

SUPERCONDUCTIVITY, MAGNETISM AND THEIR INTERPLAY IN TWO-DIMENSION

Thesis by

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In partial fulfillment of the requirements
for the degree of
Doctor of Philosophy



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April 2023

CERTIFICATE

Certified that the work incorporated in the thesis entitled "*Superconductivity, Magnetism and their Interplay in two-dimension*" Submitted by Chandan Kumar Singh was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.



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Date: 04/04/2023

DECLARATION

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



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ACKNOWLEDGEMENTS

Without the assistance of numerous individuals who have aided in my personal and professional development, this thesis would not have been achievable. I extend my gratitude for your support and wish you a happy and healthy future.

I would like to express my sincere gratitude to Dr. Mukul Kabir, my Ph.D. supervisor, above all else. Dr. Kabir's unwavering dedication to hard work and pursuit of excellence has been truly inspiring, and learning from him has been a delightful experience overall. I am grateful for the freedom and encouragement he provided me to explore problems to a satisfying conclusion, and his idea of involving his students in experimental collaborations has been incredibly rewarding for us. Dr. Kabir was always available to discuss both academic and non-academic matters, regardless of the time of day. I am grateful to him for his guidance and patience throughout the various stages of my Ph.D. journey.

I would like to express my gratitude to Dr. Goutam Sheet from IISER Mohali, India for providing me with the opportunity to simulate his experimental results. With his guidance, I was able to successfully complete three projects and gain valuable experience. I would like to express my heartfelt gratitude to Dr. Sanjay Nayak, Dr. Martin Dahlqvist, Dr. Johanna Rosen, Dr. Per Eklund, and Dr. Jens Birch from Linkoping University, Sweden, with whom I collaborated to study superconductivity in doped ZrB_2 . I am truly grateful for their invaluable contributions to this work, and for allowing it to be included in my thesis. I would like to express my sincere gratitude to Dr. G.J. Sreejith for his invaluable contributions in helping me write codes for the tight-binding Hamiltonians. His guidance and support were critical in achieving the results we obtained on topological superconductivity in van der Waals heterostructure. I would also like to extend my heartfelt appreciation to my friend, Dr. Surjit Sarkar from Concordia University, Canada, who gen-

erously taught me Python programming and helped me establish accurate tight-binding codes for various materials. His moral support during challenging times was invaluable and beyond words. I want to thank my collaborators, Dr. Atikur Rahman, Ms Neetu Prajesh and Prof. R Bhoomi Shankar, for allowing me to participate in their research works. I thank my research advisory committee members, Dr. Sunil Nair and Dr. Prasenjit Gosh, for their valuable suggestions and support during my PhD journey.

I want to thank past and present members of Dr. Mukul Kabir's Group with whom I have discussed a lot and their valuable suggestions play an important role in my research work. I am incredibly grateful to have such esteemed seniors like Dr. Rohit Babar, Dr. Srilatha Arra, Dr. Tilak Das, Dr. Ramya Iyer, Dr. Nitin Wadnerkar, Dr. Upendra Kumar, and Dr. Ashis Kundu who have generously shared their vast knowledge, invaluable experience, and provided guidance that has helped me tremendously. I am also blessed to have such extremely generous and supportive juniors like Bhagyashree Bhat, Deepak Kumar Roy, Basavraja G, Anupama S, Ashutosh Anand, Danish Pannu Kaur, Rohan Maniar, who played a crucial role in providing invaluable support during my PhD work. I want to thank Nisha Kurkure for her help in providing technical support to access the supercomputing facility at IISER Pune. To get the paperwork in the institute and the physics department, Prabhakar Anagare and Dhanashree Sheth helped me generously.

I am very thankful to IISER Pune and I-HUB Quantum Technology Foundation for providing financial support during my PhD. I acknowledge the computational support provided by CDAC-Pune, IUAC computing facility, CCMS Tohoku University Japan, Computing facility at SNBNCBS Kolkata, Athena and Param Bhrama Supercomputers at IISER Pune. These computing facilities are necessary for this thesis to be possible.

I do mention my lovable dear friends; without them any of my journey could

not have conclusive end. I receive enormous support whenever situations are critical, especially the last three years during the pandemic and I do not have words to describe their support. I am very thankful to my dear friends Sarkar, Sarvesh, Priti, Jay, Shubhendra, Mayank, Aman, Ravindra, Prashant, Samir, Rahul Deogharia, Wijay, Ashish, Vinay Suram, Shannon, Saddam, Sanjit, Udaya, Neetu, Vinay, Shatruhan, Kamal, Ashok, Bappa, Madan, Aditi, Yashwant, Ganesh, Bala, Sandhya, Deepak, Avirup, Ramya, Rohit, Shri latha, Tilak. Their contributions are priceless and equally important to me.

As the family comes last, but their contribution is my existence. I always learn the basics of humanity from my family, who constantly motivate me whenever required. My absence from their lives is the price they have paid, which is priceless. I have received much love from my father, mother and four of my sisters, Devyani, Puja, Rupam and Mamta.

Satisfaction lies in the effort, not in the attainment, full effort is full victory

Mahatma Gandhi

The thesis dedicated to my grandfather Late Shri Palakdhari Singh, my father
Ajay Kumar Singh and my mother Umda devi

SYNOPSIS

Quantum states of matter, which can exhibit remarkable physical phenomena such as superconductivity, magnetism, and topological order, have captivated physicists for decades. The ability to understand, control, and manipulate these states is not only a fundamental scientific pursuit but also has significant technological implications. Further, the interface of two materials with distinct quantum states can lead to the emergence of novel phenomena that are not present in either of the individual materials. The thesis explores some of these aspects to study superconductivity, manipulate magnetism in two-dimension and investigate emergent Majorana zero modes that may arise at the interface of two-dimensional heterostructures of superconductors and ferromagnets.

Chapter 1 lays out the fundamentals of magnetism and superconductivity and concludes by discussing the emergence of potential new quantum states at their interface, including topological superconductivity. This chapter sets the stage for the research questions explored throughout the thesis.

Chapter 2 provides a brief overview of the theoretical frameworks utilised throughout this thesis. We discuss the many-body problem and density functional theory, followed by a description of the density functional perturbation theory and an introduction to the Wannier function. Additionally, we describe the Eliashberg-Migdal formalism for studying superconductivity from first principles, including electron-phonon interaction. Finally, we conclude with the utilization of an anisotropic Heisenberg Hamiltonian to investigate two-dimensional magnetic materials.

Chapter 3 of the thesis explores various aspects related to tip-induced superconductivity, including its absence, emergence, and enhancement, using first principles methods. The focus is on CuFeSb, which has narrow Fe- d states and high

DOS at the Fermi level and becomes a ferromagnetic metal due to the Stoner instability. The chapter explains how an improvement in electron-phonon interactions leads to a five-fold enhancement in superconductivity for hcp-Zr under the Ag-tip. In contrast, insufficient electron-phonon interactions, protected Dirac points, and a large experimental transition temperature (T_c) suggest the possibility of topological superconductivity in ZrSiS under the Ag-tip.

Chapter 4 focuses on the origin of superconductivity in V (or electron) doped ZrB₂ using the Migdal-Eliashberg formalism. The chapter examines the electron-phonon interaction (λ) for different levels of charge and vanadium doping in ZrB₂. The study shows that with increasing doping concentration, the electron-phonon coupling (λ) enhances. However, the superconducting transition temperature remains one order of magnitude lower compared to the experimental transition temperature. Based on these findings, it is concluded that V (or electron) doped ZrB₂ is not a phonon-mediated superconductor.

Chapter 5 introduces a long-range anisotropic Heisenberg (XXZ) model, which offers a complete theoretical understanding of magnetism in two dimensions and can explain the available experimental data qualitatively and quantitatively. The chapter demonstrates that magnetic interactions beyond the first neighbour are of significant importance. After rigorously comparing the model with experimental data, it is predicted that the ferromagnetic Curie temperature in CrI₃ can be electrically tunable, and a remarkable five-fold increase can be achieved by ionic gating. The chapter also discusses the detailed microscopic mechanism and the effects of strain and chemical doping.

Chapter 6 explores the magnetic properties of monolayer CrBr₃ using the first-principles Heisenberg XXZ model that we have developed and discussed in Chapter 5. The study shows that the magnetic ordering can be dramatically manipulated up to room temperature through external modulation of exchange and anisotropic

magnetic interactions by gate-induced charge carrier doping. The nontrivial phase diagram triggered by the doping results in high-temperature ferromagnetism associated with a substantial increase in effective ferromagnetic exchange and overall magnetic anisotropy under experimentally attainable hole doping. The chapter concludes that the gate-tuneable room temperature ferromagnetism in CrX_3 presents new possibilities in electrically controlled spintronic and magnetoelectric devices based on atomically thin crystals.

Chapter 7 focuses on the study of a superconductor/ferromagnetic (SC/FM) van der Waals (vdW) heterostructure, which is perceived to be a cleaner system for investigating Majorana zero modes (MZMs). Specifically, we concentrate on the $\text{NbSe}_2/\text{CrI}_3$ heterostructure, utilizing first-principles calculations in combination with tight-binding and Bogoliubov-de Gennes Hamiltonians. It indicates that the Berry curvature present in NbSe_2 acts as an internal magnetic field, leading to spin splitting and spin-flip at the valley points K and K' . After incorporating spin-orbit coupling in our analysis, we observed that the in-plane Cr moment has no impact on the valley splitting, whereas the perpendicular Cr-spin plays a significant role and acts as a magnetic field. In the superconducting state, we noticed the appearance of six pairs of nodal points within the hexagonal Brillouin zone under an applied in-plane magnetic field. Moreover, a Majorana flat band arises on the armchair edge of the NbSe_2 nano-ribbon but vanishes on the zigzag edge. Based on our findings, we conclude that vdW SC/FM heterostructures hold great promise as a platform for exploring and realizing Majorana zero modes.

Chapter 8 serves as a summary of the thesis and offers a perspective on future research possibilities.

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Chapter 1

Introduction

1.1 Superconductivity

1.1.1 Experimental breakthrough

In 1911, Kammerligh Onnes observed a sudden drop in the d.c. resistance of mercury (Hg) at 4.2 K (1). The resistance of mercury has nearly vanished at the transition temperature (T_c) [Fig.1.1]. This phenomena in which some of the materials show nearly zero resistance at the critical temperature is known as Superconductivity, and these materials are called superconductors (2). At the transition temperature, a normal metallic state moves to a superconducting state through a second-order phase transition. In a normal metal, the electrical resistance is caused by electron scattering, produced by crystal impurities, crystal defects and thermal vibrations. However, in superconductors, two electrons form the Cooper pairs, creating a finite energy spectrum gap. Below the transition temperature, pairing energy becomes larger than the thermal vibrations, and the Cooper pairs are not scattered and create a macroscopic quantum state with precisely zero resistance. Another way to identify the superconductors by the Meissner effect (3; 4) in which a superconductor expels all magnetic field lines and shows perfect diamagnetism [see Fig.1.2].

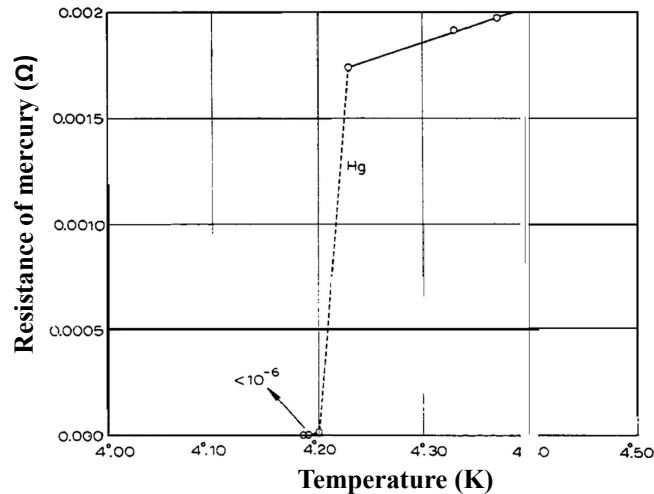


Figure 1.1: Groundbreaking unveiling of superconductivity: A graph showcasing the correlation between mercury (Hg) resistance (measured in Ohms) and temperature (measured in Kelvin). Figure reprinted from (5) by permission of IOP Publishing Ltd.

1.1.2 Theoretical discription: BCS theory

The milestone proposal of a microscopic theory of superconductivity by Bardeen, Cooper, and Shrieffer (BCS) in 1957 (6). Half a century after the discovery of superconductivity, BCS unveiled that electron attractions can lead to instabilities in the Fermi liquid state, forming correlated electron pairs known as Cooper pairs (7). Fröhlich's prior research had demonstrated the possibility of electron-electron attraction through virtual phonon exchange (8). This electron-phonon interaction frequently serves as the driving force behind pairing in various superconductors.

The BCS mechanism of superconductivity: The conduction electrons deform the crystal lattice, causing stabilization through electron-phonon interactions (6). The ionic lattice of a metal consists of positive ions immersed in a sea of conduction electrons. When a negative conduction electron moves through the array of positive ions, it slightly attracts the positive ions towards it [Fig.1.3(b)]. As a result, a region of excess positive charge is created behind the moving electron, attracting a

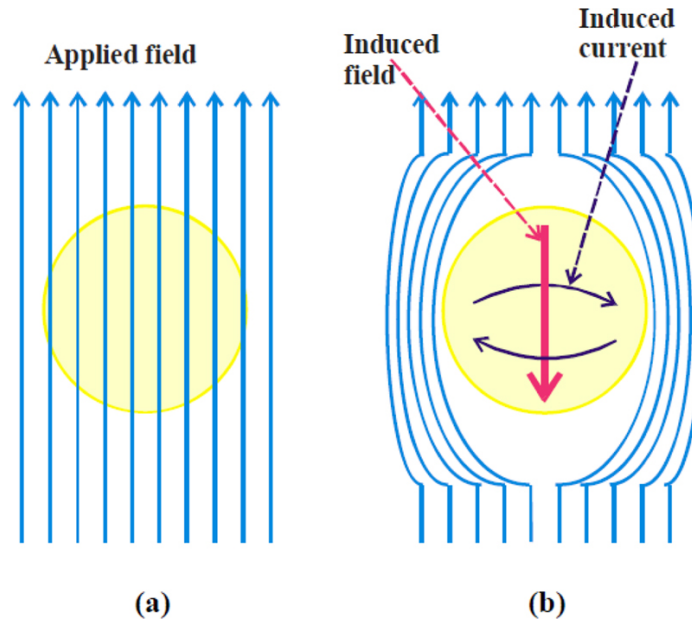


Figure 1.2: (a) Magnetic flux lines passing through the normal metallic material (b) The Meissner Effect, characterized by the expulsion of magnetic flux lines by a superconducting material. Figure reprinted from (5) by permission of IOP Publishing Ltd.

second passing electron. This leads to coupling the two electrons through virtual phonons of the ionic lattice (8).

The formation of a Cooper pair: In the BCS theory, a Cooper pair is composed of two electrons (spin singlets) with equal and opposite momentum and spin [see Fig. 1.3(a)]. Thus, its angular momentum is zero ($S = 0$), and it obeys the Bose-Einstein statistics, allowing all pairs to occupy a single quantum state. Breaking a Cooper pair requires an energy of $2\Delta_0$, where Δ_0 is the superconducting gap. The energy relation for the superconducting gap Δ_0 in BCS superconductors is $2\Delta_0 = 3.52k_B T_c$, and the value of Δ_0 decreases as the temperature of the material increases to its T_c value, eventually reaching zero (6; 7).

The BCS theory has remarkable success in explaining many of the basic features of superconductivity, but it has some significant limitations. Some of the drawbacks of the BCS theory include:

- 1. Limited applicability:** The BCS theory was originally developed to explain the superconductivity in conventional, low-temperature superconductors like aluminium and lead. However, it has limited applicability to high-temperature superconductors, which exhibit superconductivity at much higher temperatures than conventional superconductors.
- 2. Exclusion of electron-electron interactions:** The BCS theory focuses solely on the interaction between electrons and lattice vibrations and neglects other electron-electron interactions that may be important in some superconductors.
- 3. Works only for s-wave superconductivity:** The BCS theory can only explain s-wave superconductivity, where the wavefunction of the Cooper pairs is isotropic and spherically symmetrical (7). It cannot explain other types of superconductivity, such as p-wave or d-wave superconductivity, where the wave function has a more complex structure.
- 4. Fails to explain superconductivity in strong-electron-phonon coupling limit:** The BCS theory is based on the weak-coupling approximation, which assumes that the interaction between electrons and phonons is weak. However, many superconductors exhibit strong-coupling superconductivity, where the interaction between electrons and phonons is much stronger. The BCS theory cannot explain these materials.

