}_i = \frac{p_i}{m_i}$$
 and $p_i = F_i - \gamma_i p_i + f_i$ (1.36a,b)

where γ_i is the friction coefficient, f_i represents the force simulating the random motions by the damping of particles, and F_i represents the force induced on atom *i* due to the interactive potential of the ensemble.

1.7.2 Bader Charge Analysis

The scheme of representing electronic charge density present in the molecules or crystals on individual atoms is described as a Bader partitioning scheme. In the Bader scheme (within the local density approximation), the total energy of the system is given by the equation:

$$E_{tot} = \Sigma_n f_n \varepsilon_n + E_{Ion-Ion} + E_{d.c}$$
(1.37)

where f_n defines the occupancy of n^{th} Kohn-Sham orbital and ε_n defines the eigenvalue of f_n , $E_{Ion-Ion}$ represents the sum of ion-ion interactions and $E_{d.c}$ represents the double-counting energy, which is defined as

$$E_{d.c} = \int_{\rho} \left(-\frac{1}{2} V_{Ha}(\rho) - V_{XC}(\rho) + E_{XC}(\rho) \right) dr$$
(1.38)

The $\Sigma_n f_n \varepsilon_n$ is the band energy and related to the density and Hamiltonian matrix as

$$\Sigma_n f_n \varepsilon_n = \Sigma_{i\alpha,j\beta} = \rho_{i\alpha j\beta} H_{i\alpha j\beta}$$
(1.39)

The right-hand side of the above expression is defined by assigning the on-site and bonding contributions to an individual atom.

$$E_{band,i} = \sum_{\alpha,\beta} \rho_{i\alpha j\beta} H_{i\alpha j\beta} + \sum_{\substack{\alpha,j\beta\\i\neq j}} \rho_{i\alpha j\beta} H_{i\alpha j\beta} \qquad s \qquad (1.40)$$

The ion-ion interaction energy is divided among the two atoms (half to each ion), involved in ion-ion pair formation [56-60].

1.7.3 Crystal Orbital Hamilton Populations (COHP) Analysis

COHP tool is mainly used to describe band-structure energy in orbitalpair interactions among the pair of adjacent atoms. More broadly, it can be classified as bond-weighted density-of-states between the pair atoms. COHP tool represents the band-structure energy in bonding and antibonding contributions. From Bloch's theorem, one can obtain a band functions $\psi_i(k, r)$ for a given set of atoms.

$$\psi_i(k,r) = \sum_G C_{iG}(k) \exp\{i(k+G),r\}$$
(1.41)

Here, j denotes the band number, $C_{jG}(k)$ denotes the expansion coefficients, and G represents the reciprocal lattice vectors. The band function is a mathematical representation of a linear combination of plane waves. In other words, the electronic structure of the system defined by the band functions can also be described as a linear combination of atomic orbitals. Hence, for a j^{th} band, the LCAO function $\Phi_j(k,r)$ is related to the band function $\psi_j(k,r)$ and represented by the following expression:

$$\Phi_j(k,r) = c_{ju}(k)\phi_u(r) + c_{jv}(k)\phi_v(r)\dots\dots\approx\psi_j(k,r) \qquad (1.42)$$

where $\phi_u(r)$ is the one-electron functions (orbitals) with $c_{j,n}$ coefficients. Nonetheless, the quantification of a basis set and the band function is justified by the transfer matrix $(T_{j\mu}(k))$. This tells about

the fitness of the basis sets towards the band function and given by the relation $T_{j\mu}(k) = \langle \psi_j(k) | \phi_{\mu} \rangle$ (1.43)

Here, ϕ_{μ} is the local orbital used [61-64].

1.7.4 Phonon Dispersion

The phonon dispersion concept is related to the lattice dynamics, which extends the idea of crystal vibrations coupled through atoms with finite masses. The motion (or vibrations) in the crystals is not random but a superposition of vibrations with crystal symmetry. However, the lowering of symmetry in the crystals will sometimes make the understanding of the phonon frequencies difficult. Several factors can lower the crystal symmetry. In a crystal with an N number of atoms, there are 3N degrees of freedoms available (phonon vibrations). They are classified as acoustic and optical phonon modes. For the 3N number of vibrations, we have three acoustic modes and 3N - 3 optical phonon modes. Hence, the understanding of phonon spectra requires calculations of 3N phonon modes. In the presence of crystal symmetry (space group), some modes are coupled to each other through symmetries operations, resulting in doubly or triply degenerate phonon modes. This is again limited to the Γ -point symmetry of the crystal structure. As the movement away from the Γ -point results in reduce symmetry (point groups). For calculating force matrix, density functional perturbation theory (DFPT) and finite-difference based methods are available in the DFT codes, such as VASP and Quantum Espresso. The potential energy (V) in the phonon systems is related to the second-order force constant $(\Phi_{\alpha\beta})$ as

$$\Phi_{\alpha\beta}(jl,j'l') = \frac{\partial^2 V}{\partial r_{\alpha}(jl)\partial r_{\beta}(j'l')} = -\frac{\partial F_{\beta}(j'l')}{\partial r_{\alpha}(jl)}$$
(1.44)

Here, α and β are the cartesian indices, whereas *j* and *j'* are the indices for atoms in unit-cell, and *l* and *l'* are the unit-cell indices. The direct relation between force (*F*) and potential energy (*V*) is given by the relation [65-67] $F_{\alpha}(jl) = -\frac{\partial V}{\partial r_{\alpha}(jl)}$ (1.45)

1.7.5 Monte Carlo Simulation

From statistical mechanics, we will define the probability (ω) of a system in state u at time t as $\omega_u(t)$. Thus, we can write about the evolution of $\omega_u(t)$ in terms of rates $R(u \rightarrow v)$ as

$$\frac{d\omega_u}{dt} = \Sigma_u[\omega_v(t)R(v \to u) - \omega_u(t)R(u \to v)]$$
(1.46)

where the probabilities must obey the sum rule as

$$\Sigma_u \omega_u(t) = 1 \text{ for all } t \tag{1.47}$$

Now, if we are interested in some macroscopic parameter Q, having the value Q_u for a "u" state at time t, then we can write the expectation value of Q as $\langle Q \rangle = \sum_u Q_u \omega_u(t)$ (1.48)

Here, the calculation of the expectation value of Q is the fundamental goal of Monte-Carlo methods. In 1902, the relation between equilibrium occupation probabilities, P_u (= $\lim_{t\to\infty} \omega_u(t)$) at temperature T for a reservoir is derived by the Gibbs as $P_u = \frac{1}{z}e^{-E_u/kT}$ (1.49)

where k is the Boltzmann constant, E_u is the energy of state "u" and Z is the partition function. Equation 1.49 is also known as Boltzmann distribution. For an Ising model, the spins are assumed to be in their simplest form, represented by two values ± 1 (up and down spin) [68]. In a real magnetic system, they can interact through several exchange mechanisms, as discussed in section 1.3. In the simplest form, assuming all the interaction to be of equal magnitude (J). Under an external magnetic field (B), the Hamiltonian can be written as

$$H = -J\Sigma_{ij}S_i \cdot S_j - B\Sigma_i S_i \tag{1.50}$$

A positive (negative) value of J represents the ferromagnetic (antiferromagnetic) interactions. Here, the partition function takes the following form:

$$Z_{\beta} = \sum_{S_1 = \pm 1} \sum_{S_2 = \pm 1} - - \sum_{S_N = \pm 1} exp \left[\beta J \sum_{ij} S_i \cdot S_j + \beta B \sum_i S_i\right]$$
(1.51a)

$$\operatorname{Or} Z_{\beta} = \Sigma_{\{S_i\}} e^{-\beta H} \tag{1.51b}$$

And the configuration probability, $P_{\beta}(S_i)$ is given by the relation:

$$P_{\beta}(S_i) = e^{-\beta H} / Z_{\beta} \tag{1.52}$$

The expectation value for an arbitrary function f is gives as

$$\langle f \rangle = \Sigma_{S_i} f(S_i) P_{\beta}(S_i) \tag{1.53}$$

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An atomically thin ferromagnetic half-metallic pyrazine-fused Mn-porphyrin sheet: a slow spin relaxation system

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Chapter 2

2.1 Introduction

Recent developments in magnetic materials unfolded the fascinating paths towards the potential applications of many magneto-electronic devices [1-4]. The conventional electronic devices (semiconductorbased devices) ignore the spin properties and rely strictly on the transport of electrical charges to store information. In spintronic devices, the processing and storage of information are simultaneously controlled by electrons' spin and charge [5]. Hence, spintronic devices offer many possibilities beyond conventional electronic devices and can be used for high-capacity storage devices to quantum computers [6]. However, the application of spintronic devices often requires 100% spin polarization at the Fermi level. This is possible when one of the spin-channels is metallic, and another one is insulating. Such materials are called halfmetallic and very important for spintronic devices. Similarly, ferromagnetic ordering is an important requirement for spintronic devices. Though, most of the reported half-metallic materials are ferromagnetic with few exceptions [7-9]. Among all the reported promising half-metallic materials, organic spintronic materials deserve special attention due to their long spin coherence length and mechanical flexibility. On the other hand, two dimensional (2D) organic materials with planar surfaces are promising for spintronic devices. Since graphene discovery, [10-12] 2D main group materials have attracted considerable attention for spintronic devices due to their excellent electronic and anisotropic properties [13-16]. The porphyrin-based (PP) 2D structures have attracted considerable attention for electronic devices and have been investigated theoretically and experimentally [17-22]. However, the flat surface and thickness of metal-free 2D materials are difficult to evaluate with precision. Moreover, such main group based 2D nonmagnetic. structures are So, the high-temperature ferromagnetism in the atomically thin 2D nanosheet is one of the primary challenges for the scientific community [23]. However, metal incorporated porphyrin-based structures can be synthesized, which demonstrate interesting magnetic properties [24]. Furthermore, such porphyrin-based structures have lower metal loading (due to the distance between transition metals) than other transition metal-based organic systems. One-dimensional (1D) Zn-porphyrin arrays have recently been synthesized and reported as conducting molecules [25]. Since then, many investigations have been carried out on porphyrin-based nanostructures. Later, the shape-dependent two-dimensional extended porphyrin networks like L-shaped trimers, T-shaped tetramers, and square-shaped tetramers have been synthesized to investigate the structure-property relationship [26]. Despite all the experimental and theoretical efforts, [27-28] an infinite sheet of porphyrins is yet to be experimentally realized. However, many 1D and 2D transition metal incorporated porphyrin structures with different kinds of linkers have been synthesized [29]. Recently, Akita et al. (2012) [30] fabricated a pyrazine-fused diporphyrin through an oxidative coupling of β aminoporphyrins. Moreover, they predicted strong aromaticity (planarity) in the pyrazine ring. Hence, such a nitrogen-rich pyrazinefused porphyrin system could be a promising material compared to the benzene-fused porphyrins for optoelectronic and spintronic devices. Furthermore, it will be interesting to observe whether electrons can be freely transported through the linked pyrazine and pyrrole rings. Therefore, motivated by these experimental findings and previous reports, we have proposed a 2D pyrazine-fused porphyrin monolayer (PP) and 3*d* transition (Cr to Zn) metal incorporated systems (TM-PP) for their possible applications in spintronic devices. In the present work, we have performed a detailed study to understand the electronic and magnetic properties of first-row transition metal incorporated porphyrin derivatives (TM-PP). First-row transition metals are considered as they are not only abundant but also show better magnetic properties. The stability of the planar TM-PP sheets is particularly important for their synthesis and practical applications. Thus, the stability of these sheets is evaluated from the energetic (binding energy of TM-PPs), mechanical (stress vs. strain), and thermal (molecular dynamics simulation) studies. Furthermore, the structural (geometry, oxidation state), electronic (spinpolarized density of states, band structures, work functions), and magnetic (exchange energy, Curie temperature, magnetic anisotropy energy) properties are studied to assess their importance in spintronic devices. The magnetic anisotropic energy (MAE) is an important parameter for spintronic devices [5]. Their origin is always found to be dependent on many factors such as crystallinity, shape, stress, spin-orbit coupling, and so on. We have calculated the MAE (magnetic anisotropy energy) in the ground state and a strain-dependent environment to understand the behavior of spin-orbit coupling and magnetic moment under strain. We have also performed electronic structure and band structure calculations to predict the half-metallic state's stability under external stress.

2.2 Computational Details

We have used spin-polarized density functional theory (DFT) calculations as implemented in the Vienna Ab Initio Simulation Package (VASP) [31-34]. The plane-augmented wave (PAW) [35-36] method is used for electron-ion interactions. The GGA PBE [37-38] functional is used for the exchange-correlation calculations. K-Point convergence is carried out for the total energy calculations, and a set of $6 \times 6 \times 4$ Monkhorst-Pack k-points is found to be good enough for the total energy calculations. All the geometric structures are fully optimized until the Hellmann-Feynman forces on each atom are less than 0.003 $eVÅ^{-1}$ and the total energy convergence criterion is set at $10^{-6} eV$. We have used the conjugate-gradient algorithm to optimize lattice parameters and relaxing ions to their respective ground state in TM-PP structures. The conjugate-gradient algorithm uses line minimization, which involves several trial steps [39]. For truncation of plane-wave basis sets, an energy cutoff of 470 eV is used to represent Kohn–Sham wave functions with a smearing width of 0.001 eV for correct occupation numbers in electronic states. The integration of Brillouin zones is carried out using a Monkhorst-Pack k-points [40] grid of $11 \times 11 \times 7$ for electronic structure calculations. To avoid selfinteraction errors within GGA potentials, we have also adopted the

GGA+U (DFT+U) [41-42] approach and compared our results with GGA, which are found to be consistent with GGA. The values of the Hubbard parameter (U) and exchange parameter (J) are set at 4.0 eV and 1.0 eV, respectively [28,43–47]. These U and J values reproduce better electronic structures and magnetic moment for metal-porphyrin frameworks. We have also performed HSE06 (Heyd–Scuseria–Ernzerhof) [48–50] calculations for Mn-PP's exact electronic structures and compared them with GGA+U and GGA calculations. The Bader charge analysis [51–53] is performed using the Henkelman programme [54] by the near-grid algorithm refine-edge method. For the calculation of exchange energies, we have created a supercell of $2 \times 2 \times 1$ for the Mn-PP structure, and a set of $4 \times 4 \times 1$ k points carries out integration of Brillouin zones. We have plotted the spin density difference (SDD) [55] to find the Mn-PP structure's spin localization. The SDD is calculated using the following formula.

$$\rho_{SDD} = \rho_{UP} - \rho_{DOWN} \tag{2.1}$$

where ρ_{UP} and ρ_{DOWN} are the up and down electron spin densities, respectively. The electron spin density's direct mapping is measured by the neutron diffraction in electron spin resonance (ESR) spectroscopy [56].

For visualizing the behavior of bands in the 2D-Mn-PP structure, we have performed band structure calculations along the $\Gamma - M - X - \Gamma$ path in the Brillouin zone. To predict the TM-PP framework's thermal stability, we have performed molecular dynamics simulation using the Nose'-thermostat algorithm at 300 K [57]. With the inclusion of spin-orbit coupling (SOC), we have tried to link the TM-PP structure and magnetic moment (in the presence of a magnetic field) to explain the magnetic anisotropy (MA). The total energy of a system in collinear calculations (absence of a magnetic field) does not depend on the orientation or the direction of the magnetic field. The magnetic anisotropy energy (MAE) for the TM-PPs can be obtained using the following expression: $MAE = E_{||} - E_{\perp}$ (2.2) where

 E_{\parallel} and E_{\perp} are the total energies for in-plane (parallel) and out-plane (perpendicular) directions with respect to the TM-PP plane. The positive (negative) value of MAE describes the easy axis of the TM-PP system. We have performed non-collinear calculations for TM-PPs in parallel and perpendicular magnetization directions of the TM-PP plane. In general, the MAE values of any system are in the order of 10^{-3} - 10^{-6} eV and thus the energy convergence criteria (for non-collinear calculation) are set at 10^{-7} eV. We have applied strain to understand the Mn-PP framework's mechanical stability (behavior of external stress). Furthermore, the electronic properties of the Mn-PP framework are studied under strain.