Examples of superconductors exhibiting some limitations include high-temperature superconductors like $\text{YBa}_2\text{Cu}_3\text{O}_7$, which exhibit superconductivity ($T_c = 93 \text{ K}$) (9) at much higher temperatures than conventional superconductors and cannot be explained by the BCS theory. Another example is MgB_2 with $T_c = 39 \text{ K}$ (10), which is a multi-band superconductor that exhibits both weak-coupling and strong-coupling superconductivity and cannot be explained by the BCS theory alone (11–16).

In addition to the abovementioned reasons, various superconductors exist in which phonons do not mediate the pairing mechanism. One example is the cuprate-based

superconductors, where the CuO_2 layers are responsible for the superconducting state (17). Although the exact process that drives superconductivity in these materials is not fully understood, the pairing is believed to be primarily *d*-wave (18). It is currently recognized that a non-phonon process plays a crucial role in the occurrence of superconductivity in cuprate-based superconductors (19).

In conclusion, the BCS theory of superconductivity is a landmark theory that has provided great insight into the mechanism of superconductivity in conventional, low-temperature superconductors. However, it has several limitations and does not apply to all superconductors.

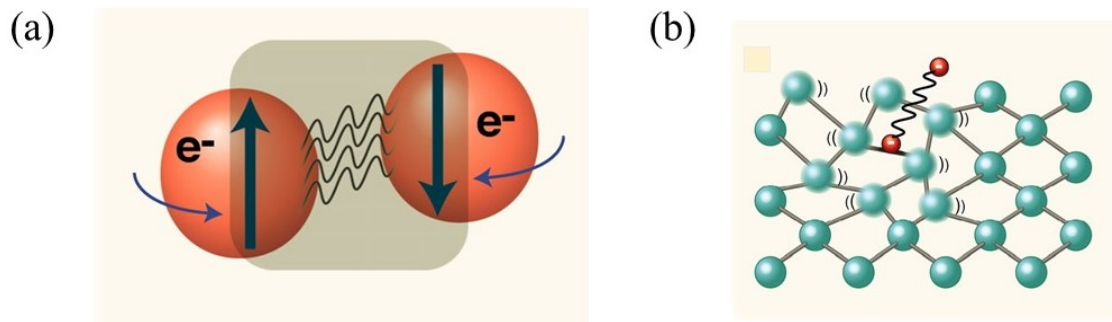


Figure 1.3: A schematic depiction of a Cooper pair and phonon mediated electron-electron interaction (a) A Cooper pair consisting of a spin-up and spin-down electron (represented by thick arrows) that combine to form a composite with a total spin of zero. In most superconductors, the average distance between the Cooper pairs is relatively large compared to their size. The wavy line represents the attraction between the electrons, which is mediated by lattice vibrations (phonons). (b) When an electron (represented by red circles) collides with the lattice (represented by green circles), it induces a vibration. The second electron is influenced by this vibration and therefore perceives the presence of the first electron, leading to an attractive interaction between the electrons. Figure reprinted from (20) by permission of AAAS.

1.1.3 Phonon-mediated superconductivity in high T_c materials

The Migdal-Eliashberg (ME) theory (21; 22) is utilized within a first-principles approach to evaluate critical characteristics of conventional superconducting materials, such as the strength of the electron-phonon interaction (λ), the size of the superconducting gap (Δ), and the superconducting transition temperature (T_c). It is considered the strong coupling extension of BCS theory. Migdal's theorem forms the basis of this theory, which asserts that vertex corrections can be disregarded when the electronic energy scale (D) greatly exceeds the phonon energy scale (ω_0). This condition remains valid even when the effective electron-phonon coupling constant (λ) greatly exceeds unity, as long as the product of (ω_0/D) and λ is much less than one. The Eliashberg spectral function ($\alpha^2F(\omega)$) is employed to accurately compute the strength of electron-phonon interactions (λ), while the Allen-Dynes-McMillan equation (23; 24) is utilized to determine the superconducting transition temperature (T_c). This approach treats the repulsive Coulomb interaction (μ^*) as a parameter. However, accurately predicting superconducting properties through fully *ab initio* methods is still difficult, so most studies rely on semi-empirical formulas like McMillan or Allen-Dynes (23; 24) to estimate the critical temperature.

After the development of the first principles theory of superconductivity based on ME formalism, several superconducting materials were investigated or proposed. The key role or ambition of *ab initio* theoretical calculation of electron-phonon physics and superconductivity to design new materials to host high temperature or room temperature superconductivity. After the discovery of superconductivity, many elemental materials were studied. Later, iron-based superconductors were discovered with higher transition temperatures than elemental ones. Then comes the cuprates materials, which raises the superconducting transition, starting with around 50 K and moving to near 150 K [see Fig.1.4].

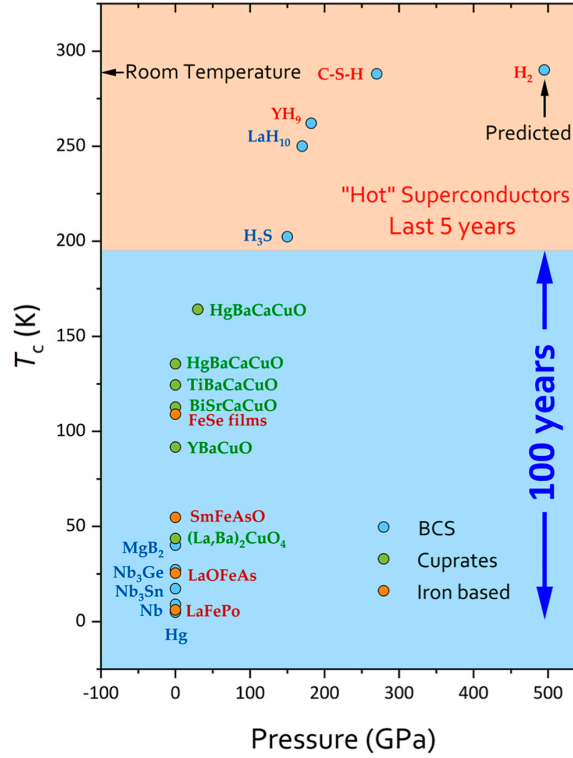


Figure 1.4: The plot shows the relationship between the superconducting T_c and pressure, with the use of high pressure techniques increasing the chances of discovering room temperature superconductivity (RTSC). The preservation of high T_c superconductivity under reduced pressure is indicated by three red labels and a corresponding red arrow. Figure reprinted from (25) by IOP Publishing Ltd under Open Access license.

A significant breakthrough in phonon-mediated superconductivity occurred with the discovery of superconductivity in MgB_2 at the transition temperature of $T_c = 39$ K (10). Subsequently, extensive experimental and theoretical investigations were conducted over the following decade, culminating in the current understanding that MgB_2 exhibits two-gap electron-phonon interactions and anisotropic properties, thereby establishing it as a superconductor of great interest (11–16). Theoretical calculations of the isotropic Eliashberg function $\alpha^2F(\omega)$ revealed two distinct peaks at different phonon frequencies (ω), resulting in two separate regions in the momentum-dependent electron-phonon coupling strength (λ_k) (16). These distinct contributions to the electron-phonon coupling are associated with the π

and σ sheets of the Fermi surface (13), reflecting the anisotropic distribution of electron-phonon interactions (16). An anisotropic solution to the Eliashberg equation was thus obtained, which yielded a two-gap structure (11; 16) corresponding to the π and σ bands, with both gaps closing at the transition temperature of $T_c = 50$ K (16), in agreement with experimental observations (15). However, the use of an isotropic Coulomb repulsion parameter (11), as well as the exclusion of anharmonic effects (26) and nonadiabatic corrections (27) in the *ab initio* calculations, may account for the discrepancy between the calculated and experimental transition temperatures.

1.1.4 Tip-induced superconductivity

Superconductivity can be induced by the carrier and elemental doping (28–33), applying pressure (34–39) to non-superconducting materials. Recently, another novel way to induce superconductivity was observed in which a superconducting phase appeared at the mesoscopic junction of Cd_3As_2 and sharp tips of metallic silver (Ag). This new superconducting phase is named tip-induced superconductivity (TISC). The emerged unconventional superconducting phase at a transition temperature (T_c) of 13 K with a 6.5 meV measured superconducting gap deviates from the conventional BCS model (40). Since the volume fraction of the superconducting phase in TISC is extremely small (contact diameter is around 100 nm) and appears only under a point contact, traditional techniques for detecting superconductivity, such as magnetization and transport measurements, are not effective (41). To establish the superconducting phase at the interface, measurements of transport properties are conducted in different contact regimes, which are described below (41):

Thermal regime: In this regime, the contact diameter (a) is larger than the inelastic mean free path ($a \gg l_{\text{in}}$). The total resistivity sharply increases near the super-

conducting transition temperature (T_c) in R vs T measurements. The dip in the differential conductance (dI/dV) vs applied bias voltage (V) plot confirms the superconducting transition.

Ballistic regime: In this regime, contact diameter a is very small, smaller than the elastic mean free path, but larger than the de-Broglie wavelength ($a_{\text{de-Broglie}} \ll a \ll l_e$). Electrons conduct without any scattering due to the small diameter. The presence of distinct Andreev double peaks, symmetric about the zero bias voltage, confirms the superconducting phase in this regime.

Intermediate regime: This contact regime is located between the thermal and ballistic regimes and is achieved by slowly withdrawing the tip from the thermal point contact. In this regime, both Andreev peaks and critical current dips appear simultaneously.

By systematically studying the evolution of spectra (dI/dV vs V) while considering different contact regimes and varying temperature and magnetic field conditions, it becomes possible to determine the precise nature of superconductivity and its underlying origin in the material. The newly discovered TISC phase is ideal for observing unconventional superconductivity when a Dirac metal or topological material is subjected to a metallic non-superconducting point contact. This confined superconducting phase is useful for observing topological superconductivity and Majorana fermions (42–44), which can host topological quantum computing. Additionally, using a non-superconducting Ag tip can enhance the transition temperature of phonon-mediated superconductors such as hcp-Zr (45). The TISC phase has recently been observed in various non-superconducting topological materials, such as $\text{Bi}_2\text{Te}_2\text{Se}$ and Bi_2Se_3 (46), as well as Dirac and Weyl semimetals including Cd_3As_2 (47), ZrSiS (48), TaAs_2 , NbAs_2 (49) and TaAs (50). Interestingly, this mesoscopic superconducting phase has also been discovered in topologically trivial materials such as doped silicon and hcp-Zr (45).

1.2 Magnetism

For centuries, people were perplexed by the enchanting attraction of lodestones to iron, and even more so by the remarkable capability of birds, fish, and insects to navigate over thousands of miles to reach their destination. Prior to the advancements in electromagnetism and quantum mechanics, it was difficult to fathom that these intriguing phenomena could be linked by a shared magnetic origin. Magnetism was first documented by the ancient Greeks, who also coined the term. The name is derived from Magnesia, a town and province in Asia Minor, with the word “magnet” having an etymological origin meaning “the stone from Magnesia”. This stone was composed of magnetite (Fe_3O_4), and it was discovered that rubbing a piece of iron with it would magnetize the iron. Magnetism is essentially founded on the movement of charges and spin of elementary particles, making it as widespread as the electron itself (51; 52).

The defining characteristic of magnetism is the presence of a structured pattern of magnetic moments across large distances, which is accompanied by a natural violation of time-reversal symmetry. This phenomenon is generally caused by the interplay between neighboring spins, known as exchange coupling, which tends to promote particular orientations between them. At temperatures of absolute zero, the orderly arrangement of magnetic moments can spread across vast distances. However, as the temperature rises, thermal fluctuations cause the misalignment of magnetic moments in adjacent regions, leading to the loss of long-range order above a critical temperature T_c . The occurrence of a phase transition at a finite temperature T_c depends on the efficacy of thermal fluctuations, which is determined by a few general parameters that are independent of the particular details of the system. The dimensionality of a system plays a crucial role in determining how thermal fluctuations affect the critical behavior of many-body systems (52–54).

Fig.1.5 illustrates the key theoretical and experimental advancements in the field of 2D magnetism. The timeline begins with Onsager's theory on 2D Ising magnet (55), and subsequent progress can be divided into three major areas. The first area involves quasi-2D magnetism observed in bulk materials, where interplanar interactions dominate and prevent long-range ordering in the third dimension (56; 57). The second area involves the identification of the first atomically thin

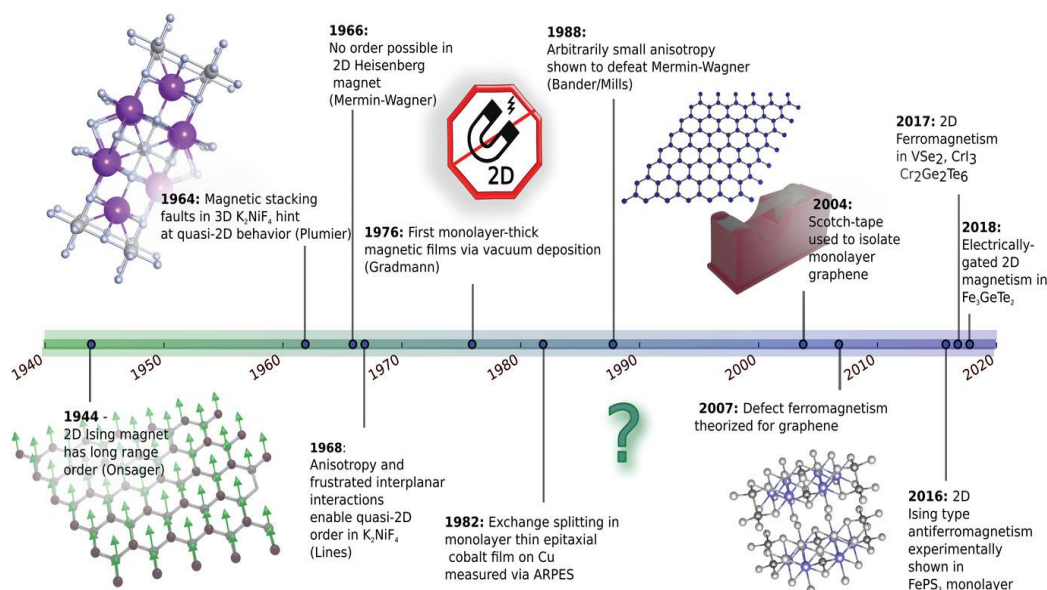


Figure 1.5: Starting from Onsager's breakthrough in 1944, this timeline highlights significant theoretical and experimental developments in the realm of 2D magnetism, ultimately leading up to the discovery of inherent 2D van der Waals (vdW) materials in 2016. Figure reprinted from (58) by permission of John Wiley and Sons.

film, which was used to test Onsager's 2D model (59) after several discoveries of thin film growth during the 1970s-1990s. The third and most recent area involves the observation of 2D magnets (60–62) following the discovery of graphene. This marks a significant advancement in the field and has led to the discovery of several other 2D magnets with unique properties. Fig.1.5 shows the Hohenberg-Mermin-Wagner theorem (63; 64) was major roadblock for the development of 2D mag-

netism. In the beginning, researchers experimented with several methods such as proximity effect (65; 66), defect modulation (67), and magnetic doping (68) in two-dimensional non-magnetic materials to achieve long-range ordering in these materials.

1.2.1 Two-dimensional magnetism: Experimental discovery

In 2016, monolayer FePS₃ (60) showed the anti-ferromagnetic ordering. After that, a long-range ferromagnetic ordering is observed in the bilayer of CrGeTe₃ and CrI₃ monolayer (61; 62). Since the discovery of Cr-based ferromagnets have been observed like CrBr₃, CrCl₃, VSe₂, VI₃ and Fe₃GeTe₂ (69–76). Monolayer CrI₃ has

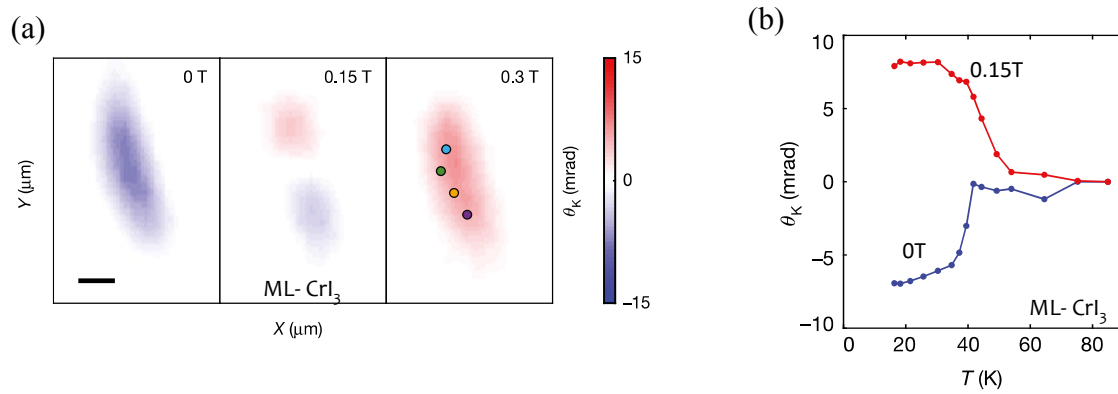


Figure 1.6: Monolayer CrI₃ investigated using MOKE measurements with varying magnetic field and temperature. (a) The Kerr rotation (θ_K) was measured with an applied magnetic field in the out-of-plane direction. (b) The Kerr rotation was plotted for a magnetic field of 0.15 T (in red) and without magnetic field (in blue) at varying temperatures. Figure reprinted from (62) by permission of Springer Nature.

hexagonal crystal structure in which the Cr³⁺ ions and I⁻ ions form the edge sharing octahedra. It shows magnetic transition (T_c) at 45 K slightly lower than T_c of bulk (61 K) (62). The polar magneto-optical Kerr effect (MOKE) experiments are performed to detect the magnetic ordering of CrI₃. A non-zero remanent Kerr ro-

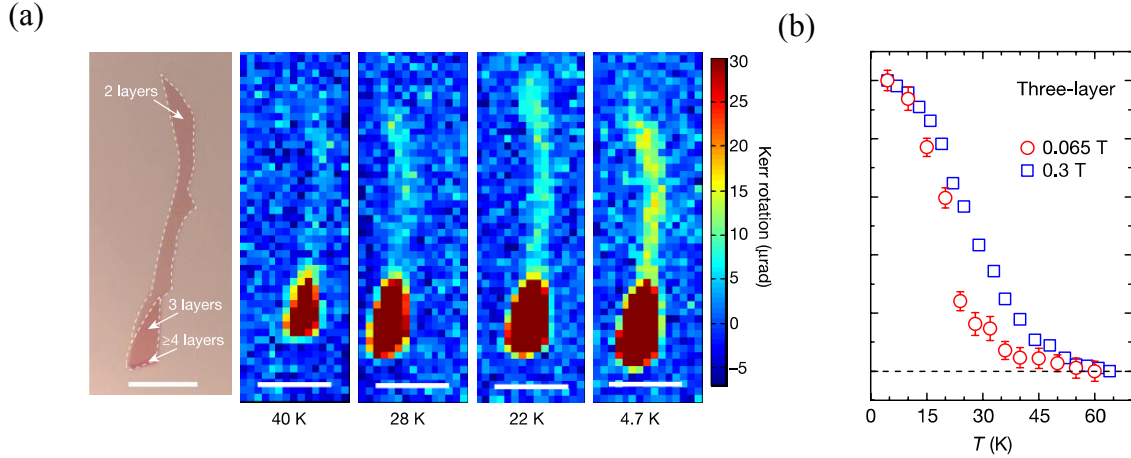


Figure 1.7: (a) The optical image shows the exfoliated $\text{Cr}_2\text{Ge}_3\text{Te}_6$ (in grey color). As the temperature is lowered from 40 K to 4.7 K, a Kerr rotation signal appears for the bilayer $\text{Cr}_2\text{Ge}_3\text{Te}_6$ under a magnetic field of 0.075 T (in blue color). (b) The Kerr rotation is plotted for two different magnetic fields with varying temperature. Figure reprinted from (61) by permission of Springer Nature.

tation in a single hysteresis loop centred around zero magnetic field ($\mu_0 H = 0$ T) indicates the existence of out-of-plane spin polarization. At zero magnetic field, all Cr spins point along the out-of-plane direction. As the field increases to 0.15 T, half of the Cr spin switches the direction. At 0.3 T, all the Cr spin aligns along the applied magnetic direction [see Fig. 1.6(a)]. The Kerr rotation is plotted as a function of temperature for zero field (blue) and 0.15 T (red), revealing the ordering temperature T_c of 45 K in the absence of a magnetic field. However, Fig. 1.6(b) shows that T_c is enhanced under an applied magnetic field (62). The Kerr rotation evolves as the temperature decreases from 40 K to 4.7 K in the bilayer CrGeTe_3 . At 40 K, there is nearly zero Kerr rotation, but it significantly enhances at 4.7 K. The same trend is observed for the trilayer at 4.7 K, confirming the magnetic ordering at this temperature for bilayer CrGeTe_3 under an applied magnetic field of 0.075 T. This small magnetic field stabilizes the magnetic moments [see Fig. 1.7(a)]. Furthermore, the ordering temperature also improves under an applied magnetic

field for the trilayer [see Fig. 1.7(b)] (61).

1.2.2 Hohenberg-Mermin-Wagner criteria

The Hohenberg-Mermin-Wagner theorem (63; 64) states that thermal fluctuations strongly inhibit the presence of long-range magnetic order in two-dimensional systems. These thermal fluctuations are associated with 'magnon' in a magnetic state. At a particular temperature, the 2D materials have more magnon density of states than bulk materials (61). To realize long-range order in 2D materials, thermal fluctuations must be counter-balance by magnetic anisotropy. This requires the breaking of spin-rotational symmetry. Three major mechanisms are 1. single-ion anisotropy, 2. exchange anisotropy and 3. dipolar interactions which break the spin-rotational invariance. In the infinite single-ion anisotropy, the Ising model

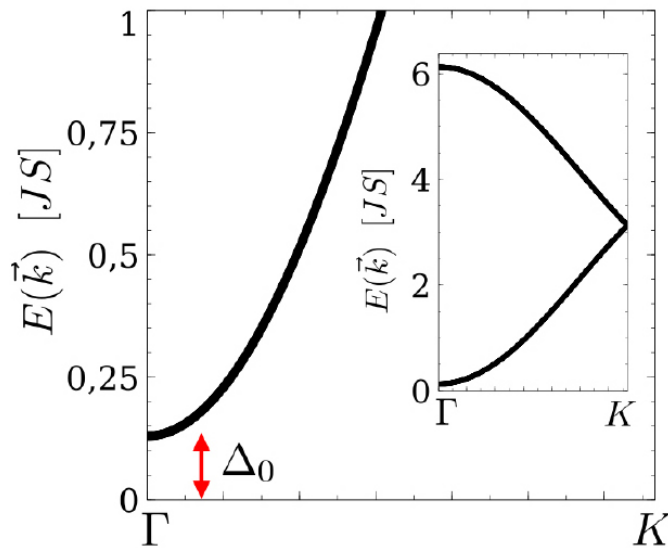


Figure 1.8: (a) An instance of the dispersion of spin waves is demonstrated, indicating a gap in the spin excitations. Figure reprinted from (77) by permission of IOP Publishing Ltd.

describes the magnetic states as explained by Onsager paper (55). Typically, very

large single-ion anisotropies arise due to the incomplete suppression of the orbital moment of the magnetic ion, which is only observed for particular oxidation states and crystal environments with low symmetry, such as surfaces (78) or rare earth atoms (79).

The magnetic anisotropy of a single ion arises due to the interaction between the spin-orbit coupling and the crystal field. For magnetic ions possessing a non-zero orbital moment, the magnetic anisotropy scales as $E_{MAE} \propto \lambda \langle L \rangle \cdot \langle S \rangle$, where λ is the spin-orbit coupling constant of the magnetic ion. However, in the event of a quenched orbital moment ($\langle L \rangle = 0$), the lowest order non-zero contribution to the magnetic anisotropy arises from quantum fluctuations of the orbital moment. It is proportional to $\frac{\lambda^2}{\Delta}$, where Δ is the energy separation between the ground state and the excited states of the ion due to the crystal field (77). Considering that $\lambda \approx 10$ meV for Cr ion (80) and Δ falls within the range of 500 meV, the energy associated with the single ion anisotropy is frequently much less than 1 meV. In the CrI₃ monolayer, single-ion anisotropy of Cr ion is related to distortion of edge shared Cr³⁺I₆[−] octahedra (77). Nevertheless, the anticipated anisotropy magnitude is low based on the small Kerr rotation and a spin reorientation field of less than 1 T (61; 62).

In addition to single-ion anisotropy, the magnetic ordering in CrX₃ (where X represents non-magnetic ligands) is also influenced by exchange anisotropy. It arises from the spin-orbit interactions of ligand atoms. In the super-exchange mechanism proposed by Anderson (81), magnetic interactions between magnetic ions happen via ligands. According to the Goodenough-Kanamori rules (82; 83), the magnetic ordering is determined by the filling of *d* levels and the cation-anion-cation angle φ . Ferromagnetic interactions reach their maximum when the angle φ equals $\angle 90^\circ$.

1.3 Interplay of Superconductivity and Magnetism

1.3.1 Van der Waals heterostructures

After the discovery of the two-dimensional (2D) material graphene (84), several other 2D atomic crystals have been identified, such as hexagonal boron nitride (hBN) (85), monolayers of metal dichalcogenides (86), and chromium trihalides (CrX_3) (61; 62). These 2D materials exhibit various properties, including metals, semiconductors, insulators, Dirac semi-metals, ferromagnetic insulators, and superconductors. It has been observed that the bilayer of these monolayers can exhibit properties that are entirely or slightly different from those of the monolayer.

Two layers of different 2D crystals are stacked together to study emergent properties, and the van der Waals (vdW) interaction acts between these layers. These materials are referred to as vdW heterostructures (87–89). These assembled materials form a complex quantum system. Their electronic states are exposed to different perturbations such as stacking, the relative angle of stacking, pressure and doping to different layers. Furthermore, the stacking of layers in vdW heterostructure enables a significantly more comprehensive range of combinations than conventionally achievable through traditional epitaxial methods. Thus, combining all these factors has resulted in a rapid increase in the complexity of atomic-layered stacks, leading to diverse research opportunities (87).

Atomic-layered stacks offer a potent approach to directly manipulate the distinct aspects or features of electrons in solids, such as the nature of quasiparticle wavefunctions or the Coulomb fields that a charged particle possesses [see Fig.1.9]. These electronic states are influenced by small feature sizes, which naturally formed, such as lateral feature size a and interlayer spacing or vdW distance d . Thus, tuning these lateral dimension a and interlayer spacing d strongly per-

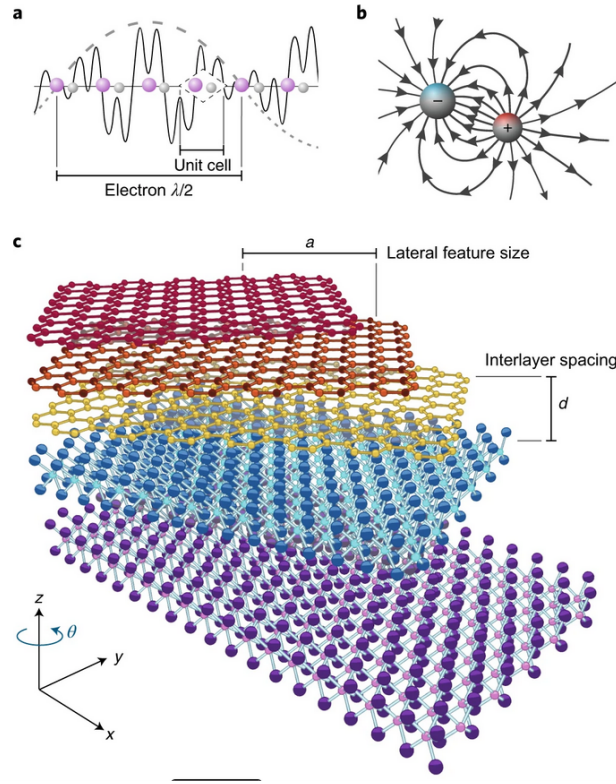


Figure 1.9: (a) This diagram presents a schematic representation of the electronic wavefunction, which serves as the fundamental unit of a crystal or crystal unit cell (depicted by a dashed blue line). It introduces a repetitive structure that alters the electron matter wave with a wavelength λ . (b) The schematic illustration of the electric field lines that represent the local Coulomb field surrounding an electron in close proximity to a positive charge. (c) The image depicts a vdW heterostructure quantum metamaterial, which is made up of individual 2D layers such as TMDs, graphene, and BN. The lateral feature size is denoted as " a ," the interlayer spacing as " d ," and the atomic-layer twist angle as θ . Figure reprinted from (87) by permission of Springer Nature.

turbed the electronic behaviour of the vdW heterostructure. A prime example of this phenomenon can be observed in a stack of van der Waals materials (as shown in Fig.1.9 c), where a slight twist in the orientation of layers can result in almost seamless adjustments to features on scales smaller than the electron wavelength. These adjustments may include atomic-scale registration changes depending on the twist angle and changes to wavelength-scale attributes such as the size of the superlattice unit cell (87).

By layering two atomic 2D layers, the periodic atomic structure within each layer combines, giving rise to a new spatial superlattice. As the Fermi energy passes through the secondary charge-neutrality points, this superlattice can exhibit ambipolar behaviour that can be adjusted to suit specific needs (90–92). The phenomenon of twisted bilayer graphene provides a striking example, where a diverse set of minibands materialize and change shape based on the twist angle (93–96). The resulting Bloch minibands can be interpreted as bands that are folded in at the edges of the superlattice Brillouin zone (94). This greatly enhances the original band structure, enabling regulation of the pattern of electron and hole filling. An impressive instance is the collection of secondary Dirac cones that arise due to the Moiré pattern present in graphene/hexagonal boron nitride stacks (97).

In recent years, several vdW heterostructures are investigated for diverse range of emerging properties such as topological superconductivity in NbSe₂/CrBr₃ (98), vdW spin-valve effect in CrI₃/graphene bilayer/CrI₃ (99), spin-valley coupling in WSe₂/CrI₃ (100), Magnon-valley Hall effect in HfS₂/CrI₃ (101).

1.3.2 Topological superconductivity in vdW heterostructure

In recent times, there has been a remarkable increase in interest in developing designer materials such as vdW heterostructures that exhibit electronic responses that are absent in naturally occurring materials. One of the primary objectives is to create topological superconductivity in these stacked layered materials. There is significant ongoing research into topological superconductors to induce and manipulate Majorana zero modes (102–105), which are crucial for achieving topological quantum information processing. Similar to topological insulator materials, the bulk is gapped in the topological superconducting state, whereas the edge has topological protected gapless states (107; 108). Several theoretical and experimental works are performed to observe topological superconductivity in order to re-

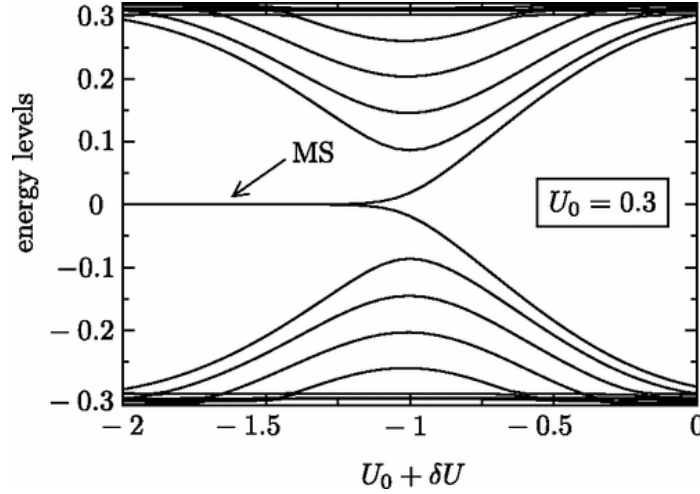


Figure 1.10: Appearance of Majorana states (MS) at the zero-energy in a BdG Hamiltonian model on a square lattice of a chiral superconductor. The emergence of MS under a defect potential $U_0 + \delta U$. Figure reprinted from (106) by permission of American Physical Society.

alize Majorana fermions (98; 109). A Majorana fermion is described as a particle which has its own antiparticle. In 1937, Ettore Majorana explained that the complex Dirac equation could be solved for a pair of real wave equations, each representing a real fermionic field without distinction of particle and antiparticle (110). These particles follow non-Abelian statistics (111–113). Majorana fermions are topologically protected in the topological superconducting state and cannot be influenced by any perturbations unless certain symmetries are broken, or the bulk energy gap is closed.