We have plotted the charge density difference to better understand charge transfer between the transition metal and Nitrogen of the porphyrin cavity. The definition of charge density difference is defined by: $\Delta \rho = \rho_{PP-TM} - \rho_{PP} - \rho_{TM}$ (2.3)

Where ρ_{PP-TM} , ρ_{PP} and ρ_{TM} are the charge densities of TM-PPs, porphyrin moiety without transition metal incorporation and the transition metal. From the analysis of charge density difference. It clearly shows the accumulation of charge on N-atom (in porphyrin moiety) and depletion of charge on the transition metal.



Figure 2.1: 2D TM-PP structures. a) Cr-PP, b)Mn-PP, c) Fe-PP, d) Co-PP, e) Ni-PP, f) Cu-PP and g) Zn-PP.

2.3 Results and Discussion

2.3.1 Geometric Properties

All the TM-PP structures have D_{4h} symmetry with a metal sitting at the center of the porphyrin ring, and the principal axis is passing through the metal center [58]. For understanding the structural properties of TM-PPs (TM = Cr, Mn, Fe, Co, Ni, Cu, and Zn), the optimized structure of all the TM-PP structures is shown in Figure 2.1. The metal-metal distances are more than 10 Å in all these structures (Table 2.1), which is in good agreement with the previously reported systems [59-60].

Table 2.1: Structural, magnetic, electronic, and energetic parameters of 2D TM-PPs systems. Here, d_{TM-TM} represents the distance between transition metal (TM) atoms, d_{TM-N} is the distance between TM and surrounding nitrogen (N) atoms, E_b is the binding energy of TM in the pore of the porphyrin moiety, M_0 is the magnetic moment per unit cell, E_g is the bandgap and Φ is the work function of TM-PP systems.

TM	Cr	Mn	Fe	Со	Ni	Cu	Zn
d_{M-M} (Å)	10.729	10.671	10.654	10.632	10.617	10.702	10.757
d_{M-N} (Å)	2.071	2.025	2.019 2.018	2.002	1.989	2.045	2.074
<i>E_b</i> (eV)	-8.96	-8.03	-8.66	-9.02	-8.98	-7.37	-6.39
$M_{0}(\mu_{B})$	4.0	3.0	2.0	1.0	-	1.0	_
E_g (eV)	0.638	Half — metal	0.487	0.851	0.863	0.425	0.851
Φ (eV)	4.750	4.183	4.505	4.896	4.951	4.972	4.817

We do not observe any in-plane shift (Table 2.1) in any of the TM-PP systems as the metal perfectly sits at the center of the porphyrin framework, and this can be confirmed from the metal–nitrogen bond distances. The Jahn-Teller distortion is not observed in the TM-PP systems, as no in-plane/out-plane shift is observed for the metal ion. The electrostatic potential (ESP) surface (using the VESTA [61]) is plotted on the total electron density surface to understand the nature of bonding between the TM and nitrogen atoms (Figure 2.2). The ESP plots show

that the TM atoms are positively charged, whereas their surrounding N atoms are negatively charged.



Figure 2.2: Electrostatic potential map for TM-PPs (Isosurface value 0.06 eV/Å^3). 1) Cr-PP, 2) Mn-PP, 3) Fe-PP, 4) Co-PP, 5) Ni-PP, 6) Cu-PP and 7) Zn-PP. The blue and red colors denote less and more electron-dense area in the electrostatic potential surface.

Bader charge analysis is also done to understand TM-PP systems' charge distribution using Atoms in Molecules (AIM) theory. Our calculated Bader charge values for TM and N atoms are given in Table 2.2. The values clearly show that TMs are positively charged, and N atoms are negatively charged. Transfer of a significant amount of charges occurs between TM and the surrounding atoms. The maximum charge transfer from metal to the pp ring occurs in Cu-PP (1.26|e|), and the minimum occurs in Cr-PP (0.91|e|). This charge transfer can be easily explained based on the electronegativity of transition metals [Cu (1.90) and Cr (1.66)]. The charge density difference plots (Figure 2.3) show the depletion of charge (cyan) on TM atoms, whereas the accumulation of charge (yellow) on N atoms of the porphyrin moiety. The distribution of charge around the porphyrin pore clearly shows the extent of overlapping between TM *d*-orbitals and N atoms (Figure 2.3). We have also calculated the binding energies for all TM-PPs, and binding energy values clearly show that all the TMs are strongly bonded to the porphyrin sheet's nitrogen atoms (Table 2.1). Now, considering the possibility of synthesizing a freestanding monolayer of TM-PP, the sheet should have enough structural stability to be isolated. Thus,

different types of stability are calculated and discussed in the following sections.



Figure 2.3: Charge density difference plot for all the TM-PPs. (Isosurface value 0.004 eV/Å^3). The yellow color shows the accumulation of charge, and the cyan color shows the depletion of charge.

Table 2.2: Net effective	charges on N and	I TM atoms from	m Bader charge
analysis.			

тм	Net effective charges								
PP	Meta	Pyrazine linker Nitrogen				Porphyrin moiety Nitrogen			
	1	N1	N2	N3	N4	N5	N6	N7	N8
No									
Meta		-1.17	-1.11	-1.17	-1.11	-1.01	-1.01	-1.01	-1.00
1									
Cr	1.26	-1.18	-1.15	-1.18	-1.15	-1.15	-1.15	-1.17	-1.17
Mn	1.25	-1.15	-1.15	-1.15	-1.14	-1.13	-1.13	-1.15	-1.15
Fe	1.15	-1.10	-1.14	-1.10	-1.14	-1.15	-1.15	-1.10	-1.10
Со	1.09	-1.10	-1.14	-1.10	-1.14	-1.15	-1.15	-1.12	-1.12
Ni	0.98	-1.10	-1.14	-1.10	-1.14	-1.14	-1.14	-1.12	-1.12
Cu	0.91	-1.18	-1.14	-1.18	-1.14	-1.10	-1.10	-1.13	-1.13
Zn	1.12	-1.18	-1.11	-1.18	-1.11	-1.13	-1.13	-1.20	-1.19

2.3.2 Thermal Stability

The role of temperature in applications like spintronics is always found to be very decisive. The TM-PP structures' thermal stability is carried
out at room temperature (300 K) using ab initio molecular dynamics (AIMD) simulation as implemented in VASP. We have considered a canonical ensemble for TM-PP $(2 \times 2 \text{ supercell})$ structures and simulated it using the Nose isotherm [57] with a time step of one femtosecond (fs) for 5 picoseconds (ps). As a 2×2 supercell of TM-PP contains 132 atoms, we have considered a gamma-centered $(1 \times 1 \times 1)$ k-point set for our calculations. Molecular dynamics calculations are carried out to find the possibility of inter-conversion to any other conformers at room temperature. We have plotted the graph between free energy and time steps for understanding the behavior of MD simulations for TM-PP (Figure 2.4). As shown in Figure 2.4, the free energy fluctuates in the range of 4 - 6 eV at 300 K. As the supercell of TM-PP contains 132 atoms during the simulation, the fluctuations are quite acceptable [62]. The Mn-PP structure remains almost planar throughout the simulation period. It suggests that the structure is stable at room temperature. Similarly, we find that all the TM-PP systems are stable though some of these structures (Co-PP, Ni-PP, Cu-PP, and Zn-PP) lose planarity during the simulation. The low thermal stability of Co-PP, Ni-PP, Cu-PP, and Zn-PP systems might be due to the decrease in ionic radii (for late TM) and increased mass. As a result, the maximum energy fluctuations (under NVT ensemble) occur for such systems.



Figure 2.4: AIMD simulations of 2×2 TM-PP sheets for 5 ps with a time step of 1 fs at 300 K.

2.3.3 Mechanical Stability

Strain technology is the most pleasing way to determine the influence of lattice distortion on the system's structural and mechanical stability. As the supercell (2×2) is fixed during the MD simulations, the effect of lattice distortion on structural stability is essential to consider. Thus, the structural stability under strain is important for their synthesis and applications. For understanding the mechanical stability of TM-PPs, we have performed stress-strain calculations to understand the behavior of TM-PPs under external stress.



Figure 2.5: A theoretical representation for strain energy. This plot can be fitted for the calculation of elastic constants.

We have used biaxial and uniaxial strains (in x-y and x directions) on TM-PP systems. The percentage of strain (ε) is calculated using the following equation:

$$\varepsilon = (a_1 - a_0)/a_0 \tag{2.4}$$

where a_0 is the optimized lattice parameter and a_1 is the lattice parameter under strain. Here, a stress-strain curve is shown in Figure 2.5 to evaluate the mechanical stability of TM-PP. Here, the parabolic curve explains the nature of external stress with respect to the total energy of the system. For evaluating the mechanical properties, we have carefully examined the effect of lattice distortion on energetic stability.

Table 2.3. Summary of elastic constants (C_{ij} in N/m) and Poisson's ratio for all the TM-PPs.

Moduli	Cr-PP	Mn-PP	Fe-PP	Co-PP	Ni-PP	Cu-PP	Zn-PP
C ₁₁	148	114	106	111	106	97	96
C ₁₂	37	24	39	31	36	44	52
C ₄₄	57	45	33	40	35	26	22
ν	0.18	0.17	0.27	0.22	0.25	0.31	0.35

The elastic energy (U per unit cell) [63-64] can be represented as:

$$U = 1/2C_{11}(\varepsilon_{xx}^2 + \varepsilon_{yy}^2) + C_{12}\varepsilon_{xx}\varepsilon_{yy} + 1/2C_{44}\varepsilon_{xy}^2$$
(2.5)

where C_{11} , C_{12} and C_{44} are the linear elastic constants whereas ε_{xx} , ε_{yy} , and ε_{xy} are the in-plane stress components along with the x, y, and xy directions. The elastic moduli can be obtained by the polynomial fit of the strain-energy graph (Figure 2.5). The main criterion for mechanical stability is $C_{44} > 0$, $C_{11} > |C_{12}|$ and $C_{11} + C_{12} > 0$ [64-66]. The value of C_{11} can be obtained from the uniaxial deformation of the structure, whereas C_{12} can be calculated from the biaxial deformation under polynomial fitting. For isotropic elastic systems, the two shear moduli $(C_{11} - C_{12})/2$ and C_{44} are equal. For Mn-PP, the calculated values of C_{11} , C_{12} and C_{44} are 114, 24, and 45 Nm^{-1} . Hence, TM-PP satisfies all the required criteria for mechanical stability. The first criterion (C_{11} + $C_{12} > 0$) is related to the bulk modulus, which is necessary for bulk phases. But in the case of monolayers, $C_{11} > |C_{12}|$ and $C_{44} > 0$ was found to play a more subtle role in explaining the stability. The former involves the bending and stretching of bonds, whereas the latter requires the shearing of bonds. Poisson's ratio (PR) ν for square lattices can be expressed as $\nu = C_{12}/(C_{11} + C_{12})$. The computed value for Poisson's ratio is given in Table 2.3. The value of shear motion (PR) shows the resemblances between the Mn-PP structure and other metal-nitrides, [65], and the value of Poisson's ratio is quite comparable to graphene [67]. Similarly, we have also calculated the mechanical stability parameters for all the TM-PPs, and we find that all the TM-PP systems are mechanically stable.

2.3.4 Work function

For introducing TM-PPs in real applications like spintronics, it is important for materials to make contact with other materials. Work function (Φ) mainly depends on the electronic chemical potential and surface dipoles. Because of the absence of any surface dipoles (no functionalization or unsatisfied valencies or any electric double layer), the contribution from surface dipoles vanishes in 2D TM-PPs. The work function (Φ) is calculated as follows:

Work function
$$(\Phi) = E_{(vacuum)} - E_F$$
 (2.6)

where $E_{(vacuum)}$ and E_F are the potentials at the vacuum level and the Fermi level, respectively. The values of the work function for all the TM-PPs are summarized in Table 2.1. The lower work function value of the Mn-PP system compared to other TM-PPs reveals the presence of loosely bound electrons around the Fermi level. It shows that an electron's ejection from the Mn-PP surface will be easier compared to other TM-PPs. From the work function value, we can easily predict the TM-PP framework's settling on other electrodes having a similar work function. It is crucial in device fabrication, which involves using other materials as external electrodes or solid supports for TM-PP in applications like spintronics.

2.3.5 Electronic and Magnetic Properties

The incorporation of transition metals into the pore of a porphyrin framework can improve the system's magnetic/electronic properties *[8,21]*. So, we have performed spin-polarized calculations for TM-PP structures. It is found that all the TM-PP (except Ni-PP and Zn-PP) systems are magnetic (Figure 2.6). The calculated magnetic moments are 4.0, 3.0, 2.0, 1.0, and 1.0 μ_B per TM for Cr-PP, Mn-PP, Fe-PP, Co-PP, and Cu-PP (Table 1) systems, respectively *[68]*.



Figure 2.6: Spin-polarized density of states. (Blue represents the up-spin component and Red represents the down-spin component).

This can be explained by the *d*-electronic configuration of the metal ion. We have observed that most of the magnetic moment is carried by the metal ion. At the same time, the surrounding nitrogen atoms are polarized anti-ferromagnetically with the metal ion except in the case of Cu-PP. In the Cu-PP case, a similar kind of polarization between Cu and nitrogen (bonded to Cu) has already been reported in earlier works [8,58]. With the help of the calculated magnetic moments (Table 2.1), we have confirmed the oxidation state of TM(II) of the metal center in the square-planar geometry. We have found the half-metallic electronic structure for Mn-PP (Figure 2.6), with a bandgap of 0.80 eV in one of the spin channels.

Thus, one of the spin channels is metallic, whereas the other one is semiconducting. Interestingly, we find that the bandgaps are higher in pyrazine fused structures than in the previously studied benzene fused systems. Furthermore, Mn-PP shows a strong half-metallicity compared to previously reported systems [8,21,69-72]. We have also shown the band-structure plot for Mn-PP in Figure 2.7.1. The electronegativity of N-atoms can be linked with this phenomenon. Because of which metal orbitals below the Fermi level are stabilized further by the indirect (conjugation) exchange of electrons and more separation results between valence and conduction bands. So, we find that the pyrazine fused Mn-PP framework can be a promising spintronic device. Thus, N atoms in the linker (pyrazine) might be playing an important role in the high bandgap [68]. Although GGA calculations may underestimate the bandgap to a more considerable extent, the bandgap's value is significant for predicting any material's half-metallic nature. We have performed hybrid-functional calculations to confirm the exact position and the width of the gap in the electronic structure for Mn-PP. Our HSE06 level of calculations gives a bandgap of 1.04 eV for Mn-PP in one of the spinchannels, and the system turns out to be half-metallic (Figure 2.7.2). Thus, both levels of theories show that Mn-PP is a half-metallic system. For understanding the behavior of bands, we have investigated the spinresolved band-structure for all the TM-PP structures using the GGA+U level of theory.



Figure 2.7: 1) Spin-polarized band-structure for Mn-PP, 2) Density of states of Mn-PP using HSE06 level of theory, 3) Partial DOS of C and N 2p orbitals, and 4) Partial DOS of Mn 3d orbitals. Here, the Fermi level is set to zero.