A recent study reported that Majorana fermions could exist with a system where the bulk is gapless (114). For example, Majorana flat bands [see Fig.1.10] can be found on the edges of two-dimensional nodal superconductors. The Majorana flat band at zero energy is also observed in NbSe₂ under an in-plane magnetic field (115). To realize Majorana flat band and topological superconductivity, vdW heterostructure is a better candidate as it has a high-quality interface. Recently, a topological superconducting state has been reported in NbSe₂/CrI₃ vdW het-

erostructure (98).

1.4 Goals of the thesis

Understanding the theoretical aspects of superconductivity is crucial for improving its transition temperature and comprehending the intricate pairing mechanisms involved. Over the years, numerous phonon-mediated superconductors such as Pb (116), MgB_2 (11; 16), and CaB_2 (117) have been studied based on the first-principles theory of superconductivity. The main goal in this field of research is to design materials with high T_c superconductivity under ambient conditions or at high pressures. Furthermore, it is important to use first-principles calculations to model tip-induced superconductivity and establish whether the emerged superconducting phase at the interface is conventional or unconventional. The first part of the thesis is devoted to this topic.

Two-dimensional magnetic materials exhibit promising potential to address not only the fundamental and emergent physics but also have promising potential for various technological applications, including spintronics, information processing and data storage. However, the technological applicability of most known two-dimensional magnets is limited since they operate at cryogenic temperatures. The thesis addressed a reasonable way to manipulate the microscopic magnetic interactions that can be manipulated externally, which in turn, significantly elevates magnetic ordering temperatures. Specifically, we consider the famous Cr-based trihalides as example cases to investigate the effects of chemical doping, strain and electrical gating.

Bringing two materials with different quantum states in close proximity can lead to the emergence of novel quantum states that cannot be found in either of the individual materials. This has opened up exciting opportunities for develop-

ing new types of quantum devices and technologies. One example of such emergent quantum states is the appearance of topological superconductivity. When a topological insulator is brought into contact with a superconductor, the superconductivity can induce a novel type of superconductivity called topological superconductivity. This can lead to the emergence of exotic excitations called Majorana fermions, which have been proposed as a promising platform for topological quantum computing (43; 44; 118; 119). Another example is the proximity effect between a ferromagnet and a superconductor, which can lead to the emergence of a superconducting spin-triplet state. This can result in the generation of long-range spin currents and spin accumulation, which have potential applications in spintronics and quantum computing (120; 121). This field of research generates renewed interest with the recent discovery of two-dimensional ferromagnets and atomically thin superconductors. This thesis outlines the possibility of emergent Majorana zero modes when a superconductor is placed in proximity to a magnetic insulator in vdW NbSe₂/CrI₃ heterostructures.

The upcoming chapter will delve into the necessary theoretical framework for modelling tip-induced superconductivity, two-dimensional magnetism, and topological superconductivity in various material scales. Chapter 3 will explain the absence, emergence, and enhancement of superconductivity in CuFeSb, ZrSiS, and hcp Zr, respectively, under an Ag tip. Chapter 4 will introduce the lack of phonon-mediated superconductivity in electron or V-doped ZrB₂. In Chapter 5, we will use an anisotropic Heisenberg model with long-range magnetic interactions to model 2D magnetism in CrI₃ and establish that its ordering temperature can be electrically tuneable. Chapter 6 will extend the XXZ anisotropic Heisenberg model to CrBr₃ and observe a room temperature ordering temperature under experimentally achievable hole doping. In Chapter 7, we will explain the appearance of Majorana zero-energy modes under an applied in-plane magnetic field. Lastly,

Chapter 8 will summarize this work and propose future aspects of this research.

Chapter 2

Computational Methods

This chapter briefly describes various theoretical frameworks that are adopted throughout the thesis. We begin with the many-body problem and density functional theory. Next, we discuss density functional perturbation theory and introduce the Wannier function. We also describe electron-phonon interaction within the Eliashberg-Migdal formalism to study superconductivity from the first principles. Ultimately, we conclude with an anisotropic Heisenberg Hamiltonian to investigate 2D magnetic materials.

2.1 Many-body problem

The quantum mechanical model in a condensed matter system comprises ion cores and itinerant valence electrons. However, the system's intricacy arises from numerous many-body interactions, and the overall Hamiltonian for the interacting system can be expressed as follows:

$$\mathcal{H} = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|}, \quad (2.1)$$

where $I(i)$ denotes an ion (electron), $M(m)$ stands for the mass of the ion (electron), and $\mathbf{R}(\mathbf{r})$ refers to the position of the ion (electron). The first two components of the Hamiltonian pertain to the kinetic energy of the ions and electrons, respectively. Meanwhile, the third and fourth constituents represent the Coulomb interaction energy for the interactions between ions and electrons. Finally, the electron-ion interaction is characterized by the last term. Relativistic corrections, including spin-orbit coupling, have not been taken into account. The solution to the above system is obtained through the Schrödinger equation,

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

The eigenvalue of the system is represented by E while the many-body wave function is denoted by ψ . However, due to the enormous quantity of quantum numbers, which amounts to approximately 10^{23} , finding an immediate solution is not feasible. Thus, it is essential to employ approximate methods.

The electrons are much lighter than the ions, including the nucleus ($M/m \sim 10^4$), resulting in a substantial difference in mass and kinetic energy. Consequently, the ions move more slowly than the electrons. The electrons can, therefore, respond

nearly instantly to any ionic motion. This separation of electronic and ionic degrees of freedom, known as the Born-Oppenheimer adiabatic approximation (122; 123), allows for the assumption that the electrons in a system experience an instantaneous potential created by the ions, which are assumed to have fixed spatial positions. As a result, the effective electronic Hamiltonian can be expressed as follows:

$$\mathcal{H} = \left[-\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{i,I} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + V_{\text{ion}}, \quad (2.2)$$

The above Hamiltonian consists of four terms. The first term describes the kinetic energy of the electrons; the second term represents the interaction between the electrons; the third term accounts for the attractive Coulomb interaction among the electrons and static ions, and the fourth term is the additive energy for the ion-ion interaction, calculated using the Born-Oppenheimer approximation. The electronic structure of the system is primarily determined by the electronic part of the Hamiltonian represented in Eq. 2.2. However, many-body electron-electron interactions necessitate further simplification using a mean-field approach.

Later, Hartree proposed that the many-body electronic wave function Φ can be expressed as a product of orthonormal one-electron wave functions φ to simplify the many-body electron-electron interactions (124).

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \varphi_1(\mathbf{r}_1) \varphi_k(\mathbf{r}_2) \dots \varphi_N(\mathbf{r}_N) \equiv \prod_k \varphi_k(\mathbf{r}_k). \quad (2.3)$$

This approach assumes that each electron moves in an average field created by the ions and all other electrons. Each one-electron wave function φ_k satisfies an independent Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \nabla_k^2 + V(\mathbf{r}) \right] \varphi_k(\mathbf{r}) + e^2 \sum_{j(\neq k)} \int \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \varphi_k(\mathbf{r}) = E_k \varphi_k(\mathbf{r}), \quad (2.4)$$

The resulting total energy can be calculated as follows,

$$E = \sum_k E_k - \frac{e^2}{2} \int \int \frac{\rho_k(\mathbf{r})\rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'.$$

The second term in the above equation represents the Hartree energy, which accounts for the doubly counted electron-electron interaction. Here, $\rho(\mathbf{r}) = |\varphi(\mathbf{r})|^2$ represents the electron density. In this approach, the Hartree equation is solved using a self-consistent approach, where the total energy is minimized with respect to the wave function or electron density. However, the Hartree wave function in Eq.(2.3) is incompatible with the Pauli principle since the fermionic wave function Φ must be antisymmetric and change sign when two particles are spatially interchanged. Furthermore, the Hartree approximation fails to incorporate exchange, correlation, and screening effects.

To resolve this inconsistency, the Hartree-Fock approximation assumes that the many-body wave function Φ is a single Slater determinant of N single-particle spin-orbitals φ , (125)

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(q_1) & \varphi_2(q_1) & \cdots & \varphi_N(q_1) \\ \varphi_1(q_2) & \varphi_2(q_2) & \cdots & \varphi_N(q_2) \\ \vdots & \vdots & \vdots & \vdots \\ \varphi_1(q_N) & \varphi_2(q_N) & \cdots & \varphi_N(q_N) \end{vmatrix}. \quad (2.5)$$

Here, the variable q represents electronic coordinates and spin, serving as a composite index. The Pauli exclusion principle can be effectively captured by utilizing this straightforward ansatz for the many-body wave function. The total energy is then computed using diverse orthonormal sets of φ . The resulting set of one-electron equations resemble those of single-particle Schrödinger equations, and the Hartree-Fock equation can be derived from this process, as outlined

in (126).

$$\left[-\frac{\hbar^2}{2m} \nabla_k^2 + V(\mathbf{r}) + e^2 \sum_j \int \frac{|\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \varphi_k(\mathbf{r}) - e^2 \sum_j \int \frac{\varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \varphi_j(\mathbf{r}) = E_k \varphi_k(\mathbf{r}). \quad (2.6)$$

The initial three terms within the equation resemble those found in the Hartree equation. However, an added exchange term arises due to considering the Pauli exclusion principle. This exchange interaction results in electrons of similar spins avoiding one another and being encompassed by an exchange hole. Although the Hartree-Fock approximation corresponds to the conventional view of electronic structure regarding single electrons, it fails to account for electron correlation by assuming the wave function is a single determinant. As a result, the Hartree-Fock theory is inadequate for making precise quantitative predictions, but it can provide qualitatively accurate results for a variety of materials.

2.2 Fundamentals of density functional theory

The computational cost of utilizing Slater determinant expansion-based methods to solve the many-body Schrödinger equation is enormous, which poses a significant challenge in addressing larger and more intricate problems. To tackle this, density functional theory (DFT) presents a promising alternative that converts the electron-electron interaction many-body problem into a single-body problem with no interaction. DFT is based on the Thomas-Fermi (TF) model of electronic structure (127; 128), which employs the electron density $n(\mathbf{r})$ as the primary variable instead of the wave function. The TF equation establishes a relationship between the ground-state electron density $n(\mathbf{r})$ and the external potential $V(\mathbf{r})$,

$$\frac{1}{2}(3\pi^2)^{2/3}n(\mathbf{r})^{2/3} + V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \mu = 0, \quad (2.7)$$

Here, μ is denoted as chemical potential. Despite its usefulness, the TF model has several limitations that hinder its ability to explain chemical bonding, primarily due to the crude approximation of kinetic energy. Additionally, the model relies on classical approximations of electron-electron interaction, neglecting crucial quantum phenomena such as exchange interaction.

DFT, a contemporary approach to describing quantum systems, adopts the TF model's utilization of the density $n(\mathbf{r})$ as the fundamental variable. The Hohenberg-Kohn theorem, a mathematically rigorous principle, affirms that the ground-state density $n(\mathbf{r})$ of an interacting electron system in an external potential $v(\mathbf{r})$ uniquely determines this potential. From the Schrödinger equation solution, the density $n(\mathbf{r})$ implicitly determines all properties derivable from the many-body Hamiltonian. The kinetic and interaction energies are functionals of density $n(\mathbf{r})$, and a universal functional $F[n(\mathbf{r})]$ is defined as,

$$F[n(\mathbf{r})] = \langle \Psi | T[n(\mathbf{r})] + U[n(\mathbf{r})] | \Psi \rangle, \quad (2.8)$$

Here, $|\Psi\rangle$ represent the ground-state wave function, and $T[n(\mathbf{r})]$ and $U[n(\mathbf{r})]$ refer to the kinetic and interaction energy functionals, respectively. The corresponding energy functional for a given external potential $v(\mathbf{r})$ is,

$$E_v[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]. \quad (2.9)$$

The Hohenberg-Kohn variational theorem (129) states that, for any trial density function $n_{tr}(\mathbf{r})$ satisfying the conditions $\int n_{tr}(\mathbf{r})d\mathbf{r} = N$ and $n_{tr}(\mathbf{r}) \geq 0$ for all $\mathbf{r}$, the inequality $E_0 \leq E_v[n_{tr}]$ holds. Here, $E_0 = E_v[n_0]$, where n_0 is the true ground-state electron density. However, the kinetic energy T is crudely approximated by the

earlier-described TF theory, which results in significant errors. The self-consistent Kohn-Sham approach can be used to address this limitation.

2.2.1 Kohn-Sham approach

The Kohn-Sham approach maps the interacting many-body system to a non-interacting system with the same density. In this approach, the non-interacting electrons experience a local effective external potential $V_{\text{eff}}(\mathbf{r})$ and are described by the Kohn-Sham equation, which is a single-particle equation given by,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad (2.10)$$

where ε_i are the initial energies of the corresponding Kohn-Sham orbital φ_i . The density of the N -particle system can be expressed as,

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2. \quad (2.11)$$

The total energy of the system is given by,

$$E[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \Delta T[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_X[n(\mathbf{r})] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}, \quad (2.12)$$

where $T_s[n(\mathbf{r})]$ is the kinetic energy of the non-interacting system, $\Delta T[n(\mathbf{r})]$ is the difference between the kinetic energy of the interacting and non-interacting systems, $E_H[n(\mathbf{r})]$ is the classical electrostatic energy of the system, $E_X[n(\mathbf{r})]$ is the exchange-correlation energy, and $v_{\text{ext}}(\mathbf{r})$ is the external potential acting on the system.

The ground-state kinetic energy is only approximated for non-interacting electrons, which leads to an incomplete description. The resulting discrepancy is denoted as ΔT and is the primary source of correlation energy. Additionally, the

electron-electron interaction energy is approximated using both Coulomb Hartree and quantum mechanical exchange energies, represented as E_H and E_X , respectively. Finally, the last term accounts for the interaction with the external potential. The expression for the non-interacting kinetic energy is given by,

$$T_s[n(\mathbf{r})] = \sum_{i=1}^n \int \varphi_i^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \varphi_i(\mathbf{r}) d\mathbf{r}, \quad (2.13)$$

The Hartree energy is defined as,

$$E_H[n] = \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}', \quad (2.14)$$

and the exchange-correlation energy is represented as $E_{XC}[n] = E_X[n] + \Delta T[n]$. To obtain the effective potential V_{eff} , the total energy is varied with respect to the KS orbitals,

$$V_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})}, \quad (2.15)$$

where the last term denotes the exchange-correlation potential. The error in the kinetic energy due to the approximation is $\Delta T[n]$, which is the origin of correlation energy.

The ground state energy corresponding to the system is given by,

$$E[n(\mathbf{r})] = \sum_i \varepsilon_i - \int v_{\text{ext}} n(\mathbf{r}) d\mathbf{r} + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int \frac{\delta E_{XC}[n]}{\delta n(\mathbf{r})} n(\mathbf{r}) d\mathbf{r}. \quad (2.16)$$

It is worth noting that in the absence of exchange-correlation, the Kohn-Sham equations reduce to the self-consistent Hartree equations.

2.2.2 Exchange-correlation functional

The Kohn-Sham equation gives the kinetic energy functional $T[n(\mathbf{r})]$, while the exchange-correlation functional $E_{XC}[n(\mathbf{r})]$ is unknown. The exchange-correlation energy can be written as,

$$E_{XC}[n(\mathbf{r})] = \Delta T[n(\mathbf{r})] + E_X[n(\mathbf{r})], \quad (2.17)$$

where $\Delta T[n(\mathbf{r})]$ represents the difference between the true and the auxiliary non-interacting systems' kinetic energies, and $E_X[n(\mathbf{r})]$ accounts for the electron-electron and Hartree energies. This exchange-correlation term is viewed as the "hole" that reduces the likelihood of finding an adjacent electron, incorporating the Pauli exclusion principle. However, it does not yet account for the self-interaction of an electron with its own density.

2.2.3 Local density approximation (LDA)

Hohenberg and Kohn demonstrated that if the electron density $n(\mathbf{r})$ varies slowly with $\mathbf{r}$, the exchange-correlation energy $E_{XC}[n]$ can be expressed as follows,

$$E_{XC}^{LDA}[n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{XC}^{LDA}[n(\mathbf{r})] d\mathbf{r}, \quad (2.18)$$

where $\varepsilon_{XC}^{LDA}[n]$ is the exchange plus correlation energy per electron in a homogeneous electron gas with electron density $n(\mathbf{r})$. The exchange part is given by $\varepsilon_X^{LDA}[n] = 3/4\pi(3\pi^2n)^{1/3}$. The correlation part can be obtained using representations by Perdew and Wang (130), Perdew and Zunger (131), or earlier ones by Hedin and Lundquist (132) and Wigner (133). The exchange-correlation potential

is obtained from the derivative of E_{XC}^{LDA} within LDA as follows,

$$v_{XC}^{LDA} = \frac{\delta E_{XC}^{LDA}}{\delta n} \quad (2.19)$$

$$= \varepsilon_{XC}[n(\mathbf{r})] + n(\mathbf{r}) \frac{\partial \varepsilon_{XC}[n(\mathbf{r})]}{\partial n}. \quad (2.20)$$

2.2.4 Generalized gradient approximation (GGA)

The generalized gradient approximation (GGA) function is based on the density and its gradient and is defined as:

$$E_{XC}^{GGA}[n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{XC}^{GGA}[n(\mathbf{r}), |\nabla n(\mathbf{r})|] d\mathbf{r}. \quad (2.21)$$

The GGA functions developed by Perdew and Wang (130) and Perdew, Burke, and Ernzerhof (PBE) (134) are commonly used. The exchange-correlation potential in Cartesian coordinates is given by:

$$v_{XC}^{GGA}[n(\mathbf{r})] = \left[\frac{\partial}{\partial n} - \sum_{i=1}^3 \nabla_i \frac{\partial}{\partial \nabla_i n} \right] n(\mathbf{r}) \varepsilon_{XC}^{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|), \quad (2.22)$$

which is dependent on the first and second radial derivatives of the density.

2.3 Density functional perturbation theory

Density Functional Perturbation Theory (DFPT) is a theoretical framework used to calculate the vibrational properties of materials. It extends the concepts of density functional theory (DFT) to include the response of the system to small perturbations, such as atomic displacements. DFPT enables the calculation of phonon frequencies and eigenvectors, as well as other related properties such as Born effective charges and infrared and Raman spectra.

The DFT calculations involve the computation of the total potential energy of

electrons and ions, represented by $U(\tau_{\kappa p})$, within the framework of the Born-von-Karman (BvK) supercell. This total energy corresponds to the ground state energy of the electrons, while the ions are considered classical particles that are fixed at the coordinates $\tau_{\kappa p}$. To calculate lattice vibrations (phonons), the total potential energy U is studied under the harmonic approximation. Expanding the total potential energy U to second order involves considering the energy contributions due to displacements $\Delta\tau_{\kappa\alpha p}$ of ions in the BvK supercell from the equilibrium positions $\tau_{\kappa p}^0$. This expansion is expressed as:

$$U = U_0 + \frac{1}{2} \sum_{\substack{\kappa\alpha p \\ \kappa'\alpha'p'}} \frac{\partial^2 U}{\partial \tau_{\kappa\alpha p} \partial \tau_{\kappa'\alpha'p'}} \Delta\tau_{\kappa\alpha p} \Delta\tau_{\kappa'\alpha'p'}, \quad (2.23)$$

Here, U_0 is the total energy of the system with ions at the equilibrium position. By taking the second derivatives of the total energy in Eq.(2.23) with respect to $\tau_{\kappa\alpha p}$, one obtains a matrix of force constants, expressed as:

$$C_{\kappa\alpha p, \kappa'\alpha'p'} = \partial^2 U / \partial \tau_{\kappa\alpha p} \partial \tau_{\kappa'\alpha'p'}. \quad (2.24)$$

By using Eq.(2.23) and Eq.(2.24), the Hamiltonian for ions, treated as quantum particles, is written as:

$$\hat{H}_p = \frac{1}{2} \sum_{\substack{\kappa\alpha p \\ \kappa'\alpha'p'}} C_{\kappa\alpha p, \kappa'\alpha'p'} \Delta\tau_{\kappa\alpha p} \Delta\tau_{\kappa'\alpha'p'} - \sum_{\kappa\alpha p} \frac{\hbar^2}{2M_\kappa} \frac{\partial^2}{\partial \tau_{\kappa\alpha p}^2}. \quad (2.25)$$

The Hamiltonian mentioned in Eq.(2.23) is based on two approximations: the first one is the harmonic approximation, which assumes that the potential energy surface can be approximated as a quadratic function around the equilibrium geometry. The second approximation is the Born-Oppenheimer adiabatic approximation, which assumes that the motion of the electrons and nuclei can be decoupled

and treated separately, as the nuclei are much heavier and slower than the electrons. Therefore, the Hamiltonian in Eq. (2.23) relies on the combined assumptions of the harmonic approximation and the Born-Oppenheimer adiabatic approximation (122; 123).

2.4 Wannier function

Wannier functions are a set of localized basis functions used to describe the electronic wavefunction of a solid in terms of its constituent atoms. They are named after the physicist Gregory Wannier, who developed the concept in the 1930s (135; 136). Wannier functions are constructed by projecting the Bloch states (periodic solutions of the Schrödinger equation in a crystal lattice) onto a set of maximally localized orbitals, which are then transformed into real-space wavefunctions. This provides a more intuitive and physically meaningful description of the electronic structure, as well as a more efficient basis set for calculations involving localized interactions, such as electron-phonon coupling or magnetic interactions. Wannier functions have numerous applications in condensed matter physics, including the calculation of topological invariants.

In the band theory of crystalline solids, the electronic ground state is represented in terms of extended Bloch functions $\psi_{nk}(r)$ for the electrons in n -th band with crystal momentum k . The effective crystal Hamiltonian commutes with the translational operation, the Bloch functions $\psi_{nk}(\mathbf{r})$ are expressed as,

$$\psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}. \quad (2.26)$$

In the above equation, u_{nk} is the periodic part of the Bloch wavefunction with a periodicity similar to the crystal Hamiltonian. The plain wave term $e^{i\mathbf{k}\cdot\mathbf{r}}$ delocalizes the electronic wavefunction and acts as an envelope function at different crys-

tal momentum values k . The Bloch orbitals $\psi_{nk}(\mathbf{r})$ span the reciprocal space and describe the delocalize electronic properties. In an alternate approach, localized orbitals can be formed by the unitary transformation of the Bloch orbitals. These orbitals are referred to as Wannier functions (135) and are constructed using the following expression,

$$w_0(\mathbf{r}) = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} \psi_{nk}(\mathbf{r}), \quad (2.27)$$

where V is the volume of the primitive unit cell and integration performed over the Brillouin zone (BZ), the Wannier function in Eq. 2.27 is located in the primitive unit cell. By multiplying a phase factor $e^{-i\mathbf{k}\cdot\mathbf{R}}$ into the integrand of Eq. 2.27, where $\mathbf{R}$ is a real-space lattice vector, we can define the Wannier function for band n in cell $\mathbf{R}$ as follows (135):

$$|\mathbf{R}_n\rangle = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k}\cdot\mathbf{R}} |\psi_{n\mathbf{k}}\rangle. \quad (2.28)$$

The Wannier functions are a set of functions that are orthonormal, meaning that their inner products with each other are zero. Additionally, if we have two Wannier functions located in the cell with lattice vectors $\mathbf{R}$ and $\mathbf{R}'$, they can be related to each other by the lattice vector $\mathbf{R} - \mathbf{R}'$. Using the Wannier functions, we can construct the Bloch function by taking the inverse Fourier transform of a Wannier function. The Bloch function is expressed as:

$$|\psi_{n\mathbf{k}}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\mathbf{R}_n\rangle. \quad (2.29)$$

The Eqs. 2.28 and 2.29 describe a unitary transformation that maps Bloch states to Wannier states, implying that both sets of states are equally valid in describing the band subspace. It should be noted that while the Wannier functions may not be eigenstates of the Hamiltonian, they still form a complete orthonormal basis in the

subspace.

The Wannier function for the multiple bands with eigenvalues $\epsilon_{n\mathbf{k}}$ and corresponding eigenstates $\psi_{n\mathbf{k}}$ is defined as,

$$w_{mp}(\mathbf{r}) = \frac{1}{\sqrt{N_p}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R}_p)} U_{nm\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r}). \quad (2.30)$$

To obtain localized Wannier orbitals from the corresponding band eigenstates, the Wannier function is optimized to be maximally localized. The degree of localization of the Wannier function can be quantified using its spread, which is given by,

$$\Omega = \sum_n [\langle 0n | r^2 | 0n \rangle - \langle 0n | r | 0n \rangle^2] = \sum_n [\langle r^2 \rangle_n - \langle r \rangle_n^2]. \quad (2.31)$$

The Wannier functions that are optimized to be maximally localized are commonly referred to as Maximally Localized Wannier Functions (MLWFs) (137), and can be obtained using software such as Wannier90 (138). These MLWFs are often used to evaluate electron-phonon matrix elements (139–141), which can be expressed as:

$$g_{mn\mathbf{k}\alpha}(\mathbf{R}_p, \mathbf{R}_{p'}) = \langle w_{m0}(\mathbf{r}) | \left. \frac{\partial V^{\text{KS}}}{\partial \tau_{\mathbf{k}\alpha}}(\mathbf{r} - \mathbf{R}_{p'}) \right| | w_{n0}(\mathbf{r} - \mathbf{R}_p) \rangle_{sc}, \quad (2.32)$$

where $g_{mn\mathbf{k}\alpha}(\mathbf{R}_p, \mathbf{R}_{p'})$ is the electron-phonon matrix element in the Wannier function representation with m and n as band indices and k and α as branch indices. These matrix elements are calculated by the integral over the Born-von Karman supercell, indicated by 'sc' in Equation 2.32. The Wannier functions $|w_{m0}(\mathbf{r})\rangle$ and $|w_{n0}(\mathbf{r} - \mathbf{R}_p)\rangle$ are centred in the unit cell at the origin of the reference frame and the centre of cell $\mathbf{R}_p$. The standard electron-phonon matrix element $g_{mn\gamma}(\mathbf{k}, \mathbf{q})$ is calculated by the Fourier transform of Equation 2.32. To achieve an accurate evaluation of electron-phonon interactions using the Wannier function method, the

matrix element $g_{mn\mathbf{k}\alpha}(\mathbf{R}_p, \mathbf{R}_{p'})$ should decay rapidly with distance $|\mathbf{R}_p|$ and $|\mathbf{R}_{p'}|$. This spatial decay is dictated by the localization of the electronic Wannier function (140; 141). The EPW code (142) utilizes this approach to compute the electron-phonon coupling strength in materials.

2.5 Migdal-Eliashberg theory

Migdal-Eliashberg theory is a theoretical framework used to describe the interaction between electrons and lattice vibrations (phonons) in materials. It is named after the physicists Arkady Migdal and Georgii Eliashberg, who developed the concept in the 1950s (21; 22). The theory extends the concepts of BCS theory, which describes the interaction between electrons in a superconductor, to include the effects of lattice vibrations. Migdal-Eliashberg theory enables calculating various properties of superconductors, such as the critical temperature and the energy gap, as well as other related properties, such as the temperature dependence of resistivity and specific heat.

The evaluation of the isotropic Eliashberg spectral function ($\alpha^2F(\omega)$) in the Migdal-Eliashberg theory is given by the following expression,

$$\alpha^2F(\omega) = \frac{1}{N(E_F)} \sum_{mn\gamma} \int \frac{d\mathbf{k}}{\Omega_{BZ}} \int \frac{d\mathbf{q}}{\Omega_{BZ}} |g_{mn\gamma}(\mathbf{k}, \mathbf{q})|^2 \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_F) \times \delta(\omega - \omega_{\mathbf{q}\gamma}). \quad (2.33)$$

The Eq.2.33 involves the electronic density of states (DOS) at the Fermi level, denoted by $N(E_F)$, and the electron-phonon matrix elements $g_{mn\gamma}(\mathbf{k}, \mathbf{q})$ with electronic band indices m, n , and phonon band index γ . The term $\sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{BZ}} \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_F)$ in the equation is known as the nesting function (ζ_q), which is a characteristic of the Fermi surface and thus originates purely from the electronic structure (142).

The isotropic Eliashberg spectral function $\alpha^2F(\omega)$ in Eq. 2.33 incorporates materials-specific parameters and is a positive quantity that is independent of temperature. This spectral function characterizes the rate at which an electron in state ψ_{nk} scatters into any electronic state at energy ε by emitting or absorbing a phonon of energy ε' (141). The computation of the isotropic electron-phonon coupling (λ) involves the integration of $\alpha^2F(\omega)$ using the following equation,

$$\lambda = 2 \int_0^\infty \frac{\alpha^2F(\omega)}{\omega} d\omega. \quad (2.34)$$

The calculation of the logarithmically-averaged phonon frequency ($\omega_{\log}$) is done using the following equation:

$$\omega_{\log} = \exp \left[\frac{2}{\lambda} \int_0^\infty \log \omega \frac{\alpha^2F(\omega)}{\omega} d\omega \right]. \quad (2.35)$$

With the aforementioned three equations, Eq. 2.33, Eq. 2.34 and Eq. 2.34, it is possible to calculate the superconducting transition temperature (T_c) using a semi-empirical formula called the Allen-Dynes-Macmillan equation (23; 24), which is expressed as follows:

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right]. \quad (2.36)$$

The equation presented above depends on the electron-phonon coupling λ , the logarithmic average of the phonon frequencies ($\omega_{\log}$), and the reduced Coulomb pseudo potential μ^* . The latter two terms can be calculated from first principles, and the value of μ^* is usually taken as a parameter that varies between 0.1-0.2 in different phonon-mediated superconductors.

The assumption made by the Migdal-Eliashberg theory is that the phonon energy scale ω_0 is significantly smaller than the electronic energy scale D , which

leads to the neglect of vertex corrections. The assumption remains valid even for stronger electron-phonon coupling λ , as long as $(\omega_0/D)\lambda \ll 1$. Therefore, it is intriguing to understand how superconductivity can arise from weak electron-phonon coupling when significant Coulomb repulsion is present. In this context, it was shown by Morel and Anderson that retardation effects play a crucial role in this phenomenon (143). Due to the difference in energy scales between electrons and phonons, the destructive effects of the Coulomb interaction on superconductivity can be significantly reduced. The Migdal-Eliashberg theory addresses this by introducing a strongly reduced Coulomb pseudo potential μ^* , given by,

$$\mu^* = \frac{\mu}{1 + \mu \log \left(\frac{D}{\omega_0} \right)}, \quad (2.37)$$

where $\mu = \rho_0 U$, U is a typical Coulomb interaction, ρ_0 is the density of states at the Fermi energy, D is half the band width, and $\omega_0 \ll D$. Even when μ is large, the value of μ^* can be small due to the logarithmic term in the denominator. The anisotropic Migdal-Eliashberg theory (21; 22), formulated using finite-temperature Green's functions, presents a field-theoretic approach to superconducting pairing and serves as a first-principles technique for computing the critical temperature of superconductivity. This theory was introduced by Migdal (21) in 1958 and further developed by Eliashberg (22) in 1960. The Migdal-Eliashberg theory involves the solution of two interdependent equations, namely,

$$\begin{aligned} \mathcal{Z}_{n\mathbf{k}}(i\omega_j) &= 1 + \frac{\pi k_B T}{N_F} \sum_{n'\mathbf{k}'j'} \frac{\omega_{j'}/\omega_j}{\sqrt{\hbar^2 \omega_{j'}^2 + \Delta_{n'\mathbf{k}'}^2(i\omega_{j'})}} \\ &\times \lambda_{n\mathbf{k},n'\mathbf{k}'}(i\omega_j - i\omega_{j'}) \delta(\varepsilon_{n'\mathbf{k}'} - \varepsilon_F). \end{aligned} \quad (2.38)$$

$$\begin{aligned} \mathcal{Z}_{n\mathbf{k}}(i\omega_j)\Delta_{n\mathbf{k}}(i\omega_j) &= \frac{\pi k_B T}{N_F} \sum_{n'\mathbf{k}'j'} \frac{\Delta_{n'\mathbf{k}'}(i\omega_{j'})}{\sqrt{\hbar^2 \omega_{j'}^2 + \Delta_{n'\mathbf{k}'}^2(i\omega_{j'})}} \\ &\times [\lambda_{n\mathbf{k},n'\mathbf{k}'}(i\omega_j - i\omega_{j'}) - N_F V_{n\mathbf{k},n'\mathbf{k}'}] \delta(\varepsilon_{n'\mathbf{k}'} - \varepsilon_F). \end{aligned} \quad (2.39)$$

Here, $\sum_{\mathbf{k}'}$ is evaluated by the integration of Brilluon zone, $\mathcal{Z}_{n\mathbf{k}}(i\omega_j)$ is the quasi-particle renormalization function and $\Delta_{n\mathbf{k}}(i\omega_j)$ is represented as superconducting gap functional. The anistropic Migdal-Eliashberg equation provide frequency dependent version of Eq.2.34, and expressed as:

$$\lambda_{n\mathbf{k},n'\mathbf{k}'}(i\omega_j) = \frac{N_F}{\hbar} \sum_v \frac{2\omega_{\mathbf{q}v}}{\omega_{\mathbf{q}v}^2 + \omega^2} |g_{nn'v}(\mathbf{k}, \mathbf{q})|^2. \quad (2.40)$$

The highest temperature that allows for a nontrivial solution, i.e., a solution where $\Delta_{n\mathbf{k}}(i\omega_j) \neq 0$, gives the superconducting critical temperature.