We know that under the influence of a crystal-field environment, squareplanar-coordinated *d*-bands split into four bands. For describing the magnetic behavior of manganese metal in the porphyrin moiety, we have examined (Fig. 2.7) the spin-polarized partial-density of states (PDOS). With the help of the occupancy of *d*-orbitals in Mn-PP, we can easily interpret the filling of electrons, hence the magnetic moment of Mn-PP. In the PP-moiety, Mn is in the +II oxidation state with a d^5 electronic configuration and a magnetic moment of $3 \mu_B$ /Mn. For explaining the half-metallic electronic structure of Mn-PP, we have considered the PDOS of Mn, C, and N separately. Upon examining the PDOS of C and N, we have found the dispersed states of highly delocalized 2p orbitals of C and N across the Fermi level for only one spin channel (Figure 2.7.3). In the case of partial DOS of Mn 3d orbitals (Figure 2.7.4), we have found the degenerated delocalized states for d_{xz} and d_{yz} orbitals (forming the d_{π} bands) whereas other orbitals $(d_{xy}, d_{z^2} \text{ and } d_{x^2-y^2})$ are completely localized. From the splitting of d-orbitals in a crystalfield environment, it is found that the $d_{x^2-y^2}$ orbital is completely unoccupied, and sequential filling of five electrons in other orbitals results in three unpaired electrons. The occupancy of these five electrons is as follows: d_{π}^3 (d_{xz}^2 and d_{yz}^1 or d_{xz}^1 and d_{yz}^2), $d_{z^2}^1$, d_{xy}^1 , and $d_{x^2-y^2}^0$. We have also plotted the spin density difference (SDD) plot to better visualize the accumulated density in ferromagnetic Mn-PP. The SDD plot for Mn-PP clearly shows the accumulation of up-spin density on Mn atoms, whereas the N atoms in the Mn-PP structure are populated with down-spin density (Figure 2.8).



Figure 2.8: Spin density difference for ferromagnetic Mn-PP structure (Isosurface value $0.007 \text{ eV}/\text{Å}^3$). The yellow color shows up-spin density, whereas cyan color shows down-spin density.

2.3.6 Curie Temperature

According to our structural and magnetic moment calculation (Table 2.1 and Figure 2.7), Mn-PP is found to be only half-metallic. As half-

metallic structures are important for spintronic devices, we have considered the Mn-PP system for further studies. Thus, we have further evaluated the magnetic ground state of the Mn-PP sheet. For the calculation of exchange energies (magnetic behavior), we adopted a supercell of 2×2 for Mn-PP. The following two magnetic state configurations are considered in our calculations: the ferromagnetic and anti-ferromagnetic phase. The exchange energy is calculated by the difference in energy for ferromagnetic spin configurations and antiferromagnetic spin configurations ($E_{ex} = E_{FM} - E_{AFM}$). The positive (negative) E_{ex} represents the stable anti-ferromagnetic (ferromagnetic) phase. For calculation of the Curie temperature, we consider the 2D Ising model Hamiltonian on a square lattice with the nearest neighbor (NN) interactions and next-nearest neighbor (NNN) interactions as shown in Figure 9:

$$H = -J_{NN}\Sigma_{i,j}S_i \cdot S_j - J_{NNN}\Sigma_{i,k}S_i \cdot S_k$$
(2.7)

where S_i represents the (\pm) Ising spin on the square lattice with respect to the nearest neighbor and J represents the exchange parameters between S_i and the nearest neighbor to the Ising spin.



Figure 2.9: Ising model considering both nearest and next-nearest exchange interactions. Each lattice point represents a magnetic Mn atom.

As shown in Figure 2.9, we have considered both the exchange interactions to explain the exact value of *J* parameters. Because of an increase in the distance of neighboring sites from the Ising spin state (σ_i) , other interactions are negligible in the scale of magnitude.

 J_{NN} and J_{NNN} can be calculated by using the following equations: [73]

$$E_{FM} = -8(J_{NN} + J_{NNN})$$
(2.8)

$$E_{AFM} = 8(J_{NN} - J_{NNN})$$
(2.9)

$$E_{AFM2} = 8J_{NNN} \tag{2.10}$$

$$J_{NN} = (E_{AFM} - E_{FM})/16$$
(2.11)

$$J_{NNN} = [2(E_{AFM2} - E_{FM}) - (E_{AFM} - E_{FM})]/32$$
(2.12)

From the above expressions, the values of exchange parameters (J_{NN} and J_{NNN}) is calculated for Mn-PP. The exact value of *J* depends on the relation $H = -J_{NN}\sum_{i,j}S_i \cdot S_j - J_{NNN}\sum_{i,k}S_i \cdot S_k$, where J_{NN} and J_{NNN} are obtained from summations, as all the interactions weigh equally and are identical for each Ising spin on the 2D square lattice. The exact value of *J* is basically obtained from the summation of all the possible exchange values ($\sum_{i=0}^{n}J_i$). The 2D Ising model is solved analytically to obtain the exact Curie temperature with the help Onsager equation, which shows the dependence of *J* on T_c in the relation $\frac{k_BT_c}{J} = 2.2691$. We have calculated the exchange parameter (*J*) for the spin-polarized Mn-PP, and the value of *J* is calculated to be 0.0102312 eV. The calculated value of Curie temperature is 269 K, which is higher than that of the previously reported similar frameworks [8,9,70].

2.3.7 Strain vs. Magnetism

In the case of half-metallic ferromagnets, the direct channel for electronspin interaction is blocked [74]. Hence no direct channel is present for spin-flip scattering, resulting in slow demagnetization over conventional ferromagnets. So, it becomes imperative to understand the effect of strain on the half-metallicity and anisotropy energy for Mn-PP. To understand this, we have performed band-structure calculations under strain to find whether the half-metallicity is conserved under strain or not (Figure 2.10).



Figure 2.10: Band-structure for Mn-PP showing the effect of compressive (C) and tensile (T) strain on the half-metallicity. With compressive strain, the half-metallicity is sustained in the Mn-PP. In contrast, with an increase in tensile strain, the degeneracy is readily lifted in the *d*-bands results in an insulating state.

We can easily conclude from the band-structure calculation that under compressive strain, Mn-PP can retain its half-metallicity. However, under tensile strain, the half-metallicity is lost under 2% of strain. The possible cause for the loss in half-metallicity is the disruption of d_{π} bonds due to the weakening of coordination spheres around the Mn atom. We have observed the change in the magnetic ground-state for Mn-PP under 2%, 3%, and 4% tensile strain from a low-spin state of 3 μ_B to a high-spin state of 5 μ_B [27]. The change in the magnetic moment for the corresponding structures can be unraveled with the help of PDOS (Figure 2.11). From the PDOS of strained systems, we can see that the localized $d_{x^2-y^2}$ orbital is stabilized (Figure 2.12) because of the weakening of coordination spheres around the metal-nitrogen moiety.



Figure 2.11: Partial DOS Mn-PP under compressive and tensile strain.

Hence, the d_{π} band which carries the extra odd electron is now free to occupy the $d_{x^2-y^2}$ orbital (appears as a flat band above the Fermi level in the band-structure). We have considered $\Gamma - M - \Gamma$ in the Brillouin zone for a better understanding of the behavior of half-metallicity on the M-point. We have also calculated the magnetic anisotropy energy (MAE) under strain for all the structures to understand the behavior of stress on the Mn-PP's anisotropy energy. As shown in Figure 2.13, the (MAE) value calculated for Mn-PP is 3.11 meV. The calculated value is quite promising for application in spintronics [75]. We have observed a decrease in the MAE value from 3.11 meV (unstrained state) to 1.31 meV (4% compressive strain) under the compressive biaxial strain. However, in the case of tensile strain, we have observed some unusual behavior of MAE on Mn-PP systems.



Figure 2.12: Qualitative description of d-orbitals and magnetic moments under normal and tensile (2%) strain conditions.

The enhancement of spin-orbit coupling has already been presented in many previous cases, which results in an increase in the MAE value under the tensile strain [76].



Figure 2. 13: Variation of MAE of monolayer Mn-PP under the biaxial strain. There is a transition from a high spin state to a low spin state with 2% of tensile strain.

Slow relaxations in the low spin $(3 \mu_B)$ complexes are quite known rather than in high spin complexes $(5 \mu_B)$ [76], which can be easily seen in Figure 2.13 up to 1% tensile (T-1%) strain. Similarly, high spin complexes are known to show fast relaxation, [77] and hence lower anisotropy energy (from T-3% to T-4%). But there are some previous reports on single molecular magnets (SMM) to show slow relaxation for even a high spin state [78]. The Mn-PP structure shows a similar behavior under a tensile strain of 2%. This behavior's simple reason is unquenched SOC while transforming from the low spin state to the high spin state (Figure 2.14). Mixing the higher spin state with unquenched SOC under external stress shows a feasible way to achieve higher MAE values without incorporating higher transition elements into organometallic frameworks.



Figure 2.14: Variation of E_{SOC} under strain for perpendicular (outplane) and parallel (in-plane) direction of Mn-PP

2.4 Conclusion

Spin-polarized density functional theory (GGA+U) calculations are performed on the TM-PP (TM = Cr to Zn) systems for possible spintronic devices. All the TM-PP systems are magnetic (magnetic moments from 4.0 μ_B to 1.0 μ_B for Cr to Cu) and show excellent mechanical and thermal stabilities. Among all the TM-PPs, Mn-PP was reported to be a ferromagnetic half-metallic material. Furthermore, the pyrazine fused Mn-PP system shows strong half-metallicity compared to the previously studied benzene fused porphyrin frameworks. More importantly, the Mn-PP system has strong anisotropic energy (3.11 meV per Mn) compared to the previously studied systems, and such high anisotropy energy is excellent for the slow spin relaxation mechanism. Our calculations show that the 100% spin polarization and slower spin relaxation in Mn-PP, due to higher anisotropy energy and non-direct electron-spin relaxation. Furthermore, the Mn-PP system's halfmetallicity (100% spin polarization) is retained under significant strains (compressive and tensile). However, such a Mn-PP system can be converted into a semiconductor under excessive strain. Furthermore, the Curie temperature and work function calculations are performed and compared with previously studied porphyrin-based systems because of their importance as spintronic materials. We hope our work will motivate and guide experimentalists to synthesize fused porphyrin structures for their possible applications in spintronic devices.

Note: This is copyrighted material from Royal Society of Chemistry, Journal of Material Chemistry C, 2016, 4, 9069-9077 (DOI: 10.1039/c6tc03438a).

2.5 References

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Double-ExchangeMagneticInteractionsinHigh-TemperatureFerromagneticIronChalcogenideMonolayers

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Chapter 3

3.1 Introduction

Ferromagnetic insulators (FMIs) are the primary candidates for the fabrication of magnetic devices such as magnetic tunneling junction (MTJs), quantum spintronic devices, magnetic sensors, and so on. Among all these FMIs, highly symmetric ferromagnetic insulators with high Curie temperature are very important for magneto-resistance based devices [1]. A ferromagnetic system with high Curie temperature can be achieved through magnetic impurities, but the crystal loses its symmetry due to such impurities [2-3]. Besides, the loss in symmetry directly affects the fabrication of multi-layered structures due to lattice mismatch [4-7]. But dopant-free FMIs are still difficult to realize for any practical applications [8-9] due to undesirable physical properties such as low Curie temperature and low-availability. Also, the symmetric ordering of magnetic ions in a lattice provides a stabilized charge-ordering, which disfavors the insulating state. Therefore, attaining strong magnetism without disturbing their highly symmetric ground state is quite a difficult task. One of our study's main objectives is to find a highly symmetric ferromagnetic material with a high Curie temperature. In this regard, two different magnetic states in the same material with varying ligand field are quite interesting.

The discovery of 2D materials [10-12] has opened a wide range of possibilities for tuning and fabricating devices at a nano-scale [13]. Among the 2D materials, the transition-metal chalcogenides (TMCs) are promising candidates for the creation of next-generation spin-based transistors because of their abundances and interesting magnetic properties [14-15]. For example, they are readily available in the form of oxides and sulfides with different stoichiometries and show fascinating properties such as superconductivity, spintronics, Mott transitions and optoelectronics properties [16-20].

Iron-based TMCs are very promising due to their natural occurrence and abundance in nature. Fe_3S_4 is a well-known example of iron-based

chalcogenides, which naturally occurs in greigite form. The other natural occurring form of Fe₃S₄ is smythite [21-22]. Smythite does not have any tetrahedral voids like in greigite (Figure 3.1) [23], which makes physics interesting. In this work, we have considered the smythite due to its well-known lamellar structure. We predict that the lamellar form of Fe₃S₄ can provide new insights for magnetism and spintronics. Because in smythite, Fe can have two different possible oxidation states with varying multiplicities of spin. For example, octahedral (O_h) Fe(II) can have low spin (ls) $t_{2g}^6 e_g^0$ or high spin (hs) $t_{2g}^4 e_g^2$ electronic configuration with S = 0 or 2. Similarly, Fe_{0h} (III) can have $t_{2g}^5 e_g^0$ (ls) or $t_{2g}^3 e_g^2(hs)$ electronic configuration with spin S = $\frac{1}{2}$ or $\frac{5}{2}$. Here, the ligand environment around the Fe is important for *d*-orbital degeneracy and band ordering, which provides a playground to manipulate the electronic or magnetic properties.

In TMC, the intrinsic charge transfer and coulombic interactions are very important for charge ordering and chemical bonding. These factors directly affect the occupation in d orbitals and energy ordering of t_{2q} and e_g orbitals. Because of the strong correlation of electrons in partially/half-filled d orbitals, the insulating behavior may emerge compared to the classical d band model of insulators (with no delectrons). This correlation may induce the interdependence between charge, spin, and orbital moment ordering. Hence, magnetic ordering cannot be determined by the interpretation of a single parameter. However, these parameters' dependence provides the tunability of electronic, magnetic, and optical properties by applying some perturbations in the form of cation size, bond lengths, or bond angles. In TMC, the valence p-orbitals (from chalcogenides) and d-orbitals (from transition-metal) may interact to form strong chemical bonds. Due to their differences in electronegativity, the d orbitals of earlier transitionmetals $(d^0 \text{ to } d^3)$ may lie higher in energy compared to the late transition-metals $(d^7 \text{ to } d^9)$, which in turn may favor the formation of

stronger metal-chalcogenide bonds with late transition metals. Such strong interaction may favor the strong p - d mixing.

In the Hubbard model picture (ionic model), the $d^m - d^n$ excitations are caused by coulombic repulsion parameter *U*. However, in the case of d - p excitations (more covalent), the charge transfer (CT) energy (Δ) plays an important role. The CT energy plays a crucial role in determining the band ordering [24]. The CT energy depends upon the relative electronegativity of ligand orbitals and ionization energy of metal cation. But when we are dealing with TM having the electronic configuration d^4 to d^6 , there will be a competition between CT (Δ) and Coulombic repulsion *U* [25].

The electronic and magnetic properties of the smythite 2D layer and the effect of electronic-correlation on the degeneracy of *d* orbitals have been investigated to understand the origin of magnetic properties and the nature of the insulating/semiconducting state in 2D smythite layer Fe_3S_4 . The crude electron localization provided by Hubbard *U* model shows the importance of exact electron-correlation for describing the chemical bonding, magnetic properties, and electronic properties. We have tried to explain the crystal field splitting and Jahn-Teller distortion in the Hubbard *U* model. We have also tried to explain the importance of the double-exchange mechanism (DE) responsible for the magnetic interactions. We have also checked whether pressure could play any role in improving their magnetic properties. The non-collinear spin model is used to study the spin ordering and the magnetic anisotropy energy.

3.2 Computational Details

We have investigated the electron-correlation and effect of external strain in a 2D smythite lattice in this work. (S)DFT calculations are performed as implemented in VASP [26-27] within the GGA-PBE [28] approximation.



Figure 3. 1: 1) Greigite structure (with tetrahedral and octahedral voids) and 2D smythite layered structure with corresponding Bader charges (red color). 2) Fe_3S_4 (smythite) in octahedral phase surrounding Fe_A and two anti bi-prismatic phases around the Fe_B . The difference in chemical potentials results in a distorted structure with different bond-lengths of $Fe_A - S_1$, $Fe_A - S_2$, $Fe_B - S_1$ and $Fe_B - S_2$.