2.6 Spin Hamiltonian

The spin Hamiltonian is a mathematical model used to describe the magnetic behavior material. In the context of 2D materials, the spin Hamiltonian is a simplified model that mostly includes exchange interactions among the spins and anisotropy, which describes the dependence of the spin energy on its orientation relative to the crystal lattice. By solving the spin Hamiltonian, researchers can predict important properties such as the magnetic ordering temperature and the nature of magnetic excitations in 2D materials. The Ising and Heisenberg Hamiltonians are two common mathematical models used to describe the interactions between spins in magnetic materials.

The Ising Hamiltonian is a simple model that assumes the spins are fixed along one direction (for example, up or down). In contrast, the Heisenberg Hamiltonian is a more complex model that allows the spins to point in any direction in space.

The Heisenberg Hamiltonian is a powerful tool for understanding the behavior of spins in magnetic materials and has played a central role in the development of modern spintronics and magnetic data storage technologies.

The Ising spin Hamiltonian (144) treated spin as classical particles, is expressed as:

$$H_I = -J \sum_{i,j} s_i s_j - h \sum_i s_i, \quad (2.41)$$

where H_I is the Hamiltonian, J is the exchange interaction between nearest-neighbour spins, h is the strength of the external magnetic field, s_i and s_j are the spin variables at sites i and j , respectively. The summation is taken over all pairs of nearest-neighbour spins.

The anisotropic Heisenberg spin Hamiltonian is typically expressed as:

$$H_{xyz} = \sum_{i,j} \left[J_x s_i^x s_j^x + J_y s_i^y s_j^y + J_z s_i^z s_j^z + D_i (s_i^z)^2 \right] + \sum_{i,j} K_{ij} s_i^\alpha s_j^\beta, \quad (2.42)$$

Here H_{xyz} is the Hamiltonian, J_x , J_y , and J_z are the exchange coupling constants along the x , y , and z directions, respectively, s_i^x , s_i^y , and s_i^z are the x , y , and z components of the spin at site i , respectively, D_i is the single-ion anisotropy parameter at site i , K_{ij} is the Kitaev interaction constant between nearest-neighbor spins i and j , and s_i^α and s_j^β are the components of the spins at sites i and j , respectively, along the α and β directions. The summation is taken over all pairs of neighbouring spins.

Chapter 3

Absence, Emergence and Enhancement of Superconductivity

This chapter explores the superconducting property of three bulk materials (CuFeSb, ZrSiS, and hcp-Zr) at the confined interface under a sharp metallic tip. We explain the experimental observations using electronic structures, the density of states, and electron-phonon coupling. First, we studied CuFeSb, which is isostructural to iron-based superconductors such as LiFeAs and NaFeAs. It is a ferromagnetic metal with high transport spin polarization. We found that the Stoner instability occurs due to the narrow Fe- d states at the Fermi energy (E_F) and the very high density of states, causing CuFeSb to become a ferromagnetic metal. The calculated transport spin polarization is 46%, which agrees with the experiment. In another project, we investigated the emergence of superconductivity in the nodal-line semimetal ZrSiS. In this case, local superconductivity with a large transition temperature of 7.5 K was observed under the Ag-tip. While we observed a mild increase in the density of states and electron-phonon coupling due to the macroscopic tip, Migdal-Eliashberg theory predicts a T_c of 63 mK, which is orders of magnitude smaller than the experimental value. Therefore, the observed superconductivity may be unconventional and possibly topological since we observe protected Dirac points in ZrSiS/Ag-tip. However, further investigations are required to identify the mechanism. Lastly, we investigated the superconductivity

of hcp-Zr, which has a transition temperature of 0.51 K. We found that the local superconductivity increased several-fold under the Ag-tip due to a substantial increase in Zr density of states at E_F and increased electron-phonon coupling λ resulting from an order of magnitude increase in Fermi surface nesting. Within the Migdal-Eliashberg theory, the quantitative predictions of T_c are in excellent agreement with the experiment. The results from this chapter appeared in the following articles [Appl. Phys. Lett. 108, 242411 \(2016\)](#), [J. Phys. Condens. Matter 30 255002 \(2018\)](#) and [J. Phys. Condens. Matter 31 485707 \(2019\)](#).

The work presented in this chapter resulted from a long-standing collaboration led by Dr Goutam Sheet from IISER Mohali. We provided the necessary theoretical support to this collaboration in understanding tip-induced superconductivity, and this chapter only includes the theoretical investigation. On the experimental side, the collaboration involved colleagues from various institutes; Anshu Sirohi, Preetha Saha, Sirshendu Gayen, Abhishek Gaurav, Shubhra Jyotsna, Mohammad Aslam, Shekhar Das, Ritesh Kumar, Soumya Datta, Soumyadip Halder, Leena Aggarwal from IISER Mohali; Gohil S. Thakur, Zeba Haque, L. C. Gupta, Dr Ashok K. Ganguli from IIT Delhi; and Ratnadwip Singha, Arnab Pariari, Dr Prabhat Mandal from SINP Kolkata. Due to the theory-experiment nature of the present work, some of the results presented here may have appeared in the experimental thesis of Anshu Sirohi, Leena Aggarwal, and Mohammad Aslam, IISER Mohali.

3.1 Introduction

In Iron-based superconductors, spin fluctuations are an essential part of the pairing mechanism. The magnetic ground state and the spin-fluctuations of the parent compounds of iron-based chalcogenides and pnictide superconductors are key features to explain the coupling between spin-fluctuation and superconducting order (145–149). Most of the iron-based chalcogenides and pnictides, such as LiFeAs (150; 151), NaFeAs (152; 153), have anti-ferromagnetic ground state in the pristine form and moves to superconducting state due to charge doping. In these materials, the antiferromagnetism is supported by the spin-density waves, which is correlated with the Fermi surface nesting (154–157). In recent experiments, CuFeSb (158) and MgFeGe (159; 160), which are isostructural to 111 iron pnictides superconductors have shown ferromagnetism. This observation drew attention to the study of the degree of spin polarization, the origin of ferromagnetism and the spin-resolved Fermi surface of CuFeSb. We employ the First principle methods to explain the absence of superconductivity in CuFeSb and validate our experimental observation on the degree of spin-polarization. Our theoretical calculations explain the origin of the unique ferromagnetic ground state of CuFeSb.

In the next work, we have investigated the emerged superconducting phase at the interface of the Dirac semi-metal ZrSiS and metallic silver (Ag) tip. It has been conceived that topological superconductivity can be discovered by inducing superconductivity in non-trivial topological materials and possible realization of Majorana fermions (161–164). Several methods such as, chemical doping (31–33) and applying pressure (35–39) on the topological materials are proposed. This leads to the discovery of superconductivity in many topological materials using chemical doping in Cu-intercalated Bi₂Se₃ (32) and applying pressure on Bi₂Se₃ (36).

However, these techniques worked only on a few topological materials. Recently, a new method to induced superconductivity, called tip-induced superconductivity (TISC), is discovered where unconventional superconductivity is observed at the interface of topological materials (such as Dirac and Weyl semi-metals) and the metallic tip (40; 165). The observed TISC phase appears only under a point contact and provides better scope for observing topological superconductivity. In this work, we have observed an emerged superconducting phase at $T_c = 7.5$ K for the ZrSiS/Ag interface. To explain these results, we have evaluated the electronic structures, density of states and electron-phonon coupling for the pristine ZrSiS and its interface. We have established that emerged superconducting phase is not phonon-mediated due to insufficient electron-phonon coupling strength, whereas intact topological bands near the Fermi level hint towards the possibility of topological superconductivity at the ZrSiS/Ag interface.

In another project, we explain the enhancement of superconductivity in hcp-Zr under the Ag tip by evaluating the electron-phonon interactions within the Migdal-Eliashberg approximation. The tip-induced superconductivity (see the section) at the mesoscopic contact of two non-superconducting materials is essential to study the conventional and unconventional superconducting state (166; 167). This confined superconducting state either emerged or enhanced under the metallic tip (168; 169). In SrTiO₃/LaAlO₃ interface (170), two-dimensional electrons gas shows superconductivity at sub-Kelvin temperature. In contrast, the superconducting transition temperature (T_c) increases several folds at the point contacts on SrRuO₄ and FeSe (171–177). Several robust unconventional superconductivities is emerged by the point contact on the Dirac and the Weyl semi-metals (40; 165). Motivated by these observations, we have performed Andreev reflection spectroscopy for the hcp-Zr under metallic tip in thermal and intermediate point contact regimes. We have observed a five-fold enhancement in T_c at the interface.

To explain our experimental results, we have computed the electronic structure, phonon dispersion, Eliashberg spectral function and electron-phonon interactions for the hcp-Zr and hcp-Zr with Ag tip with the first-principles method. We have explained that the electron-phonon coupling has been improved under the Ag tip, which leads to the enhancement of T_c under the Ag tip.

3.2 Absence of superconductivity in CuFeSb

3.2.1 Experimental observation on CuFeSb

CuFeSb crystallizes in the tetragonal symmetry with space group P4/nmm [see Fig.3.1(a)]. The crystal structure is isostructural to other Fe-based superconductors. In this type of lattice, Sb and Fe organize as anti-PbO type layers, whereas Fe and Sb atoms form a distorted tetrahedral network. The interstitial sites of Sb layers are occupied by the Cu ions [see Fig.3.1(a)]. It is formed by the solid state reaction at high temperatures of the elements Cu, Fe and Sb. The lattice parameter of CuFeSb [$a = 3.9117(3)$ Å and $c = 6.2619(4)$ Å] is derived from the refinement. To establish the magnetic nature, the temperature-dependent magnetization experiment is performed for the 50-400 K temperature range. The ferromagnetic transition at $T_c \approx 376$ K is observed, which is consistent with a published value (158) [$T_c \approx 375$ K]. An ordered magnetic moment of $1.76 \mu_B$ at 2 K is close to the reported value (158).

To study spin-polarization in CuFeSb, the spin-resolved Andreev reflection spectroscopy experiment is performed. In this measurement, Andreev reflection spectra (dI/dV vs V) are observed for a ballistic point contact between a typical metal and a superconductor. In this type of contact, the Fermi-level becomes spin-polarized if the metal is a ferromagnet (156). This implies that the density of states of the up-spin channel ($N_\uparrow$) is not equal to the density of states of the down-spin chan-

nel ($N_{\downarrow}$) at the Fermi level. Therefore, these remaining electrons ($N_{\uparrow} - N_{\downarrow}$) do not show Andreev reflection as they do not get the accessible state in the opposite spin band. Therefore, Andreev reflection is suppressed in a point contact between a conventional superconductor and a ferromagnetic metal (178–180). The observed Andreev reflection spectra are analyzed by the BTK theory using four fitting parameters such as superconducting gap (Δ), intermediate spin-polarization P_t and two dimensionless parameters Z and Γ . The measured spin-polarization P_t is 47 %. This spin-polarization is measured using two conventional superconductors, Nb and Pb, as a point contact tip. The measured degree of spin-polarization remains unchanged under both the superconducting tip (181).

To explain the origin of the ferromagnetic ground state of CuFeSb and validate the spin-polarisation degree, we have performed *ab initio* calculations and calculated spin-resolved band structure and magnetic and non-magnetic density of states. We have also evaluated the transport spin-polarization for the ballistic contact regime, and a detailed discussion of these results will be provided in the next section.

3.2.2 Origin of ferromagnetic state in CuFeSb

The first-principles calculations were performed within spin-polarized density functional theory (DFT) (182; 183) using projector augmented wave formalism (184) with kinetic-energy cut-off of 370 eV for the wave functions. The exchange-correlation is described with Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (134) and the reciprocal space integration was carried out using $31 \times 31 \times 17$ Monkhorst-Pack k-point sampling. Atomic positions as well as the volume and shape of the unit cell were relaxed until the force components on each atom are less than 0.01 eV/Å. The structural parameters of the optimized tetragonal [$P4/nmm$, shown in Fig. 3.1(a)] CuFeSb are in excellent agreement with the current and previous (158) experimental measurements (Table 3.1). The CuFeSb crystal structure

Table 3.1: Refined structural parameters for CuFeSb obtained at 300K, which is below the ferromagnetic transition temperature. The number in the square bracket indicates the number of symmetric bond lengths. Calculated structural parameters within DFT-PBE formalism are in excellent agreement with the present and previous experimental measurements (158)

$P4/nmm$: $a = b = 3.9117(3) \text{ \AA}$, $c = 6.2619(4) \text{ \AA}$ 300K $a = b = 3.9347(2) \text{ \AA}$, $c = 6.2515(4) \text{ \AA}$ 400K Ref. (158) $a = b = 3.91 \text{ \AA}$, $c = 6.32 \text{ \AA}$ (DFT-PBE)						
		x	y	z	$B (\text{\AA}^2)$	Wyckoff positions
Atomic coordinates	Cu	0.25	0.25	0.7127(3)	1.68(6)	2c
	Fe	0.75	0.25	0	1.69(1)	2b
	Sb	0.25	0.25	0.2981(1)	1.19(4)	2c
		Bond lengths ($\text{\AA}$)			Sb-Fe-Sb angles ($^\circ$)	
	Fe-Sb [4]	Fe-Fe [4]	Cu-Sb [1]	Cu-Sb [4]	α	β
Experiment	2.704(1)	2.766(1)	2.596(3)	2.767(2)	92.68(2)	118.47(2)
Ref. (158)	2.693(1)	2.782(2)	2.660(3)	2.784(2)	93.86(5)	117.80(3)
DFT-PBE	2.72	2.77	2.69	2.77	91.98	118.86

is analogous to other iron pnictides and chalcogenides, though there are some striking differences from the superconducting ones (185). For example, while compared with the superconducting LiFeAs, (a) the Sb-Fe-Sb angles are substantially different than As-Fe-As angles, and (b) the Fe-Sb bond length is significantly larger (Table 3.1). Thus, the height of Sb (As) from the Fe plane is strikingly different for CuFeSb [$z_{\text{Sb}}=1.89 \text{ \AA}$ (DFT-PBE), and $1.87 \text{ \AA}$ (experiment)] and LiFeAs ($z_{\text{As}}=1.51 \text{ \AA}$), (185) and this z_{anion} is predicted to play an important role in determining the electronic structure (186). Although CuFeSb is isostructural to other iron pnictides and chalcogenides, the electronic and magnetic structures are

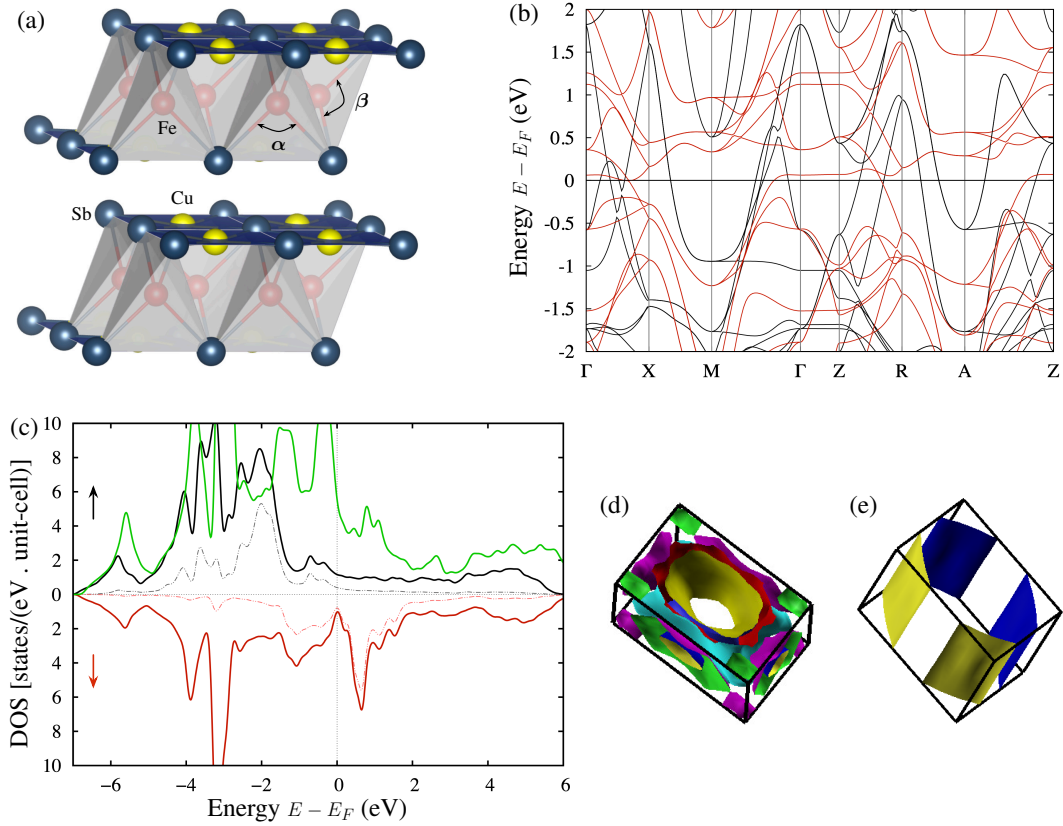


Figure 3.1: (a) Crystal structure of CuFeSb, which has tetragonal $P4/nmm$ symmetry. Different Sb–Fe–Sb angles, α , and β are indicated. (b) Calculated spin-polarized band structure within density functional theory indicates CuFeSb to be metallic. Bands corresponding to the up (down) channel is indicated in black (red) color. (c) The nonmagnetic (green line) and ferromagnetic DOS for CuFeSb. For nonmagnetic DOS, the conduction band is very narrow, which is entirely of Fe-*d* character, and the number of states at the Fermi level is very high, resulting in a ferromagnetic Fe-layer. The dashed lines for the spin-polarized DOS indicate the Fe-*d* character for up (black) and down (red) spin electrons. Spin-polarized Fermi surfaces are shown in (d) for up and (e) for down spin electrons. Figure reprinted from (181) by permission of AIP Publishing.

calculated to be completely different due to the profound difference in structural parameters discussed above. A large class of iron pnictides and chalcogenides are found to be antiferromagnetic and superconducting in ambient or pressured or chemically modified environments (187; 188). In remarkable contrast, we find CuFeSb to be a ferromagnetic metal. Calculated band structure and density of states (DOS) are shown in Fig. 3.1(b) and (c), which indicate CuFeSb to be metallic.

Present theoretical results are in good agreement with earlier magnetization and neutron scattering measurements, with 375 K transition temperature. (158) Calculated Fe moment ($m_{\text{Fe}} = 2.4 \mu_B$) is larger than the experimental moment ($1.85 \mu_B$) at 20 K, which further increases with decreasing temperature. (158) However, the calculated m_{Fe} is comparable to the earlier theoretical prediction for FeSeTe ($2.94 \mu_B$ with $z_{\text{Te}} = 1.81 \text{ \AA}$) (186). The nonmagnetic DOS in Fig. 3.1(c) reveals that the conduction electrons at the Fermi level are of Fe- d character and belong to a narrow band with a large density of states, and due to this Stoner instability, the Fe layer becomes ferromagnetic. It would be interesting to compare the DOS at the Fermi level $N(E_F)$ for CuFeSb, which is a metallic ferromagnet, with the superconducting counterparts. The nonmagnetic $N(E_F)$ is found to be 5.6 eV^{-1} per unit cell for CuFeSb [Fig. 3.1(c)], which is significantly larger than superconducting LiFeAs (4.5 eV^{-1}), and other Fe-based superconductors (189–191). In contrast, $N(E_F)$ is comparable to MgFeAs, which is isoelectronic to LiFeAs but non-superconducting similar to CuFeSb (192). The large number of states at the Fermi level and in the vicinity is conventionally connected to the number of condensed Cooper pairs, which enhance superconductivity. However, for CuFeSb, the narrow d band near the Fermi level and very high $N(E_F)$, the magnetic Stoner instability takes over, and the Fe-layer becomes ferromagnetic. This is similar to the case in ferromagnetic MgFeAs (192).

Next, we calculate the transport spin polarization P_t , which is in excellent agreement with the present spin-resolved Andreev reflection spectroscopy measurement. Within classical Bloch-Boltzmann transport theory, P_t can be defined in terms of spin-dependent current densities, and in general, (193)

$$P_t^n = \frac{\langle N(E_F) v_F^n \rangle_{\uparrow} - \langle N(E_F) v_F^n \rangle_{\downarrow}}{\langle N(E_F) v_F^n \rangle_{\uparrow} + \langle N(E_F) v_F^n \rangle_{\downarrow}},$$

where v_F is the spin-polarized Fermi velocity of electrons, thus by definition, P_t^n is connected to the spin polarization measured in various experiments, spin-resolved photoemission ($n = 0$) and point-contact spectroscopy in ballistic ($n = 1$) and diffusive ($n = 2$) regimes. In the present experimental setup, P_t has been measured in the ballistic regime. We calculated the spin-polarized DOS, which is shown in Fig. 3.1(c), along with the spin-polarized Fermi surface [Fig. 3.1(d) and (e)]. Similar to the non-magnetic case, the conduction electrons at the Fermi level have Fe- d character. Further, $N_\uparrow(E_F)$ is found to be 12.6% larger than $N_\downarrow(E_F)$ for ferromagnetic CuFeSb. In addition to this imbalance in $N_\sigma(E_F)$, the average Fermi velocity $\langle v_F \rangle_\sigma$ contributes to P_t in the ballistic regime. We find $\langle v_F \rangle_\uparrow > \langle v_F \rangle_\downarrow$, and the calculated average Fermi velocity for the up and down channel is 6.44×10^5 and 2.68×10^5 m/s, respectively. These results in a transport spin polarization, $P_t = 46\%$, which is in excellent agreement with the present Andreev reflection spectroscopy measurement.

3.3 Emergence of superconductivity in the semi-metal ZrSiS

3.3.1 Appearance of superconductivity

ZrSiS with P4/nmm tetragonal crystal structure is a Dirac semi-metal. It exhibits multiple Dirac points near the Fermi level (194). It has a robust and unusually very high linear dispersion up to the energy of 2 eV, which is rare to observe in other topological materials (195–197). Due to very high linear dispersion, electronic features of ZrSiS remain insensitive to external perturbations like lattice distortion or carrier doping. In this work, we observe a novel and emerging tip-induced superconducting phase at T_c of 7.5 K and the superconducting gap ($\Delta(T = 0)$) ≈ 1 meV

(48). The non-existence of 'zero-resistivity' is not a hallmark of superconductivity at the confined point contact region. In the ZrSiS/Ag interface, the disappearance of the Andreev peak in the Andreev reflection spectroscopy measurement in the thermal regime of transport confirms the superconducting transition at T_c of 7.5 K (48). As the superconductivity emerged in the non-trivial topological semi-metal ZrSiS, it is essential to understand the nature and origin of this superconducting state. We have calculated electronic band structures, the density of states and electron-phonon coupling for the pristine ZrSiS and its interface with metallic Ag tip. We have discussed these results in detail in the next section.

3.3.2 Possible topological superconductivity in ZrSiS

To gain a microscopic understanding of the observed superconductivity, we have carried out first-principles calculations to investigate the electronic structure and electron-phonon coupling in ZrSiS under a mesoscopic metallic tip. Our first-principles calculations are based on density functional theory within the projector augmented wave formalism (182–184). The wave functions were expanded in the plane wave basis with 400 eV cutoff. The structures were fully optimized using $31 \times 31 \times 19$ Monkhorst-Pack (198) k -grid to sample the Brillouin zone. The Perdew-Burke-Ernzerhof functional form of generalized gradient approximation was used to describe the exchange-correlation energy (134). Calculated lattice parameters for bulk $P4/nmm$ ZrSiS (Fig. 3.2(a), $a = 3.55$ and $c = 8.14$ Å) are in excellent agreement with the experimental results (195). The electronic structure of bulk ZrSiS hosts several Dirac cones along ΓX , $M\Gamma$ and AZ lines [Fig. 3.2(b)]. Further, Dirac-like crossings are observed below the Fermi level at the X and R points [Fig. 3.2(b)], which are protected by non-symmorphic symmetry of the ZrSiS crystal (195) and are unaffected by the inclusion of spin-orbit coupling in the calculation (see Fig. 3.4). Note that the Dirac cones along the ΓX , $M\Gamma$ and AZ define

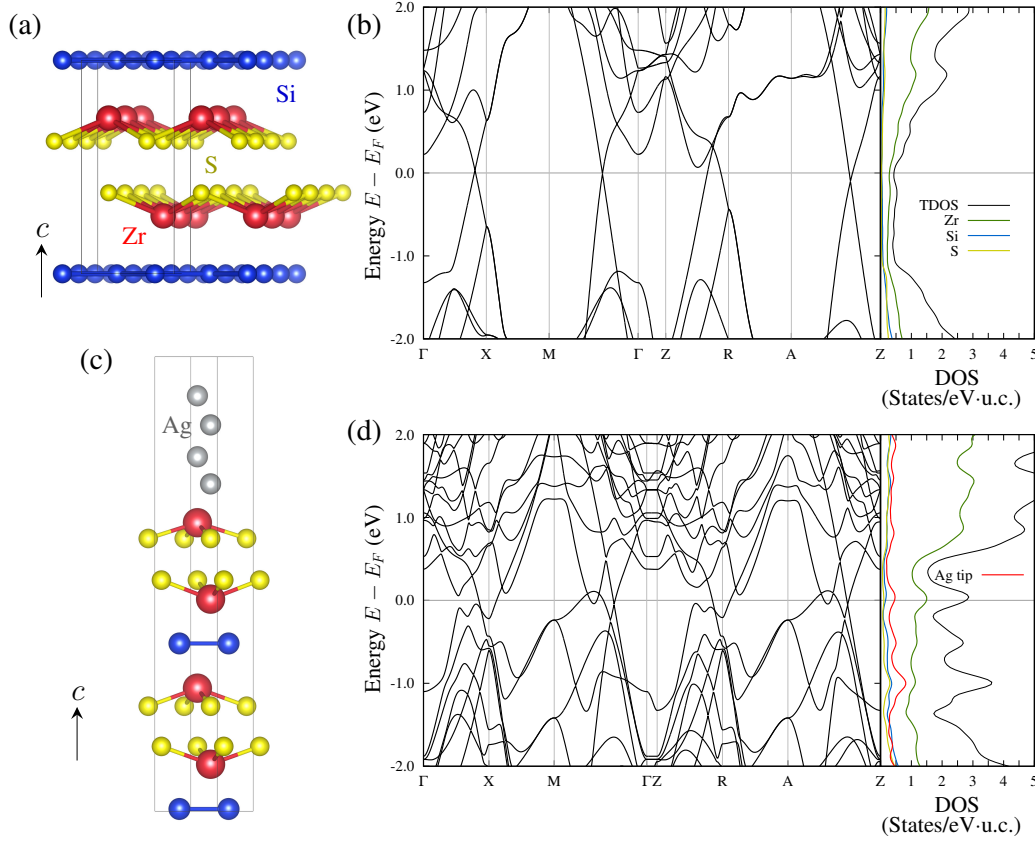


Figure 3.2: The crystal lattice and band structure of ZrSiS without and with Ag-tip. (a) ZrSiS crystallizes in a tetragonal $P4/nmm$ structure. The Zr and S layers are sandwiched between the Si square nets in a fashion that the two neighbouring S layers are between the Zr layers. Calculated lattice parameters are in excellent agreement with experimental data. (b) Calculated band structure of ZrSiS without spin-orbit coupling showing Dirac cones along ΓX , $M\Gamma$ and AZ lines of the Brillouin zone. The corresponding DOS indicate Zr- d character around the Fermi level. (c) The $1 \times 1 \times 3$ [ZrSiS]₄Ag₄ superlattice to investigate the effect of Ag-tip. (d) The superlattice band structure shows Dirac cones along the $M\Gamma$ and AZ lines. The resulting DOS at the E_F show a substantial increase. Figure reprinted from (48) by permission of IOP Publishing Ltd.

ZrSiS as nodal line semimetal, while the Dirac points ~ 0.5 eV below the Fermi energy at X and R points are different. However, due to the C_{2v} symmetry lines, the Dirac cones at the Fermi level open up a small gap ~ 35 meV, while the spin-orbit coupling is considered (see Fig. 3.4). The density of states (DOS) is found to be 0.86 states/eV·unit-cell at E_F , which is dominated by Zr- d character. To investigate the effects of metallic Ag point contacts on the electronic structure of ZrSiS, we have

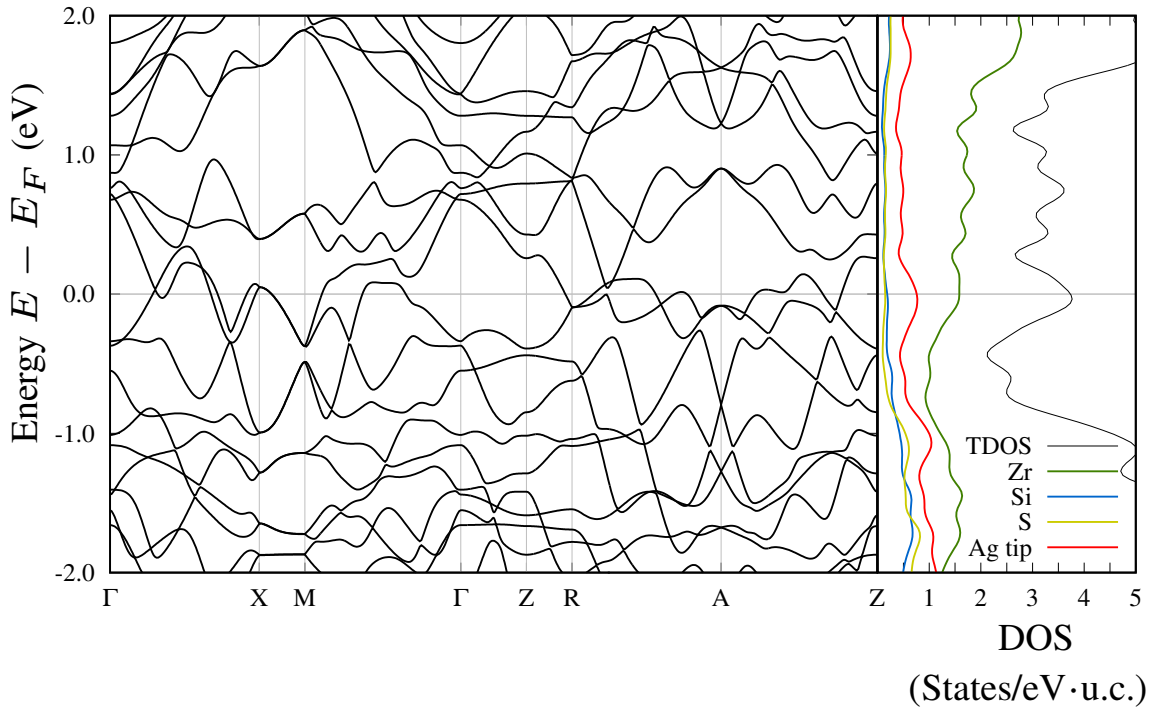


Figure 3.3: Calculated band structure for the $3 \times 1 \times 1$ $[\text{ZrSiS}]_4\text{Ag}_6$ superlattice indicating destruction of all the Dirac points. Figure reprinted from (48) by permission of IOP Publishing Ltd.