Figure 3.2: Optimized unit cell of Smythite with interlayer spacing of 3.512 Å.

The lattice parameters are obtained by comparing the optimized structure from hybrid functionals such as the HSE06, HSE03, PBE0, and B3LYP [29-31]. We have considered different U (Dudarev et al. approach) [32] values ranging from -1 to 8 eV in step size of 0.25 eV, to reach the same magnetic ground state (Table 3.1) as predicted by Hybrid-functionals. We have used a fixed value (1 eV) of the exchange interaction parameter (j) in all the calculations. The plane-wave basis sets and an energy cut-off of 520 eV are used for solving the Kohn-Sham equations. We have sampled the reciprocal space by employing a k-point mesh of $8 \times 8 \times 1$. The tetrahedron method with Bloch correction is used to calculate electronic structure with a smearing of 1 meV and k-point mesh of $13 \times 13 \times 1$. The total energy and ionic forces are converged up to 10^{-8} eV and -0.001 eV/Å. We have also performed the molecular dynamics and phonon calculations to interpret the system's thermal and dynamic stability, respectively. The localized wannier functions are calculated from Bloch states obtained through VASP, and the tight-binding band-structure is produced by using wannier90 code [33].

3.3 Results and Discussion

3.3.1 Structure and Stability

In transition-metal chalcogenides, a perfect O_h environment splits the fivefold degenerated *d* orbitals into two sets of threefold t_{2g} and twofold e_g orbitals. The in-plane/out-plane distortion such as Jahn Teller distortion can cause a further reduction in the O_h symmetry to D_{3d}/C_3 . For this, we have restricted ourselves to mixed hybridized systems like smythite (Fe₃S₄). This bulk smythite structure is known to show ferromagnetic ordering [34-36] and naturally occurs in the hexagonal phase having $R\bar{3}m$ (166) space group. The bulk structure of smythite is layered, containing three septuple layers of iron and sulfur (Figure 3.2). The interlayer spacing between the two septuple layers is 3.512 Å (Figure 3.2). This work has considered a 2D model of smythite for studying the electronic and magnetic properties.

Table 3.1: The magnetic moment (atom resolved and total), bond lengths, lattice parameters, and bandgap of 2D smythite. Please see Figure 3.1 for numberings.

Exchange correlation	Magnetic moment		Fe_A			Lattica		
	(µB)			$-S_1(S_2)$	Fe_B	Fe_B	parameters	Band
	Fe _A	Fe _B	μ_B	(Å)	$-S_1$	$ \begin{array}{c c} -S_1 & -S_2 \\ (\text{\AA}) & (\text{\AA}) \end{array} $	a (and b)	gap (eV)
			(total)	In-plane	(Å)		in Å	
				(out-plane)				
GGA	2.84	1.29	5.75	2.41	2.37	2.24	3.294	Metallic
PBE0	3.49	1.36	6.00	2.47(2.49)	2.41	2.25	3.382	1.50
HSE03	3.48	1.37	6.00	2.48(2.49)	2.41	2.25	3.378	0.95
B3LYP	3.41	1.29	5.90	2.49(2.50)	2.44	2.27	3.410	1.22
HSE06	3.49	1.29	6.00	2.48(2.49)	2.41	2.26	3.375	1.05

Smythite have four different kinds of Fe – S bonds ($Fe_A - S_1 = 2.48$ Å, $Fe_A - S_2 = 2.49$ Å, $Fe_B - S_1 = 2.41$ Å, and $Fe_B - S_2 = 2.24$ Å) as shown in Figure 3.1 and Table 3.1, which easily lifts the degeneracy of the *d*-orbitals in the O_h environment. The sulfur atoms around the Fe_B form anti bi-prismatic arrangement and a distorted octahedron around Fe_A (Figure 3.1). The calculated bond lengths with the help of hybrid functionals (HFs) (Table 3.1) suggest such a distorted structure, whereas GGA failed to do so. We have calculated the exfoliation energy ($E_{exf}(n)$) for one septuple layer of smythite by using the following relation:

$$E_{exf}(n) = \frac{E_{iso}(n) - E_{bulk}/m}{A}$$
(3.1)

Where $E_{iso}(n)$ is the energy of an isolated layer, E_{bulk} is the energy of m layers of bulk and A is the molecular surface area. The calculated value of exfoliation energy is 0.0134 eV/A, which suggests weak interlayer interactions in bulk smythite. Furthermore, we have calculated Bader [37-39] charges to understand different iron-sulfur bonds present in the 2D smythite lattice. From Bader charge analysis (Figure 3.1), it

has been clear that the crystal field is different for Fe_A and Fe_B. Therefore, there are two different Fe centers present in the 2D smythite structure. Hence, the crystal field around metal splits the regular octahedron of bulk smythite to D_{4h} (Fe_A) and C_{3v} (Fe_B), where D_{4h} belongs to a regular out-plane Jahn-Teller octahedron and C_{3v} is a capped octahedron.

Because of the natural abundance of smythite ($\leq 25^{\circ}$ C) and compositional similarity to greigite, [36] we have carefully studied the dynamical and thermal stability. We have not observed any imaginary modes at the Γ point in phonon dispersion (Figure 3.3.1). However, we have observed slightly negative acoustic modes between K- Γ point. We have also simulated the Langevin *NVT* thermostat of 252 atoms having 373 K temperature (Figure 3.3.2).



Figure 3.3: 1) Phonon dispersion of 2D Smythite lattice and, 2) AIMD simulation of 2D Smythite at 373 K with 252 atoms for 10 ps with a step of 1fs.

The molecular dynamics calculations are performed in search of any phase evolution or transformation. From molecular dynamics calculation, we have observed the in-plane (along Fe_A) lattice distortion. However, we have not observed any structural deformation or transformation. The above room temperature molecular dynamics shows that the further heating at higher temperature can result in the formation of tetrahedral pockets or empty voids within the Smythite [7, 21-22].

3.3.2 Magnetic and Electronic Properties

Our GGA calculations show that Fe_3S_4 is metallic with a total magnetic moment of 5.75 μ B per unit cell. However, in transition metal chalcogenides, the strong localization of electrons is well known, [40] which cause the substantial gain in many-body character in their wavefunction.



Figure 3.4: 1) Magnetic moments under applied U. 2) Impact of localized Hubbard (U) on the magnetic moment.

Hence GGA alone cannot describe their electronic and magnetic properties [41]. To account for this electronic localization in Smythite, we have used the Hubbard (U) approach of Dudarev *et al.* as implemented in VASP. We have applied the same U value on both the metal centers. On applying the U beyond 3 eV on the Fe site, we have got the spin transition from a $Fe_A^{II}(high spin)$ to $Fe_A^{II}(low spin)$ and Fe_B^{III} (low spin) to Fe_B^{III} (high spin) (Figure 3.4.1). Then we have compared the total and localized magnetic moments obtained from GGA+U and hybrid functionals. The GGA+U calculated localized magnetic moment values do not match those calculated using hybrid functionals (HFs). Then we have varied the U value as a step function at the Fe_A site by keeping the U value fix on Fe_B site. On varying the U_A from 1.5 to 8.5 eV at the Fe_A site, we have observed an increase in total magnetic moment values (Figure 3.4.2). However, there is a little gain $(\sim 0.11 \mu B)$ in magnetic moment value at Fe_B site. However, at larger values of U_A (up to 7.5 eV) and U_B (up to 3.0 eV), the system tends to
deviate from magnetic ground-state (6.00 μB) obtained from hybrid functional calculations.



Figure 3. **5**: Magnetic moment of Sulfur atom present at the surface with different DFT methods.



Figure 3.6: 1) HSE06 Band-Structure of Fe_3S_4 , showing the VB states contributing by *p* states of S and CB states contributing by *d* states of Fe. 2) Electronic structure of Fe_3S_4 , where black color denotes up spin and green color denotes down spin channel.

On carefully analyzing the localized magnetic moments, we have observed that the magnetic moment of S atoms (at the surface) is coupled antiferromagnetically with the other localized magnetic moments (Figure 3.5). Finally, we have calculated the electronic structure for 2D Smythite with different types of hybrid functionals (Table 3.1) and obtained a bandgap of 1.05 eV. From HSE calculations, we have observed that the electronic gap lies in between the valence band maxima (consists of S p-orbitals) of up spin and conduction band minima of down spin (consists of Fe *d*-orbitals) channel (Figure 3.6.1). As both the Fe ions are feeling different crystal field/ligand field (CF/LF) due to the ligand environment, DFT+U method can not account for exact electronic localization/delocalization between VB and CB. The maximum bandgap obtained by DFT+U is only 0.17 eV [41]. However, this electronic gap opens due to different electron localization provided by the U parameter. We have carefully analyzed the continuity of density of states of 3s and 3p orbitals of the sulfur atom in Figure 3.7. If we look at the LDOS of S atoms, the *p*-band center of the S-atoms (inner) is nearly stabilized by 1 eV or more compared to the S-atoms of the surface. However, the cation state also loses its degeneracy due to Jahn-Teller distortion (Figure 3.8) and contributes a significantly less contribution at valance band maxima.



Figure 3.7: Spin-polarized PDOS of S atoms in Fe_3S_4 . Blue color line represents the inner sulfur atoms, whereas red color line represents the S atoms present at the surface.



Figure 3.8: PDOS of Fe (localized on *d*-orbitals). Fe_A *d* states are more stabilized over Fe_B.

Hence, from electronic structure calculations, we have concluded that the transition is mostly charge-transfer (p - d) types in this system. Because around the Fermi energy, the p - d states equally contribute towards the process like hopping, charge transfer, and magnetism. Hence, from here on, we have preceded all our calculations within the HSE06 framework for exact electronic localization and correlation.

3.3.3 Exchange model and Ferromagnetism

We have divided the exchange mechanism into two parts to understand the magnetic interactions involved in the smythite structure. In the first part, only in-lattice (molecular approach) magnetic interactions are considered. However, in the second part, we have considered the periodic approach with only possible nearest neighbors (NN) to account for the exact exchange mechanism needed for triangular lattices [42]. Because of weak SOC in 3*d* transition elements, the important role is played by crystal-field (CF) or ligand-field (LF) and Jahn-Teller distortions. Hence the non-collinear magnetic models in 3*d* TM materials are not strong enough to overcome the LF and Jahn-Teller model. Here, we have employed the collinear magnetic model and constrained the spins in parallel and antiparallel directions. In simple words, the spins at sites *i* and *j* are assumed in such a way that $S_i \cdot S_j = \pm 1$. Based on the Heisenberg spin model, the corresponding Hamiltonian is

 $H = J_1 \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j + J_3 \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j + \dots)$ (3.2)where J_1 , J_2 and J_3 are the exchange interactions parameter [43]. The exchange parameter J can be obtained by calculating the relative energy differences between ferromagnetic (FM), ferrimagnetic (FiM) and antiferromagnetic states (AFM). The same Hamiltonian can be used for both the molecular approach (MA) and the periodic approach (PA). We have calculated the possible exchange parameters (I) to determine the exact magnetic ground state in Fe₃S₄. In Figure 4, we can see the different possible exchange matrices within the unit-cell and the neighbor periodic lattice. Out of eight possible spin configurations, we have only three sets of indistinguishable spin configurations. The competing nature among super-exchange (Fe_{*B*} $\stackrel{S}{\leftrightarrow}$ Fe_{*B*} and Fe_{*A*} $\stackrel{S}{\leftrightarrow}$ Fe_{*A*}), double-exchange $(Fe_B \stackrel{D}{\leftrightarrow} Fe_A)$ and direct-exchange $(Fe_B \leftrightarrow Fe_A)$ will decide the nature of magnetism. We have carefully discussed the magnetism and exchange pathways by considering the molecular approach and periodic approach to explain these exchanges among the ions. The presence of three magnetic centers in Fe₃S₄ (unit-cell) diminishes the possibility of an antiferromagnetic configuration in the collinear model. So, we have divided the exchange pathways into different magnetic states, as shown in Figure 3.9. Because of the absence of any periodic images (along z) for these exchange interactions (J_{ln}) . The corresponding system can be considered as an isolated molecule. The corresponding DFT energies for these magnetic configurations are fitted to Heisenberg Hamiltonian. As we can see in Figure 3.9, because of the different oxidation state of Fe_A and Fe_B , there will only be two possible paths for nearest neighbor interaction $(J_{l1} \text{ and } *J_{l1})$ and one path for second NN interaction (J_{l2}) .



Figure 3.9: Exchange pathways for molecular (MA) and periodic approaches (PA); Three possible exchange paths in MA approach and geometrical parameters considered for study the magnetism.

These interactions are energetically competing and help in determining the actual magnetic ground state. Here the ${}^*J_{l1}$ will be the doubleexchange path for NN, J_{l1} will be the direct-exchange path for NN and J_{l2} will be NNN interactions. Based on the simple spin model, we have eight possible spin configurations in which three configurations are indistinguishable in terms of DFT energies. These three spin configurations are FM ($\uparrow\uparrow\uparrow$), FiM1 ($\downarrow\uparrow\uparrow$), and FiM2 ($\uparrow\downarrow\uparrow$). The corresponding energies related to those configurations can be written in the form of

$$E_{FM}^{MA} = E_0 + 2J_{lc} + J_{l2} , E_{FiM1}^{MA} = E_0 + J_{lc} + J'_{l2} + J'_{lc} , \text{ and}$$

$$E_{FiM2}^{MA} = E_0 + 2J'_{lc} + J_{l2}$$
(3.3)

Where J' and J denote the $\downarrow\uparrow$ and $\uparrow\uparrow$ spin coupling and J_{lc} includes both the double-exchange and direct-exchange contribution (J_{lc} = J_{l1} + *J_{l1}). The E₀ is the ground state energy for the non-interaction spin model. The relative DFT energies for the configuration $E_{FiM1}^{MA}(4.0 \,\mu B)$ and E_{FiM2}^{MA} (2.0 μB) are 0.048 eV and 0.103 eV compared to E_{FM}^{MA} (6.00 μB). These values show that the *FM* is a most stable magnetic ground state. We have applied $\pm 3\%$ strain on Fe₃S₄ to observe the

difference between $\uparrow\downarrow\uparrow$, $\uparrow\uparrow\downarrow$ and $\uparrow\uparrow\uparrow$ coupling. We have plotted the difference between J_{lc} and J'_{lc} with applied strain in Figure 3.10.1. With an applied compressive strain, the parallel coupling of spin becomes more favorable. However, the second NN coupling strength $(J_{l2} - J'_{lc})$ is very weak and lies in the range of 10^{-5} eV. But the exact magnetic only be determined by the considering ground state can antiferromagnetic state. Hence, we have considered a 2×2 supercell for the calculation of exchange energy with only possible antiferromagnetic chain configuration. In the periodic approach (PA), we have considered configuration ferromagnetic and one antiferromagnetic one configuration. Here, each Fe ion has six nearest neighbors, and the second nearest neighbor is far away to be considered for calculation of *J*. The difference between the antiferromagnetic and ferromagnetic configuration is about 210.01 meV. The T_c of Smythite is calculated based on mean-field theory and Heisenberg model, where T_c is given by the relation $k_B T_c = \left(\frac{2}{3}\right) \Delta E$ [44]. Here k_B is the Boltzmann constant, and ΔE is the exchange energy per unit-cell. The calculated value of T_c is 406 K, which is significantly higher than the room temperature. Hence, 2D Smythite can be a good candidate for room temperature magnetic applications [45-46]. To understand the nature or type of magnetic interaction, we have applied a common strategy by applying mechanical strain to observe the changes in exchange energy [47-48]. However, due to the structure's complexity, we have applied up to $\pm 2\%$ lattice strain [49] to observe the effect of magnetic interaction operating in the lattice (Table 3.2).

Structure	$d_{A_{i}-B_{i}}\left(\text{\AA}\right)$	$\angle A_i \stackrel{D}{\leftrightarrow} B_i$	$\angle A_i \stackrel{D}{\leftrightarrow} B_j$	$\angle A_i \stackrel{S}{\leftrightarrow} A_j$	$\angle B_i \stackrel{S}{\leftrightarrow} B_j$	$\Delta E_{ex}($
Structure	Direct	Double	Double	Super	Super	meV)
+2%	2.92	72.2	132.8	86.8	98.4	105.85
+1%	2.95	73.7	132.9	86.0	97.6	167.80
Normal	2.96	74.5	132.9	85.1	96.3	210.01
-1%	2.97	75.0	133.0	85.3	96.3	214.48
-2%	3.00	76.3	133.6	83.6	95.1	265.74

Table 3.2: Dependence of ferromagnetic exchange energy (ΔE_{ex}) on the bond-angles and bond distances.



Figure 3. 10: 1) Competitive in-lattice interactions for ferromagnetic (\uparrow $\uparrow\uparrow$) vs ferrimagnetic ($\uparrow\downarrow\uparrow$) configurations. **2)** Virtual electron excitation and orbital overlap for DE interactions (along $\angle A_i \leftrightarrow B_j$) for hybrid orbitals.

We have considered the following parameters mentioned to explain the competing behavior: direct-exchange $(d_{A_i-B_i})$, super-exchange $(\angle A_i)$ $\stackrel{s}{\leftrightarrow} A_i \text{ and } \angle B_i \stackrel{s}{\leftrightarrow} B_j \text{ and double-exchange } (\angle A_i \stackrel{D}{\leftrightarrow} B_j \text{ and } \angle A_i \stackrel{D}{\leftrightarrow} B_i) \text{ in }$ the smythite structure. On applying the compressive strain in smythite, the ferromagnetic interactions become stronger. We have examined the magnetization between a chalcogen ion (S) and two transition metals (Fe) to explain the nature of ferromagnetic interactions. Because of electron pairing in the $d^5(\text{low})$ - $d^5(\text{low})$ spin states, we have constructed the virtual atomic orbitals to explain the possible cation-anion-cation interactions. In smythite, we have two $\sim 90^{\circ}$ cation-anion-cation centers for super-exchange and two double-exchange paths. Based on Goodenough-Kanamori rules, [50-52] any super-exchange interaction between low spin or high spin states can be discarded due to the presence of cation-anion-cation 90° angle (Table 3.2). For cation-cation interaction (direct-exchange) in insulators, the electron transfers are not favorable due to the improper overlap of orbitals (among metals) and strong binding energy of the electron on electron-deficient cation sites. However, due to the difference in cations' oxidation states, some polarization is induced at those lattice sites. This difference in polarization favors the delocalization of an electron from one site to another. Here, the overlap for DE interaction (Fe-S-Fe orbital) is more favorable due to $\sim 135^{\circ}$ cation-anion-cation angle and induced polarization. In DE interaction, the formation of Fe^{2+}/Fe^{3+} redox couple favors the transfer of the σ bonding electron from e^2 states of $t_{2g}^4 e_g^2$ (Fe²⁺) to the empty orbital e^0 of $t_{2g}^5 e_g^0$ (Fe³⁺) (Figure 3.10.2). This favors the ferromagnetic DE interactions in Fe_3S_4 and becomes more favorable with the opening of the bond angle (Table 3.2). Hence, the ferromagnetic DE interactions play a crucial role in providing the strong ferromagnetic nature of smythite structure. We have also calculated the non-collinear magnetic ground state to describe the order of spins. We have constrained the magnetic moment in out-of-plane angle (along the z axis) and varied the SOC along with Cartesian SOC vectors. We have calculated the magnetic anisotropy energy for the 2D

smythite in a constrained direction along the x (5.9 meV), y (0 meV), z (6.7 meV) axis and along 110(1.8 meV) and 111(5.3 meV) plane. The difference in MAE energy confirms the presence of weak Jahn-Teller distortion due to d^5 (low spin) and d^6 (high spin) configuration. The difference in magnetic anisotropy energy along y and z axis is about 6.7 meV. However, we have found a strong dependence of MAE on the out-plane magnetic moment and in-plane easy axis. Therefore, we have calculated the relaxation of MAE with spin quantization vectors along the x - y plane (Figure 3.11). We have plotted the angular dependence of magnetic anisotropy energy within the x - y plane. This implies that 2D Smythite has a disordered spin ordering in an in-plane and out-plane lattice.



Figure 3. 11: The minima of MAE lie along the easy xy plane. Angular dependence of MAE of Fe₃S₄ is plotted with respect to polar angle.

3.4 Conclusion

Here, we propose a Fe based (2D smythite structure) transition-metal chalcogenide for room-temperature spintronics applications. Spin-polarized calculations are performed to study the electronic and magnetic properties of a 2D smythite layer. The 2D smythite structure's electronic structure possesses a crucial dependence on the exact exchange and correlation of standard DFT theory. For this, we have used the DFT+U method. However, it fails to locate the exact magnetic

ground state. Therefore, with the help of hybrid functionals methods, we have calculated the 2D smythite layer's electronic gap, which is ~ 1.05 eV. We have found out that the 2D Smythite is a charge-transfer insulator due to mixed hybridization around Fe (d) and S (p) orbital near the Fermi energy. The system shows a Jahn-Teller distortion due to asymmetrical electronic filing in t_{2g} and e_g orbitals for both the cations. A strong ferromagnetic behavior is observed due to the presence of a double-exchange mechanism. The calculated Curie temperature value (T_c) is as high as 406 K, which suggests that the system can be used for room temperature spintronics devices. We have applied the mechanical strain for the enhancement of exchange energy. With the increase in compressive strain, the system tends to be strongly ferromagnetic due to the Fe-S-Fe DE angle opening. This enhancement in DE angle provides a better orbital overlap for Smythite. We have used a virtual orbital model to explain the nature of the DE mechanism between $Fe^{2+}(hs)/Fe^{3+}(ls)$. The presence of Jahn-Teller distortion removes the in-plane degeneracy of Smythite. To explain the spin ordering in the Smythite, we have used a non-collinear model and found out the system's in-plane easy axis. The angular dependence of MAE is studied to see the relaxation path of spins along the x - y plane. In summary, this work provides a route towards the study of complex magnetic interactions and synthesizing the strong ferromagnetic transition-metal dichalcogenides in iron-based compounds. The presence of redox couples within the same system favors the possibility of a strong ferromagnetic exchange mechanism, which in results give rise to strong room temperature ferromagnetism.

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3.5 References

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Spin-PolarizedCurrentinFerromagneticHalf-metallicTransitionMetalIodideNanowire

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Chapter 4

4.1 Introduction

Spintronics is a branch of science, which involves the usage of electronic spin to process information [1]. Spintronics devices with lowdimensionality, high spin polarization, and high-Curie temperature (T_c) are highly desirable for their practical applications [2]. Among these spintronics devices, half-metal (HM) based spintronics devices have gained enormous importance because of their $\sim 100\%$ spin polarization [3-6]. Such materials have a sharp difference in electronic density near the Fermi level for the spin-up and spin-down channels. Half-metallic systems have the potentials to provide current, which is completely spinpolarized. They can act as a spin-filter system where such electric polarization is needed. Such property is an invigorating factor while constructing spin-logic based circuits. In general, half-metallicity is an inherent property of material, but it can also be induced via defect, doping, and various other ways [7]. In both cases, the half-metallic system with a desirable Curie temperature is needed for their practical applications. Over the past few decades, many researchers have devoted their time in search of such half-metallic materials. In this regard, transition metal (TM) chalcogenides, TM-hydrides, and TM-borides based materials have been investigated [8-12].

Similarly, transition-metal chalcogenides have been known for their importance in the field of spintronics, ferroelectrics, and optics [8,13-14]. But in the past few years, metal-halides have received significant attention in the area of spintronics and ferroelectrics [14-20]. After discovering CrI₃ by Huang et al. [21], transition-metal-based halides have emerged as promising materials for spintronic devices. The weak van der Waal interactions in the TM-halides (TMXs) are important as magnetism comes out to be an inherited property of these layered structures. The exfoliation of a TM-halide monolayer is easily achievable without altering the magnetic property of the system. CrI₃ monolayer is one of the most common examples of a ferromagnetic

system with a T_c of 45K. The discovery of CrI₃ has proven the importance of metal-halides. After that, many researchers have proposed several transition-metal based dihalides and trihalides monolayers for spintronics [22].

In recent time, one dimensional (1D) nanowires (NWs) have shown their versatile applicability in the field of magnetism, thermo-electric, and so on [9,12-24]. However, attaining a remarkably high Curie temperature (T_c) is a challenging task in 1D based systems. Because it is difficult to control the growth of such materials for practical applications, and the ferromagnetic interaction is weak in such systems. But with the recent advancement in nanotechnologies, the atomic-scale tunability of simple molecular junctions becomes quite achievable [25-26]. Hence, nanowires can be grown experimentally by assembling simple molecular segments [27]. Ferromagnetic 1D nanowires or nanowires coupled with strong ferromagnets can be useful for making spin-logic circuits. These 1D systems can be used to transfer electronic signals between the logic gates, even for simple operations such as on/off. Similarly, due to the gain in the current/voltage ratio (halfmetallicity), they always improve devices' power consumption.

Inspired by the recent literature on such low dimensional materials, we have focused our search on transition-metal triiodide (TMI₃) based molecular nanowires for spintronics applications. For this, we have performed a detailed study to understand the structural, electronic, and magnetic properties of Sc to Co NWs. Different magnetic properties (exchange energy, exchange parameter, Curie temperature, and magnetic anisotropy energy) are studied to assess their importance in spintronics applications. Moreover, we have used non-equilibrium Green's function-based methods to confirm the existence of spin polarization in the half-metallic TM NW structure.

4.2 Computational Details

All the spin-polarized calculations are performed using the Vienna Ab *initio* Simulation Package (VASP) [28-29]. For the better treatment of

the exchange-correlation part, we have used Perdew-Burke-Ernzerhof (PBE) functionals within the generalized gradient approximations (GGA) [30]. For a representation of Kohn-Sham wave functions, we have used an energy cut-off of 520 eV. For optimization and relaxation of ions, we have used the conjugate-gradient algorithm. The total energy convergence criteria have been set at 10^{-06} eV and all the structures are optimized till the forces on individual atoms are reduced to 0.01 eV/Å. A distance of 18 Å is used between the two molecular wires to avoid the interaction between the periodic images. A Gamma-centered kpoint grid of $60 \times 1 \times 1$ points is used to sample the Brillouin zone. To avoid the Peierls distortion in 1D crystal, we have considered a supercell of four unit-cells for all the calculations. The Bader charge analysis is also performed with a near-grid algorithm as implemented in the Henkelman programme [31-32]. For the calculation of electronic structure, we have used a kpoint grid of $101 \times 1 \times 1$ kpoints. Several DFT functionals (hybrid and semiempirical) are used for our best system to account for the exact electron-correlation. The final electronic structure obtained from all the functionals are compared with G_0W_0 functional as implemented in VASP [33-37]. The molecular orbitals are projected for the gamma-point from the obtained wavefunction. For chemical bonding analysis, we have calculated the projected Crystal Orbital Hamilton Population (COHP) curves with the help of the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) package [30-32,38]. A total of 192 Kohn-Sham (KS) states are considered in the analysis of occupied states during the COHP analysis. The obtained wavefunction converges with 1% charge spilling for the occupied KS states. The molecular dynamics calculations have been performed within an NVT canonical ensemble with a Langevin thermostat [39]. The electronic transport properties have been studied using the non-equilibrium Green's function (NEGF) in the TranSiesta module [40-41]. The system's electronic transport properties have been studied using non-equilibrium Green's function (NEGF) within DFT in the TranSiesta module of Siesta code. For this purpose, we again

independently relaxed the junction geometry by employing GGA+PBE level of theory in the Siesta code. Norm-conserved Troullier-Martins pseudopotentials are employed to describe the interaction between the core and valence electrons. The energy cut off for the real space grid is 300 Ry. To sample the Brillouin zone integration, we employed the gamma point for the extended nanowire region and a $1 \times 1 \times 101$ within the Monkhorst-Pack scheme for electrodes with a double- ζ polarized basis set. The systems are fully relaxed by employing the generalized gradient (CG) algorithm. The tolerance in density matrix difference is 0.0001, and the residual forces on the atoms are less than 0.01 eV/Å. The current-voltage I-V characteristics curves are computed by combining the non-equilibrium Green's function (NEGF) and DFT approach, as implemented in TranSiesta packages. The proposed device is shown in Figure 4.1. This device has been divided into three parts: left (L) electrode, right (R) electrode, and a central scattering region. The electrodes are periodic in the transport direction (z is the transport direction). The electric current through the central scattering region for our proposed device is calculated by expending the Landauer-Buttiker methodology:

$$I(V_b) = \frac{2e}{h} \int_{\mu_R}^{\mu_L} T(E, V_b) \left[f(E - \mu_L) - f(E - \mu_R) \right] dE$$
(4.1)

where $T(E, V_b)$ is the transmission spectrum of the electrons entering at energy (E) from L to R electrode in the presence of an applied finite bias voltage V_b , $f(E - \mu_{L,R})$ is showing the Fermi-Dirac distribution of electrons in the L and R electrodes and $\mu_{L,R}$ the chemical potential where $\mu_{L/R} = E_F \pm V_b/2$ are moved correspondingly up and down according to the Fermi energy E_F .



Figure 4.1: Schematic presentation of the proposed device for the calculation of spin-polarized current. Color code; V: red: I: violet.

4.3 Results and Discussion

4.3.1 Structural Parameters

We have considered two configurations for the 1*D* transition-metal triiodide (TMI₃) based NWs (Figure 4.2): eclipsed (E) and staggered (S) conformers. In the case of E, the iodine atoms form a perfectly eclipsed structure along the periodic boundary direction, whereas in the case of S, the iodine atoms are in a staggered position along the periodic boundary direction. During the optimization of the TM based 1D NWs, we have observed a distorted trigonal bipyramidal geometry around the metal center. Due to the trigonal crystal field, TMI₃ NWs belong to the full prismatic group or frieze "*mm*" group [42]. Hence the *d*-orbitals degeneracy does not follow the conventional octahedral splitting. Hence, it is important to analyze all the geometrical parameters, such as metal-metal (d_{M-M}) and metal-iodine (d_{M-I}) bond lengths. We have summarized these parameters in Table 4.1.



Figure 4.2: 1) Top and side views for E- and S-types TMI₃ NWs, and 2) Calculated formation energy values for TMI₃ NWs.

In the case of type E structures, we find a decrease in average M-M bond length as we go from early to late transition metals though there is no such trend in the case of S-configurations. This indicates that the structures are distorted, and the distortion is maximum for Sconformers. Therefore, these two types of NWs differ in terms of spatial projections of I atoms around the TMs.

U		/		v 1				
NWs		Sc	Ti	V	Cr	Mn	Fe	Со
Type E	d_{M-M}	3.79	3.65	3.63	3.60	3.55	3.55	3.52
	d_{M-I}	2.90	2.82	2.78	2.76	2.80	2.79	2.72
Type S	d_{M-M}	3.52	3.23	3.30	3.30	3.38	3.26	3.23
	d_{M-I}	2.88	2.79	2.74	2.73	2.82	2.77	2.59

Table 4.1: Average metal-metal bond $(d_{M-M}, \text{Å})$, and metal-iodine bond lengths $(d_{M-I}, \text{Å})$ in E and S-types TMI₃ NWs.

4.3.2 Energetic and Thermal Stability

We have calculated the formation energy (E_f) using the following equation to understand whether such types of NWs are energetically stable or not:

$$E_f = E_{NW} - 4 \times E_{TM} - 12 \times E_I \tag{4.2}$$

where E_{NW} is the total energy of the NW, and E_{TM} and E_I are the total energy (per atom) in their respective bulk structures. Figure 1b shows the formation energies for all the studied TM based 1D NWs, and it shows that S-type of early TM based NWs are energetically more stable compared to the S-types of late TM based NWs. Our total energy values show that S-conformer is stable over E-conformer for all the studied NWs. The maximum difference in energy between the two structural types exceeded up to 0.712 eV/TM for CrI₃ NW. Such a high energy difference indicates the stabilization of S-conformers due to the staggered I atoms around the TM center. Hence, we have excluded the E-type of nanowires from our current study. Moreover, we have excluded Fe and Co-based NWs from our present study. The calculated formation energy values (more positive) suggest early TM based NWs are stable over late TM based NWs. While calculating the formation energies, we have found out a gradual decrease in the formation energies from Sc to Co. This decrease can be correlated with the electronegativity difference between the TM-I bond. As we already know, I's tendency to oxidize the late TMs decreases from left to right in a periodic table. The calculated formation energy values are very much in agreement with this. Furthermore, we have performed a Bader charge analysis (Table 4.2) to understand the nature of interaction in M-I bonds.

TMI2 NWS	Charge on Type S (in <i>e</i>)				
1111311013	TM	Ι			
Sc	+1.90	-0.62			
Ti	+1.61	-0.54			
V	+1.39	-0.47			
Cr	+1.23	-0.41			
Mn	+1.16	-0.38			

Table 4.2: The calculated average Bader charge values on TM and I in TMI_3 NWs.

From the Bader Charge analysis, we have observed a decrease in positive charge on TMs as we move from Sc (1.90e) to Mn (1.29e).



Figure 4.3: Total energy fluctuations of TMI₃ NWs ($6 \times 1 \times 1$ supercell) during the AIMD simulation at 300 K for 10 *ps* with a time step of 1 *fs*.

Such a decrease is directly proportional to the difference in the electronegativity of TM-I bonds. Furthermore, the thermal stability is evaluated with the help of *ab initio* molecular dynamics (AIMD) simulations for a period of 10ps (time step 1fs) at 300 *K*. A canonical ensemble for Sc to Mn NWs ($6 \times 1 \times 1$ supercell) is considered and simulated using the Langevin thermostat. A graph between free energy and time steps (in *ps*) has been plotted for all the systems (Figure 4.3). We have not observed any structural deformation or phase transformation during the MD simulations. Therefore, we predict that all the NWs are thermally stable at room temperature.

4.3.3 Electronic and Magnetic Properties

Transition-metal iodides are known to show fascinating electronic and magnetic properties [43]. So, we have performed spin-polarized calculations for all the nanowires. It is found out that the nanowires are magnetic, except TiI₃ and ScI₃. The calculated magnetic moments are 4.0, 3.0, and 2.0 μ_B per TM for MnI₃, CrI₃, and VI₃ NWs. This trend can be explained based on electronic configurations for transition-metal dorbitals. Under a triangular prismatic field, TM d-orbitals splits into three-sets of orbitals; $a(d_{z^2})$, $e_1(d_{xz}, d_{yz})$ and $e_2(d_{xy}, d_{x^2-y^2})$. Here, e_1 and e_2 orbitals are twofold degenerate. Similar trends are also observed for other TM-trihydrides NWs [9]. In Figure 4.4, we have shown a schematic diagram for the hybridization between TM (d) and I(p) orbitals. Based on magnetic moment values and schematic for hybridization for TMI₃, we conclude the following electronic configurations for the TMs in the TM NWs; $Sc = d^0$, $Ti = d^1$, $V = d^2$, $Cr=d^3$ and $Mn=d^4$. On carefully analyzing the localized magnetic moments, we have found out that the iodine atoms are antiferromagnetically coupled with TMs. Most of the magnetic moment is localized on the transition-metals. From LDOS analysis (Figure 4.6), we have observed that the I states are more stabilized over the transitionmetal states. Therefore, I atomic orbitals (p) appear more in the valance band edge, whereas TM atomic orbitals (d) appear more in the

conduction band. Hence, for a process like charge-transfer, most of the excitation will be $p \rightarrow d$ type in nature.



Figure 4.4: A schematic representation for the hybridization between TM s/d-orbitals and I p-orbitals.



Figure 4.5: Spin-polarized band-structure and density of states for TMI_3 NWs.

Our electronic structure plots (Figure 4.5) show that all the nanowires to be semiconducting except VI₃ NW. The calculated values of bandgap (E_g) are 1.36, 0.30, 1.30, and 0.44 eV for ScI₃, TiI₃, CrI₃, and MnI₃ NWs. As our main interest in the ferromagnetic half-metallic systems, we have also plotted the spin-resolved and orbital-resolved bandstructure for VI₃ NW (Figure 4.7). From Figure 4.7.1, it is clear that the half-metallicity originates mainly due to the spin-up electrons. On carefully examine the orbital resolved band-structure, we have found the maximum contribution at the Fermi surface belongs to the V d-orbitals (Figure 4.7.1).



Figure 4.6: Spin-polarized LDOS for TMI_3 NWs. Here, red color represents the *d*-orbitals contribution from TM, and magenta color represents the *p*-orbitals contribution from I. Here the Fermi level is set to zero and indicated by the blue dashed line.

In general, the electronic properties of transition metal-based compounds are greatly influenced by the correlation effect. To understand the robust half-metallicity in VI₃ NW, we have studied electron correlation effects in VI₃ NW using different DFT functionals (HSE06, HSE03, PBE0, SCAN (meta-GGA), and TPSS (meta-GGA)). Furthermore, we have compared all these results with the G_0W_0 electronic structure (Figure 4.8). With the meta-GGA functionals, the half-metallicity of VI₃ is found to be robust. However, with hybrid functionals (HSE06 and HSE03), a small gap of 0.4 eV opens up. On the other hand, with the PBE0 functional, the calculated bandgap is 2.0 eV. However, our G_0W_0 calculations show that VI₃ NW system is half-metallic. Previous reports show that GW-based calculations accurately describes the vanadium oxide's electronic structure compared to HSE06 [43-45]. Therefore based on our GW calculation, we can say that VI₃ NW is truly a half-metallic system.



Figure 4.7: 1) Spin- and orbital-resolved band-structures for VI₃ NW. Here, red color represents the *d*-orbitals contribution from V and magenta color represents the *p*-orbitals contribution from I. 2) Monte Carlo simulation for the calculation of Curie Temperature (T_c) for ViI₃ NW.



Figure 4.8: Spin-polarized DOS for VI_3 NW with different DFT functionals.

4.3.4 Curie Temperature

From the Ising model, we know that phase-transitions are nearly absent in the 1D system due to the absence of long-range interactions. However, in many previous works, [24] it has been observed that the long-range magnetic interactions become stable with an increase in the length of chain/wire. Here we have considered the possibilities of simple exchange interactions and the formation of a magnetic couple (magnetic dimer). To validate this, we have considered three possible magnetic ordering (Figure 4.9): one type of ferromagnetic (FM) and two types of antiferromagnetic (AFM) orderings. The presence of one more antiferromagnetic configuration is due to TM-TM dimer. On careful examination of DFT energies for the configurations mentioned in Figure 4.9, we have found out the VI₃ nanowire to be ferromagnetic with an exchange energy value of -106.37 meV. While all the other NWs are either antiferromagnetic or non-magnetic. The calculated values of exchange energies are 167.11 and 194.79 meV for CrI₃ and MnI₃, whereas ScI₃ and TiI₃ remain non-magnetic.



Figure 4.9: Possible magnetic exchange interactions in TMI₃ NWs; (FM= ferromagnetic and AMF = antiferromagnetic).

As the Curie temperature (T_c) is one of the most important criteria for the realizations of ferromagnetic materials in spintronic applications. We have performed a Monte Carlo simulation based on the Ising model. In our work, we have only considered the nearest-neighbor exchange interactions (J_{ij}) . We have considered the following Hamiltonian for the calculation of J_{ij} ;

$$H = -J\sum_{ij}S_i.S_j \tag{4.3}$$

where *S* is the spin moment per site (TM_2I_6). Here, *J* represents the exchange interactions between two adjacent sites. To calculate the exchange parameter (*J*), the following equation is used;

$$J = \frac{E_{FM} - E_{AFM}}{M^2} \tag{4.4}$$

where E_{FM} and E_{AFM} are the total energies of the NW in their ferromagnetic and anti-ferromagnetic structures. As VI₃ is a ferromagnetic system amongst all the studied systems, and the calculated value of *J* is 3.324 meV. A plot between magnetization and temperature has been given in Figure 4.7.2. The calculated value of T_c is 22.3 K. This value is quite large compared to the previously studied quasi-1D organic ferromagnet [46] though smaller than the VI₃ monolayer [47]. This is obvious as the number of exchange interactions reduces from a 2D lattice to a 1D chain.

4.3.5 Nature of magnetism

We have also applied strain on the Ti and V NWs to understand the change in their magnetic and electronic properties. The reason behind the consideration of TiI₃ NW is due to the presence of atomic magnetic moments reported by Kuzubov *et al.* [23]. They have shown the localization of *d*-electrons in TiI₃ NW packets, which results in a small magnetic moment. Here, we have applied tensile strain (ϵ) in the form of wire-length to find out the magnetic robustness in the system. For the calculation of strain, we have used the following relation;

$$\epsilon = \frac{a_1 - a_0}{a_0} \times 100 \tag{4.5}$$

where, a_1 is the wire length under strain and a_0 is the wire length of the optimized lattice. We have plotted a graph between relative energy and wire length (Figure 4.10). As shown in Figure 4.10, both the wires are mechanically stable as the total energy change is less under strain. After that, we have investigated their magnetic properties. For VI₃ NW, on increasing the wire length from 13.23 Å to 14.82 Å, we observe that the magnetic moment value increases. The increase in magnetic moments results in the increase of exchange interactions between V-V centers (Figure 4.11.1).



Figure 4.10: Variation in DFT energies and magnetic moments with wire lengths: 1) TiI₃ NW and 2) VI₃ NW.



Figure 4.11: 1) A plot between exchange energy and wire length for VI₃ NW, and 2) Projected HOMO orbital for TiI₃ NW.

With the increase in exchange interactions, the value of T_c also increases (Figure 4.11.1). However, while applying the mechanical strain on the

TiI₃ NW, we have observed a sudden change in the magnetic moment value. The magnetic moment value increases under strain. A small inflection on the relative energy plot (Figure 4.10) is observed for TiI₃ NW. At that point, a non-magnetic to magnetic transition can be observed for TiI₃ NW. Under moderate strain, the TiI₃ NW system shows anti-ferromagnetic properties. With an increase in strain, the TiI₃ NW system undergoes an anti-ferromagnetic to ferromagnetic transition. The influence of magnetic transition is also visible on the electronic structure of TiI₃. The TiI₃ NW becomes half-metallic under strain. Hence, it is clear that the ferromagnetic exchange interactions are possible for TiI₃ NWs under tensile strain.

As we have already found out that VI₃ is a ferromagnetic system with d^2 electronic configuration. But TiI₃ NW calculated to be a nonmagnetic system with d^1 electronic configuration. The electronic configuration for Ti(d^1) and V(d^2) can be written as $s^{\uparrow\downarrow} a^{\uparrow\downarrow} e_1^{\uparrow\downarrow} e_2^{\uparrow}$ and $s^{\uparrow\downarrow} a^{\uparrow\downarrow} e_1^{\uparrow\downarrow} e_2^{\uparrow\uparrow}$, which indicates that Ti should be a magnetic system with a magnetic moment value of 1 μ_B . However, TiI₃ (d^1) NW forms a nonmagnetic ground-state. To understand this behavior, we have performed a wavefunction analysis for the TiI₃ system. From the projected HOMO for Ti NWs (Figure 4.11.2), we have observed that the Ti-Ti metal interacts through the e_2 orbitals. Hence, d-orbitals come near to each other, which results in a strong d-d overlap between two Ti atoms, and the pairing of the electron becomes more feasible. To account TM-TM interactions, we have also calculated the COHP values. The calculated ICOHP values for $Ti \stackrel{2.91\text{\AA}}{\longleftrightarrow} Ti$ and $Ti \stackrel{3.55\text{\AA}}{\longleftrightarrow} Ti$ are -1.16 eV and -0.54 eV. These values represent a strong interaction between the Ti centers in the pure Ti NW. Similarly, ICOHP values are calculated for the V-V interactions in VI₃ NW (ICOHP = -0.18 eV ($V \stackrel{3.17\text{\AA}}{\longleftrightarrow} V$) and - $3.17 \times 10^{-3} \text{ eV} (V \stackrel{3.55\text{\AA}}{\longleftrightarrow} V)$. Hence, our calculated ICOHP_{TM-TM} values suggest that there is a formation of a dimer in the TiI₃ NWs. Furthermore, on carefully analyzing the -pCOHP density of states (DOS) plots for the VI₃ nanowire, we have found an equal contribution of bonding and antibonding states in forming the half-metallic gap in the nanowire. Here, the major contribution towards the bonding states comes from the V-V hybridization and anti-bonding states contribution comes from the V-I hybridization (Figure 4.12).



Figure 4.12: -pCOHP plots for VI_3 nanowire. Here, the solid line represents the up-spin channel, and the dotted line represents the down-spin channel.

Moreover, we have applied a certain amount of stress on both the Ti and V NWs (Figure 4.10) to understand the nonmagnetic/magnetic state in Ti/V NW. The sudden rise in magnetic moment values for TiI₃ shows the presence of a spin couple. A similar argument is also valid for VI₃ NW. As in both cases, the TM-TM distance increases to a large extent. The applied tensile strain weakens the orbital overlap between the two metal centers, resulting in the spin couple's deformation, and hence, the magnetic moment rises rapidly for TiI₃.

4.3.6 Transport Properties and Phonon Softening

The realization of spin-polarized currents in the ferromagnetic structures is of great interest. The decomposition of spin-currents in ferromagnetic structures can be described by a simple collinear model in which the current decomposed in two spin components; such as spin-up and spindown. However, in the presence of spin-orbit coupling (SOC), the same model cannot be applied to describe the spin-polarized currents. The spins' random orientation in the three-dimensional space makes things difficult, as we do not have any ordered spin-direction. To account these facts while calculating the transport properties, we first performed the SOC calculations and found out a small magnetic anisotropy energy (MAE) value of 0.017 meV for VI₃ NW. The observed value of MAE is smaller than the ferromagnetic exchange interactions in the NW. Hence, we have considered a collinear ferromagnetic model while calculating the spin-polarized currents in the NW. The TranSiesta module is used for the transport calculations. A spin-polarized current is calculated under the applied bias regime of 0.02-0.6 V. As shown in Figure 4.13.1, a large difference in the magnitude of the spin-polarized current is observed. The spin-polarized current remains constant for both the channels up to 0.6 V, which further proves the half-metallic nature of the NW. Hence, our transport calculations support the formation of spin-polarized currents in the agreement of ferromagnetism and halfmetallicity in the NW.

Moreover, we have performed the phonon calculations for the VI₃ NW. The motivation behind the calculation of phonon dispersion is to observe the electronic temperature's effect on the phonon dispersion. Sometimes to reduce the computational time in the DFT calculations, we increase the electronic smearing width. This change in electronic smearing produces a pseudo temperature in the DFT calculations. The effect of electronic temperature is maximum on acoustic phonons. With the increase in temperature, the phonon-phonon interactions increases due to the formation of new phonon modes. This ultimately results in thermal expansion. Here, we have calculated the phonon dispersion for the VI₃ NW at different smearing parameters (Figure 4.13.2). We have observed two negative acoustic modes at all smearing parameter. However, we do not observe any softening in phonon modes. But from the phonon dispersion, someone can argue about the stability of VI₃ nanowire. As we know from the literature, the acoustic modes' instability generally disappears while considering the phonon interactions over a large periodic image. To account for these long-range

interactions, we have performed phonon calculations for a $6 \times 1 \times 1$ supercell (Figure 4.13.3). From Figure 4.13.3, it is clear that the imaginary modes in the phonon dispersion rapidly disappear. Therefore, our phonon calculations support the dynamic stability of the VI₃ nanowire.



Figure 4. 13: 1) A *I*-*V* characteristics plot for the VI₃ (black/red colours for up-spin/down-spin channel), 2) phonon dispersion plot for VI₃ unit cell at different smearing width (σ (*eV*)), and 3) phonon dispersion plot for VI₃ in a 6 × 1 × 1 supercell.

4.4 Conclusion

Here, we report TMI₃ based NWs (TM = Sc, Ti, V, Cr, and Mn) with intriguing magnetic and electronic properties. The calculated formation energy values support the stability of early transition-metal iodide-based NWs, which is further confirmed through AIMD simulations. Amongst all the NWs, vanadium triiodide NW is calculated to be a ferromagnetic half-metallic system, whereas CrI₃ and MnI₃ NWs are antiferromagnetic, and ScI₃ and TiI₃ NWs are non-magnetic. Our phonon calculations further confirm the dynamic stability of the VI₃ NW. All the NWs are found to be either semiconducting or insulating (except VI₃). On careful examination of geometrical parameters (TM-TM bondlength), an excessive amount of lattice distortion is observable for TiI₃ and VI₃ NWs. A compelling role of TM-TM interaction is found to be the origin behind their magnetic ground-state configurations. To understand the role of TM-TM interactions, we have found out an increase in the ferromagnetic exchange interaction with the disruption
of TM-TM dimer under the tensile strain. Furthermore, the -pCOHP analysis has shown an important role of the V-V bonding and V-I antibonding hybridization towards forming a half-metallic gap. Our spintransport calculations confirm the half-metallicity nature in the VI₃ NW. Hence, our findings on one-dimensional systems provide a better platform for the researchers in developing such spin-logic based devices.

Note: This is copyrighted material from ACS Publications, Journal of Physical Chemistry C, 2019, 123, 25, 15717-15723 (DOI: acs.jpcc.9b02464).

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Evidence ofSpinHallEffectinTwo-DimensionalGlobalMinimumFe-PMonolayer

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Chapter 5

5.1 Introduction

In the past decade, the growing demand for non-volatile memory for spintronics applications has motivated the researchers to explore many forms of magnetoelectric materials. From simple monolithic multiferroics to artificial multiferroics, the emergence of magnetoelectric effect is either facilitated by the intrinsic magnetic ordering (anti-ferromagnets or paramagnets) and/or by the formation of heterostructures between ferroelectrics (or piezo electrics) and ferromagnets [1-2]. In the latter case, the tunability of magnetic anisotropy energy and/or the magnetic transition temperature (T_c) is achieved by the electrical control [3-4]. In such heterostructures, the magnetization is either governed by the magnetostriction principle or piezomagnetic effects. In both cases, the spin-orbit coupling plays a crucial role in governing such spin-logic devices [5-6].

The efficient and reliable detection of spin currents in such spin-logic devices occupies the central area of spintronics. In systems with no magnetization and the absence of an external magnetic field, the most important phenomenon is the Spin Hall effect (SHE) [7-11]. This phenomenon is driven by the intrinsic spin-orbit interactions or some external mechanism such as skew scattering or side-jump mechanism [12-13]. In perfectly ordered crystals, this phenomenon is expressed by the spin Berry curvature of the occupied electronic bands within the Fermi surface's vicinity. From electron transport theory, the SHE in ordered systems solely depends upon the eigenvectors and eigenvalues (electronic bands) in the k-space. The standard DFT methods can calculate SHE. The calculated spin-hall conductivity (SHC) in the heavier metals (such as Pt) reaches up to 2000 (\hbar/e) Ωcm^{-1} , whereas in lighter metals (such as Al), the SHC ranges only up to $-17(\hbar/e)$ Ωcm^{-1} [14]. The intrinsic mechanism (electronic band-structure) solely determines the SHE in such systems. Similarly, Zhou and coworkers have calculated the SHC in W $(-204(\hbar/e) \Omega \text{cm}^{-1})$ and Mo $(-361(\hbar/e)$ Ωcm^{-1}) based semimetals (ditellurides), which are primarily driven by the intrinsic spin-orbit coupling [9]. Due to the reduced symmetry in metal-tellurides, all the elements of spin-hall tensor are anisotropic and provide better control for the SHE driven applications [15]. Similarly, the low-dimensionality of a material limits the number of elements in the spin-hall tensor. Inspired by the literature on the importance of spinhall conductivity in spintronics applications, we have explored the lowdimensional materials in the present work. Due to weak spin-orbit couplings in 3d transition-metals [16] and early p-block elements, it is quite interesting to study the SHE in such systems. Theoretical calculations have played a significant role in the prediction of such materials. To explore such materials, it is important to study the phase diagrams of pre-existing materials to predict new materials. It basically talks about the extent of spin polarization with respect to the compositional ratio. The previous studies on the phase-diagram of Fe-P have shown some substantial stable/metastable phases that can coexist with minor energy barriers with different magnetization types (magnetic, paramagnetic, or non-magnetic). In similar reports, Wu et al. have also shown the phase stability among the different $Fe_{\gamma}P_{\gamma}$ compositions (bulk phases) [17]. In recent reports on Fe-based systems, such as Fe₃GeTe₂ [18] and Fe₃P [19], a strong interdependence has been observed between magnetization and spin-orbit coupling. The presence of magnetism in a Fe-based system is mainly driven by the Fe crystal's intrinsic magnetism. The main reason behind the consideration of Fe-based nano-architectures in the present study is due to its tendency to provide different types of magnetism. In few reports, it has been shown that the presence of nearly half-filled *d*-states and stability of iron redox pair (Fe²⁺/Fe³⁺) [20] provides additional control over magnetization, which can be further control by the applied strain. Although it has been found that to formulate the compound with Fe, a suitable counter pair is also needed. Due to the presence of rich chemistry in early *p*-block elements, we have preferred the *p*-block elements to search out a counter pair. Elements such as Boron, Carbon,

Silicon, and Phosphorous have shown excellent tendency of catenation. Among various elements, B and C are already known to form simple/hyper coordinated structures *[21-22]*. But none of the reports discuss the global (thermodynamically favorable) 2D phase that can coexist in similar compositions. The study of magnetization in such systems is appealing for scientific exploration and offers a more vibrant picture of chemical bonding between transition metals (such as Fe) and pnictides (phosphorous).

Here, our goal is to find out an exact solution for a 2D $\operatorname{Fe}_{x} \operatorname{P}_{y}$ composition. Several $\operatorname{Fe}_{x} \operatorname{P}_{y}$ compositions are considered from a Fe rich $(5 \ge x \ge y)$ to P rich $(5 \ge y \ge x)$ phase. For each $\operatorname{Fe}_{x} \operatorname{P}_{y}$ composition, a global structure is obtained with the help of global optimization tools, and their energetics are compared with previously reported $\operatorname{Fe}_{3} \operatorname{P}$ and $\operatorname{Fe}_{2} \operatorname{P}$ systems [19,23]. Phonon and Molecular dynamics simulations are also performed to ensure their stability. Under an applied strain of $\pm 2\%$, we have investigated the magneto-mechanical properties for the most stable structure. Finally, we have calculated the transport properties for the most stable system.

5.2 Computational Details

To find out the most stable two-dimensional phase of iron-phosphide $(Fe_x P_y)$, we have used the *ab initio* evolutionary USPEX algorithm as implemented in the USPEX (Universal Structure Predictor: Evolutionary Xtallography) code [24-26]. A vacuum of ~20 Å is considered to avoid the interlayer interactions to prevent the interaction between the periodic images. A slab thickness of ~3.5 Å is considered to account for the formation of multilayered structures. All the density functional theory (DFT) based calculations are performed with the Vienna ab initio Simulation Package (VASP) [27-30]. The electron-correlation part is treated with the Perdew-Burke-Ernzerh (PBE) functionals [31]. The projected augmented wave (PAW) method [32] is used to describe the electron-ion interactions. An energy cutoff of 500

eV is used to represent the Kohn-Sham (KS) wavefunctions. An energy convergence criterion of 10^{-6} eV and a force convergence criterion of 0.005 eV/Å are considered during the structural optimization. During the structural optimization, a total of 1764 k-points are used to sample the Brillouin zone along the periodic vectors. A chemical bonding analysis is performed with the COHP (crystal orbital Hamilton population) package [33-36]. The convergence for the wavefunction is achieved with 1.8% charge spilling using 128 KS states. Molecular dynamics simulations are performed within the NVT canonical ensemble with a Nöse thermostat. A phonon spectrum is also calculated along with the high-symmetry points within the DFPT (density functional perturbation theory) framework.

5.3 Results and Discussion

5.3.1 Global Optimization and Energetic Stability

The initial search of a 2D phase of iron-phosphorous (Fe-P) begins with the Fe-P phase diagram [17]. Several Fe rich bulk phases are already investigated over the past years, such as Fe₃P (Body-Centered Tetragonal), Fe₂P (Hexagonal), and FeP (Orthorhombic). Among them, Fe₃P has shown the highest Curie point (716 K) for a magnetic groundstate [19]. However, the phosphorous rich phases such as FeP₂ (orthorhombic) is also known to exist [23]. The thermodynamic stability of any 2D material plays a crucial role in their experimental realizations and device fabrications. Therefore, we have emphasized on thermodynamic stability while proposing our Fe-P based 2D material. To encounter such factors, we have included the compositions nearer to the stable thermodynamic grain boundary (FeP) reported by the researchers over the past years.



Figure 5.1: Fitness data for $Fe_x P_y$ compositions. High energy structures (positive enthalpy) are excluded from the current representation.

Hence, the following compositions Fe_5P , Fe_4P , Fe_3P , Fe_2P , FeP, FeP_2 , FeP_3 , FeP_4 , and FeP_5 are considered during the global structural minimization. Our search for each composition produced many structures during the sampling (Figure 5.1). The lowest energy structure (global structure) for each composition is shown in Figure 5.2 with their lattice parameters and monolayer thickness.



Figure 5.2: Global structures for different $Fe_x P_y$ compositions along with their geometrical parameters. The unit cell is indicated by solid black line.

After obtaining the global structures for all the compositions, their energetics is compared by calculating their formation energies (E_f) with respect to their parent elements such as Fe (*bcc*) and P (black-phosphorous). The following expression is used for the calculation of formation energy;

$$E_f = E_{\mathrm{Fe}_x \mathrm{P}_y} - x E_{\mathrm{Fe}} - y E_{\mathrm{P}}$$
(5.1)

Here, $E_{Fe_xP_y}$ is the total energy for each Fe_xP_y phase. E_{Fe} and E_P is the chemical potential for Fe and P atoms, respectively. The chemical potential (per-atom energy) for each species is calculated from their corresponding bulk-structure. To correlate the energy barrier between

the magnetic and non-magnetic calculations, the formation energies are calculated with (E_f^*) and without (E_f) spin-polarized density functional theory. A graph is plotted between the formation energy (per atom) and the atomic percentage of Phosphorous (Figure 5.3). The formation energies for pure Fe and P phases are considered as a reference point and set to 0 eV.



Figure 5.3: A plot between formation energy (per atom) and atomic % of phosphorous for 2D Fe_xP_y phases. Here, ΔE_f represent the non-spin polarized DFT energy and ΔE_f^* represent the spin-polarized DFT energy.

The calculated formation energies for Fe rich phases are much lower (more positive) compared to the P rich phases. Among all the structures, the FeP, FeP₂ and FeP₃ are found to be energetically favorable with negative formation energies. The difference between spin-polarized and non-spin polarized DFT energies exceeded up to ~0.29 eV/*atom* for Fe₄P. This difference gradually decreases as we move from Fe to P rich phases. A strong dependence of spin polarization can be seen in Fe-rich phases. On moving left in Figure 5.3 from FeP (1: 1), an increase in spin polarization is seen to provide stability among the iron-rich phases. However, phosphorous rich phases are still energetically more favorable with a formation energy value of -0.16 eV/atom (FeP₂) and 0.05 eV/atom (FeP₄). On comparing the energetics of our structures with the

previously reported 2D Fe_xP_y structures, such as Fe₃P (0.68 eV/atom) and Fe₂P (1.79 eV/atom) (Figure 5.4), the structures reported in the present work are found to be energetically more stable.



Figure 5. 4: Optimized structures of Fe_2P and Fe_3P . Here, blue sphere denotes Fe atom and red sphere denotes P atom.

The more negative formation energies for Fe_3P and Fe_2P shown in the present work suggests the formation of multilayered structures, which is contradictory to the previously reported Fe_3P and Fe_2P systems [19,23]. Also, a non-magnetic (or paramagnetic) state can be seen in Figure 2 for |1:2| composition, as the difference between the spin and non-spin DFT energies reach to 0 eV. However, energetics cannot be considered as a sole parameter to assure thermodynamic stability. Hence, it becomes crucial to study the dynamical and thermal stability of such systems.

5.3.2 Dynamic and Thermal Stability

A phonon calculation is performed within the DFPT framework for all the systems (Figure 5.5). A minimum of 500 K-point mesh is used to sample the 2D Brillouin zone (BZ). Phonon dispersion calculations are performed with the help of PHONOPY code along the high symmetry points in the 2D BZ for all the systems. Phonon spectra for all the structures are shown in Figure 5.5. The presence of large negative acoustic modes in Fe₃P (2.94*i* THz), Fe₂P (2.37*i* THz), FeP (0.84*i* THz), FeP₃ (0.96*i* THz), FeP₄ (2.99*i* THz) and FeP₅ (3.00*i* THz) indicates the instability among these structures, whereas Fe₅P and FeP₄ are found out to be dynamically stable.



Figure 5.5: Phonon dispersion for $Fe_x P_y$ phases.

In composition such as FeP_2 (0.30*i* THz), the presence of small imaginary acoustic phonon mode is also observable. However, many imaginary acoustic modes near the high symmetry points account for the instability in the structure. This phonon instability can be electronic or structural. In general, a dynamic instability arising due to the presence of high electronic density at the Fermi surface can give rise to the fascinating properties such as Ferroelectricity, Charge Density Waves (CDW), superconductivity, etc. Also, the temperature plays a significant role in stabilizing such imaginary phonon modes, which has been observed in materials such as β -Ni-Ti [37]. Sometimes computational noises during the force constant calculations also result in the higher magnitude of such modes. Such factors are controlled by accounting the long-range phonon interactions and/or sometimes anharmonicity. But the possibility of structural evolution is still valid in the viewpoint of thermal fluctuations. An AIMD calculation is performed to account the thermal stability under a Nose thermostat for 10 picoseconds (ps) at 300 K with a time step of 1 femtosecond (fs). As shown in Figure 5.6, some structural transformations (and/or) deformations are observed in Fe_xP_y phases irrelevant to their phonon spectra. A structural deformation is observed in Fe₃P, Fe₄P, FeP, and FeP₄. Surprisingly, Fe₅P and Fe₄P does have a favorable phonon spectrum, but they are unstable towards thermal fluctuations. In contrary, FeP₅ is found out to be thermally stable with positive formation energy and large negative phonon modes. Among all, only four phases (Fe₂P, FeP₂, FeP₃ and FeP₅) are thermally stable. Therefore, after discussion on the energetical, dynamical and thermal stabilities, we have considered the FeP₂ for further study due to their favorable energetics and thermodynamic stability.



Figure 5.6: AIMD simulations for all the $Fe_x P_y$ structures.

5.3.3 Electronic instability and Chemical bonding

The crystal structure of FeP_2 is consists of two buckled Fe-P atomic layers stacked on each other, forming a rectangular lattice (Figure 5.7.1). A total of two Fe atoms and four P atoms form the 1×1 unit cell. Each Fe atom is surrounded by the six P atoms forming a distorted octahedron.



Figure 5.7: 1) Geometrical parameters (bond-length and intralayer distance "d") for FeP₂.Intralayer bonds are omitted for better visualization. **2)** An atom resolved spin-polarized band-structure for FeP₂.

The calculated lattice parameters for FeP₂ are a = 4.72 Å, b = 3.39 Å, and $\gamma = 90^{\circ}$. On carefully analyzing the geometrical parameters, we have observed different types of Fe-P bonds in the FeP₂ (Figure 5.7). Based on crystal field (CF) theory, the *d*-orbital degeneracy is assumed to be removed and confirmed with the help of the orbital resolved density of states (Figure 5.8.1).



Figure 5.8: 1) LDOS plot for Fe *d*-orbitals in FeP₂. The Fermi-level is set to zero. 2) Total-DOS for FeP₂. Here, Blue color represents up-spin channel and red color represents the down-spin channel.

An atom resolved band-structure plot is also shown in Figure 5.7.2 and it shows a non-magnetic (and metallic) electronic picture. Two common features in FeP₂ band-structure is parabolic bands at the high symmetry point X (and Y) and multiple band crossing across the Fermi level. Here, the *p*-band (due to P atoms) at the X point and *d*-band (due to Fe atoms)

at the Y point provides diverse control over electronic manipulation (carrier doping etc.). The spin-polarized density of state (DOS) plot confirms the presence of high electronic density at the Fermi level. The presence of high electronic density at the Fermi surface also enforces an electronic instability, which is also seen in the phonon spectra of FeP₂. This electronic instability can be established by the larger number of anti-bonding orbitals near the Fermi for FeP₂ monolayer. To further ensure the nature of electronic instability, a COHP analysis is performed with many un-occupied Kohn-Sham states (electronic bands). At the Fermi, the maximum contribution in the DOS comes from the Fe-P and Fe-Fe anti-bonding states (Figure 5.9).



Figure 5.9: A -pCOHP plot for FeP₂ monolayer showing anti-bonding DOS states near to the Fermi-level.

As these states belongs to Fe_d - Fe_d and Fe_d - P_p , the polarization can be easily induced in such states in comparison to the P_p - P_p states. Due to the large DOS, the electronic filling among the *d*-bands is kinetically driven, and any small perturbations such as mechanical strain can also induce the magnetization. The removal of spin-degeneracy under the small mechanical perturbations can give rise to the magneto-mechanical properties and intriguing transport properties.

5.3.4 Effect of Strain

Strain plays a significant role in tuning the electronic and magnetic properties of materials. In actuality, the strain on a 2D system is generally enforced during the synthesis process. The strain is either induced by the substrate used during the synthesis or external factors. Therefore, it is important to study the electronic and magnetic properties under some perturbed environment. Here, we have investigated the magnetic properties of FeP₂ monolayer under the applied strain. Before proceeding to magneto-mechanical properties, the elastic constants are calculated with the help of strain vs energy relation to ensure the extent of mechanical stability. For the calculation of elastic stiffness constants, the following expression is used;

$$C_{ij} = \frac{1}{A_o} \left(\frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \right) \tag{5.2}$$

Here, A_o = area of x-y plane, ε = strain, and E = energy. The calculated elastic moduli are; C_{11} = 141.88 N/m, C_{22} = 99.32 N/m, C_{12} = 56.84 N/m, and C_{66} = 41.66 N/m. The criterion for the mechanical stability of a rectangular lattice is $C_{11} > 0$, $C_{66} > 0$, and C_{11} . $C_{22} > C_{12}^2$. After confirming the mechanical stability of the proposed monolayer, we have carefully examined the magnetic properties. A magnetization (and energy) vs. strain plot is shown in Figure 5.10.



Figure 5.10: A graph between % strain vs Energy (and Magnetic Moment $\{M\}$) under uniaxial (x =left; y =middle) and biaxial (x-y =right) strain.

We have not observed any sudden (or gradual) change in the magnetic moments under the compressive strain. FeP_2 monolayer remains in the non-magnetic ground-state. However, with the increase in tensile strain

(*x* or *y* or *x*-*y*), a small change in the local magnetic moment (mainly on Fe) is observed. However, we have not observed any drastic change in the electronic properties (bandgap) under the applied strain. This also suggests the strong metallicity in the FeP₂ monolayer. But, with the increase in tensile strain, a Zeeman type band splitting is observed. A few of the main reasons behind such splitting are the presence of electronic instability (due to antibonding COHP states) and large DOS in the proximity of Fermi level. Also, the tensile strain induces the magnetic moments in the FeP₂ monolayer, which reaches up to $0.357 \mu_B/uc$ for +2 % of strain. Here, the magnetic moment is mainly localized on Fe *d*-orbitals. Hence, it becomes important to understand the magnetic coupling in the FeP₂ monolayer, as this magnetic coupling governs the magnetic properties.



Figure 5.11: 1) An atom (and orbital) resolved spin-polarized bandstructure for FeP₂ under 2% tensile strain with a spin-splitting gap of 0.26 eV 2) A plot of magnetic moment vs temperature for FeP₂ (with 2% tensile strain) monolayer under mean-field theory.

5.3.5 Curie Temperature (T_c)

A spin-polarized (orbital-resolved) band-structure plot is shown in Figure 5.11.1 for +2 % of strain. A spin-splitting (Δ_Z) of 260 meV (Γ – X) is observed near the Fermi level due to the induced spin polarization. This value is much higher in comparison to electron-doped Py(BCSB)₂ (20 meV) and hole-doped GaSe monolayer (30 meV). [38] The presence of such a high value of spin-splitting can give rise to strong ferromagnetism in the FeP₂ monolayer. On carefully examine Figure 5.11.1, the spin polarization is mainly present in the *d*-bands near the Fermi (-1 to 1 *eV*) in the conduction bands (CBs) and valence bands (VBs), whereas a slight spin polarization is also seen in P *p*-bands. Because the VB at the $\Gamma - X$ point mainly belongs to the metal *d*-orbitals, the system remains stable towards carrier doping. Here, the spin-splitting between the *p*-type bands are stable towards the mechanical strain. As the spin-splitting near the Fermi level is driven by the metal *d*-bands, the study of ferromagnetism becomes more interesting. To discuss the exact nature of magnetism in FeP₂ monolayer, we have employed the Stoner model of Itinerant magnetism. In this model, the ferromagnetism in a ferromagnetic metal is described the following relation;

$$\frac{U}{1+\frac{U}{W}} \cdot D(E_F) > 1 \tag{5.3}$$

where U is equivalent to stoner parameter I (represents the on-site Coulomb repulsion), $D(E_F)$ is the density of states for 3d orbitals in non-magnetic state at Fermi and W is the d-band width. The above relation can be further simplified to validate the Stoner criterion of magnetism,

$$I.D(E_F) \ge 1 \tag{5.4}$$

where, *I* is related to the spin-splitting (Δ_i) and magnetic moment (m_i) present on the *i*-site in *l* (angular quantum number) band by the following relation;

$$\Delta_i = I. m_i \tag{5.5}$$

After observing a band-splitting of 260 meV ($\Delta_z \approx \Delta_i$) at the Γ point between two spin channels (majorly *d*-bands), we have correlated the band-splitting with Stoner parameter *I* to justify the Stoner criterion of magnetism. On subjecting the values for $D(E_F)$ and *I* in equation (3), FeP₂ monolayer with 2% tensile strain is found out to be satisfying the Stoner criteria of ferromagnetism [$I.D(E_F) \sim 1$]. For the calculation of T_c , the mean-field model is considered based on the minimization of free energy with respect to the electronic temperature. In the mean-field model, the total magnetic moment (*M*) is calculated by the following relation;

$$M = \int_{-\infty}^{E_F} \{D_{i\uparrow}(E) - D_{i\downarrow}(E)\} dE$$
(5.6)

where thermal excitations are induced by the fictitious electronic temperature (k_bT or σ), which causes the Curie transition [$D_{i\uparrow}(E_F) = D_{i\downarrow}(E_F)$]. A graph is plotted between the electron temperature (σ) and the net magnetic moment for the FeP₂ monolayer (Figure 5.11.2). The calculated value of Curie temperature is 471 K (+2% strain), which is much higher in comparison to strained CrPS₄ (90 K) electron-doped Py(BCSB)₂ (8.1 K) and hole-doped GaSe (90 K) [38-39]. Such a ferromagnetic state also retains its metallic properties. Hence, the proposed FeP₂ monolayer is non-magnetic and provides a strong ferromagnetic state. This ferromagnetic state is free from dopant induced magnetism, and it can be used for piezo-spintronic applications.

5.3.6 Topological Properties and Transport Properties

In FeP₂ monolayer, the energy bands cross the Fermi level but do not intersect each other. A topological number can be assigned to such occupied bands (Chern number), which can be non-zero under the absence of time-reversal symmetry. A Chern number can be assigned in FeP₂ bands, as no occupied band crosses the unoccupied bands along the BZ path (k-points).

Finally, we have investigated the transport properties of FeP₂ monolayer. Figure 5.12 shows the calculated SHC for the FeP₂ monolayer at Fermi energy. Here, the SHC σ_{ij}^k is a third-order tensor which comprises all the six elements of SHC tensor. Here, *s* represents the spin polarization direction, *i* represents the direction of spin-current generated by the electric-field along the *j* direction. Due to symmetry constraint in a 2D Brillouin zone, we have only two SHC tensor

elements (σ_{xy}^z and σ_{yx}^z). For the calculation of SHC, we have used the Kubo formula for the intrinsic SHC given by the following relation [15];

$$\sigma_{ij}^{s} = -\frac{e^{2}}{\hbar} \sum_{\vec{k}} \sum_{n} f_{n}(\vec{k}) \Omega_{n,ij}^{s}(\vec{k})$$
(5.7)

$$\Omega_{n,ij}^{s}(\vec{k}) = \sum_{m \neq n} \frac{2Im \langle \psi_{n,\vec{k}} | j_{i}^{s} | \psi_{m,\vec{k}} \rangle \langle \psi_{m,\vec{k}} | v_{j} | \psi_{n,\vec{k}} \rangle}{(E_{n} - E_{m})^{2}}$$
(5.8)

Here, $f_n(\vec{k})$ is the Fermi distribution function for the n^{th} band for each \vec{k} in the brillouin zone and $\vec{l} (= \{s, \vec{v}\})$ is the spin-current operator for the SHC. Due to anisotropy in the structure, the calculated values of SHC in FeP₂ monolayer under normal conditions is 34 (\hbar/e) Ωcm^{-1} (σ_{xy}^z) and $-47 (\hbar/e) \ \Omega \text{cm}^{-1} (\sigma_{yx}^z)$ at the Fermi. However, the SHC strongly depends on the Fermi energy. Tuning of Fermi energy by the applied mechanical strain is an effective way for the manipulation of SHC. The mechanical strain introduced by the substrate (or other methods) is more feasible. It does not alter the intrinsic properties by creating the charge pockets compare to the electron/hole doping. As shown in Figure 5.10, the applied compressive strain maintains the nonmagnetic ground-state of FeP₂. Hence, we have calculated the SHC for the system under +2% of (x - y) mechanical stress. The calculated values for SHC are 80 (\hbar/e) Ω cm⁻¹ (σ_{xy}^z) and -93 (\hbar/e) Ω cm⁻¹ (σ_{yx}^z) (Figure 6). The calculated SHCs with respect to Fermi energy shown in Figure 5.12. However, these values are not higher compared to some other known compounds. But FeP₂ monolayer proposed that the higher values of SHCs are possible in materials with lighter elements.



Figure 5.12: SHC tensor elements $(\sigma_{xy}^z \text{ and } \sigma_{yx}^z)$ for FeP₂ monolayer relative to the Fermi energy tuned by the strain (left = normal; right = +2%).

5.4 Conclusion

Spin-polarized density functional theory calculations are performed to locate the minimum energy $Fe_x P_y$ structures using the USPEX code. We have identified all the $Fe_x P_y$ based global minimum structures. From DFT calculations, phosphorous rich phases are found to be energetically more stable. On careful examining the dynamical and thermal properties, FeP2 is found to be energetically, thermally, and dynamically stable. Furthermore, the FeP₂ is found to be non-magnetic and metallic in nature. From COHP analysis, we have observed a small amount of electronic instability in the FeP₂ electronic structure (antibonding states at the Fermi level). On careful examination of spin-polarized structure, a strong metallicity is observed throughout the BZ path. However, the valence band and conduction bands remain separated and do not cross each other along the BZ path. To further explore the electronic instability and electronic structure of FeP_2 monolayer, we have calculated the electronic and magnetic properties of FeP2 monolayer under strain. With applied compressive strain (upto 2%), we have not

seen any change in electronic and magnetic properties. However, with increasing tensile strain, small magnetic moments arises in the FeP₂ structure. A spin-splitting of 260 meV is observed with 2% of tensile strain. This spin-splitting induces strong ferromagnetism in the FeP₂ monolayer (T_c = 421 K). Even under applied strain, there is no band crossing observed in the vicinity of Fermi level. To explore the topological properties, we have calculated the spin-hall conductivity (SHC) in the FeP₂ monolayer. In general, the spin-hall effect in the early transition-metals and early p-block elements is difficult due to the absence of strong spin-orbit coupling. However, in FeP₂ monolayer, we have calculated the SHC to be -47 (\hbar/e) Ω cm⁻¹ (σ_{yx}^z), which on applying the compressive strain increases to -93 (\hbar/e) Ω cm⁻¹ (σ_{yx}^z). We believe that our results on two-dimensional FeP₂ monolayer will be beneficial for the experimental realizations and its spintronics applications.

5.5 References

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Scope for Future Work

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Chapter 6

6.1 Scope for future work

The present doctoral thesis discusses about the atomistic origination of magnetism and modulation of electronic properties in low dimensional systems and their applications in the field of spintronics. With detailed discussion on numerous magnetic phenomena, the importance of 3dtransition metals in the field of spintronics has been very intensively studied. In this regard, the role of dimensionality has been explored in two-dimensional nanosheets (monolayer to multilayered structures) and in one-dimensional nanowire-based structures. Moreover, the changes in the spin-polarized electronic structures mainly depend upon the magnetic interactions. In this regard, we have demonstrated the strong magnetic anisotropy in 3*d* transition metal-organic frameworks, due to the localization of electronic spin in such systems. Achieving a significant value of magnetic anisotropy energy (MAE) is possible in MOFs, which is not seen in pure metals or doped structures. The influence of magnetic interaction in correlation with electronic structure is extensively studied. Apart from this, the present thesis also discussed the magnetism in a single Smythite (Fe_3S_4) layer with complex doubleexchange interactions. Furthermore, the ferromagnetic interactions and transport properties are also discussed in early 3d transition metaliodide based nanowires. The magnetic interactions in 1D systems are not commonly observed, which makes them an exciting candidate to investigate the electronic and magnetic properties. In our last chapter, we have talked about the non-magnetic interactions in Fe-based systems and discovers a small amount of SHC. This low value mainly originates due to the electronic structure of the system and easily tuned by the external perturbations. The present discussion on the electronic and magnetic properties and their importance in the field of spintronics, provides a route to experimentalists for developing more complex systems with desired properties. The present scenario in the spintronics not only requires the enhancement of physical features but also requires a cost-effective solution for daily purpose applications. In this thesis,

several aspects are intensively dealt with, which can be useful for the designing of new materials in the field of spintronics. Thus, the present thesis can provide a few conceivable outlooks for the researcher's mind.

In this regard, we believe that the understanding of the atomistic origination of electronic and magnetic phenomenon in low dimensional materials plays a crucial role in designing of multifunctional materials for spintronics. DFT plays an essential role in understanding the inherent properties such as spin-polarized electronic structure, chemical bonding, and many more.