considered $1 \times 1 \times 3$ $[\text{ZrSiS}]_4\text{Ag}_4$ (shown in Fig. 3.2(c)) and $3 \times 1 \times 1$ $[\text{ZrSiS}]_4\text{Ag}_6$ superlattice (see Fig. 3.3). The Ag-tip substantially perturbs the band structure of ZrSiS, and for both cases, we observe an enormous increase in total density of states (TDOS) at the E_F , 2.77 and 3.73 states/eV·unit-cell, respectively [see TDOS plots in Figs. 3.2 (d) and 3.3]. The increase in low-energy electrons at the Fermi energy increases the possibility of Cooper pairing, which is reflected in an increase in transition temperature according to the conventional phonon-mediated BCS theory (6). When ZrSiS was placed under the Ag tip, the DOS of Zr d states was enhanced at and around the Fermi level in both cases [see DOS plot of Zr d states in Figs. 3.2 (d) and 3.3]. In contrast, the contribution of Ag in terms of density of states at and around the Fermi level is considerably small [see DOS plot of Ag tip (in red colour) in Figs. 3.2 (d) and 3.3]. Thus, it can be surmised that a substantial increase

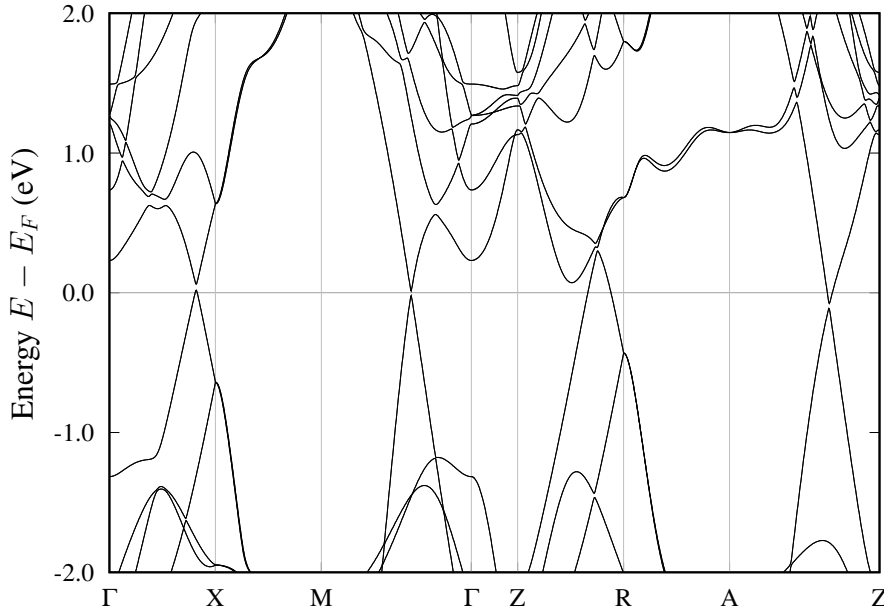


Figure 3.4: Calculated band structure of ZrSiS including spin-orbit coupling, which opens up a small gap of $\sim 35\text{meV}$ for the Dirac cones near the Fermi surface. Figure reprinted from (48) by permission of IOP Publishing Ltd.

in the carrier density around the E_F has an explicit role in observed tip-induced superconductivity in ZrSiS. Further, to investigate the microscopic mechanism of the observed superconductivity, using the EPW code,(199) we calculate the electron-phonon coupling λ , which is also positively correlated with the DOS at the Fermi energy. λ is calculated using the Eliashberg spectral function $\alpha F(\omega)$, and is used to evaluate the logarithmic average of phonon frequencies $\omega_{\ln}$.(200; 201) The calculated λ increases from 0.15 in bulk ZrSiS to 0.29 for the $1 \times 1 \times 3$ $[\text{ZrSiS}]_4\text{Ag}_4$ under the microscopic Ag-tip. However, assuming the Coulomb repulsion μ^* of 0.1, the corresponding transition temperature calculated using the Allen-Dynes modified McMillan formula (23; 24) is only 63 mK, which is two orders of magnitude smaller than the experimental T_c of 7.5 K. Thus, we argue that the observed superconductivity does not arise from the conventional phonon mediated cooper pairing. It is important to note that while the Dirac cone along the ΓX disappears due to Ag-tip insertion for $[\text{ZrSiS}]_4\text{Ag}_4$ superstructure, the Dirac cones along the $\text{M}\Gamma$ and AZ

lines are found to be protected along with the appearance of extra nesting feature (Fig. 3.2(d)). This observation hints to the co-existence of the topological character of ZrSiS along with tip-induced superconductivity, thereby opening a strong possibility of topological superconductivity at ZrSiS/Ag point contact interfaces.

3.4 Enhancement of superconductivity in the elemental Zr

3.4.1 Tip-induced superconductivity in hcp-Zr

The elemental bulk Zr has an hcp crystal structure. In pristine form, the bulk Zr shows a superconducting transition around 0.57 K (202; 203). To study the influence of metallic tips, this elemental superconductor is placed under a point contact of Ag and Pt. In the thermal contact regime, the Andreev reflection spectra (dI/dV Vs V) provide the superconducting transition temperature of around 3 K for Zr/Ag and Zr/Pt interface. The estimated superconducting gap (Δ) is about 0.51 meV evaluated by the BTK theory for the spectra observed in ballistic contact regime (45).

To understand the five-fold enhancement of T_c , we have performed first principle calculations for the pristine Zr and its interface with the Ag tip. The point contact geometry is modelled using the superlattice model. We have evaluated the electronic structures, phonon-dispersion spectrum, the Eliashberg spectral function and electron-phonon coupling for the elemental Zr and Zr/Ag interface. A detailed discussion of the theoretical results is provided in the next section.

3.4.2 Electron-phonon interaction under Ag tip

To understand the microscopic origin for the giant enhancement in superconducting temperature under mesoscopic point contact on Zr, we have conducted first principles-based calculations. Electronic structure calculations were performed within norm-conserving Troullier-Martins pseudopotential scheme (204) and local-density approximation (131; 205) implemented in QUANTUM ESPRESSO code (206). The Kohn-Sham wave functions and charge density were expanded in the plane wave basis with energy cutoffs of 60 and 240 Ry. Structures were fully relaxed until the forces on each atom were smaller than 10^{-4} Ry/Å using $12 \times 12 \times 8$ Monkhorst-Pack k -mesh (198) with 0.02 Ry Methfessel-Paxton smearing for electronic state occupancy. (207) Highly dense k -point grid of $60 \times 60 \times 60$ was used to calculate Fermi surfaces. Dynamical matrices are calculated on a $6 \times 6 \times 4$ q -mesh in the Brillouin zone using density functional perturbation theory (DFPT). (208) Further, the electron-phonon ($e - p$) coupling was calculated using the electron-phonon Wannier method (140) as implemented in the EPW code (199). Maximally localized Wannier functions are constructed on a $6 \times 6 \times 4$ k -mesh using Wannier90 code (137; 209; 210). Finally, fine electron $24 \times 24 \times 16$ k -grid and phonon $24 \times 24 \times 16$ q -grids with phonon smearing 0.3 meV were used to calculate Eliashberg spectral function.

Phonon mediated superconductivity is well described by Migdal-Eliashberg theory and the corresponding T_c is well approximated by the Allen-Dynes modified McMillan formula, (23; 24)

$$T_c = \frac{\omega_{\ln}}{1.2} \left[\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right], \quad (3.1)$$

where $\omega_{\ln}$ is the logarithmic average of phonon frequencies, λ is the $e - p$ coupling constant and μ^* is Coulomb pseudopotential. (143) The Eliashberg spectral

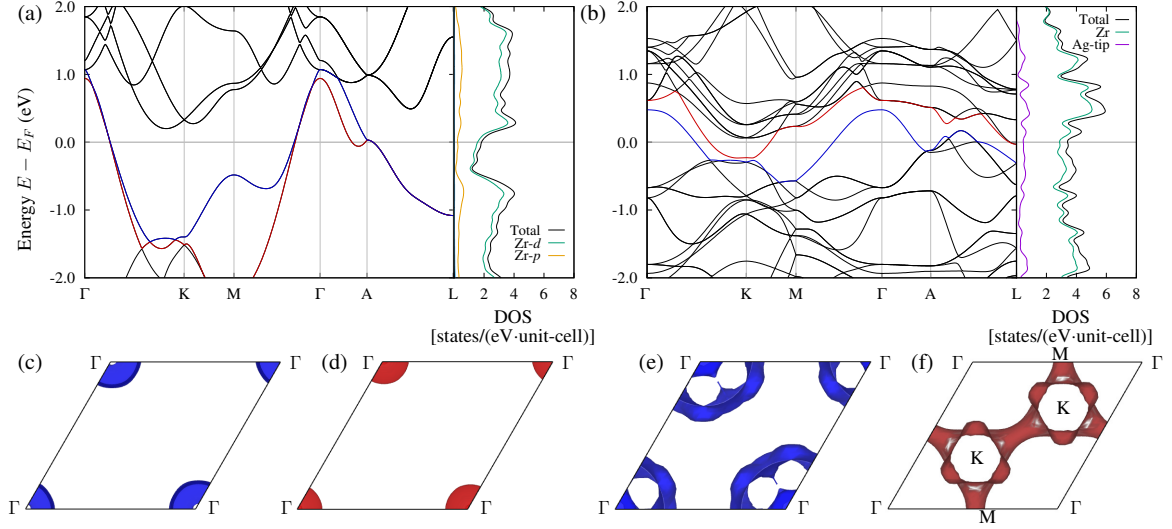


Figure 3.5: Band structures and the corresponding density of states of (a) hcp-Zr and (b) hcp-Zr/Ag-tip. While two hole-like bands cross the Fermi level for hcp-Zr, an electron pocket appears due to the introduction of an Ag-tip. The Zr-DOS at E_F is increased by 62% due to Ag tip insertion. The corresponding Fermi surfaces are shown in (c)-(f). The hole pocket in hcp-Zr/Ag-tip is larger in size, and the electron pocket at K-point is connected by a tubular network. Figure reprinted from (45) by permission of IOP Publishing Ltd.

function for the $e - p$ interaction is obtained as, (200; 201)

$$\alpha^2 F(\omega) = \frac{1}{N(E_F)} \sum_{\mathbf{k}, \mathbf{q}, \gamma} \left| \mathcal{G}_{\mathbf{k}, \mathbf{k}+\mathbf{q}, \gamma} \right|^2 \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}+\mathbf{q}}) \delta(\omega - \omega_{\mathbf{q}, \gamma}), \quad (3.2)$$

where $N(E_F)$ is the electronic density of states (DOS) at the Fermi level, $\omega_{\mathbf{q}, \gamma}$ is the phonon frequency of wave vector $\mathbf{q}$ and mode γ . The $|\mathcal{G}_{\mathbf{k}, \mathbf{k}+\mathbf{q}, \gamma}|$ is the $e - p$ matrix element for the scattering of electron between states with momenta $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$ at the Fermi level. Further λ and ω_{ln} are obtained using $\alpha^2 F(\omega)$ as $\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega$ and $\omega_{\text{ln}} = \exp[\frac{2}{\lambda} \int \frac{\alpha^2 F(\omega)}{\omega} \ln(\omega) d\omega]$.

We first discuss the picture for pure hcp-Zr and subsequently investigate the effects of elemental Ag-tip. The decomposed band structure of hcp-Zr along the high-symmetry directions of the Brillouin zone indicate two hole-like bands centred at the Γ -point [Fig. 3.5(a)], which originate mainly from the Zr- d orbitals, while

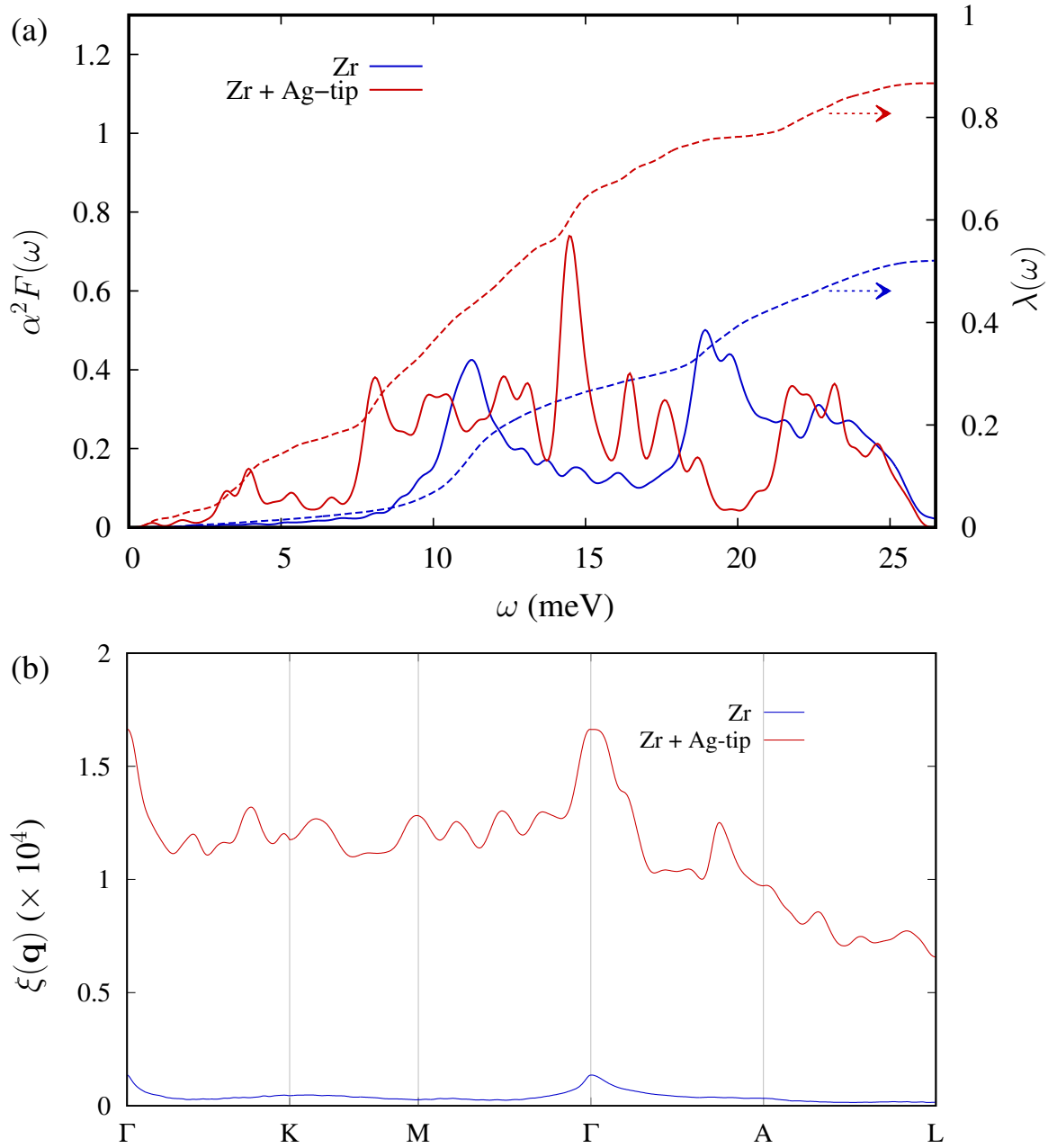


Figure 3.6: (a) Calculated Eliashberg spectral function $\alpha^2 F(\omega)$ and $\lambda(\omega)$. In addition to increased spectral weight, availability of many phonons to couple with electrons enhance $e - p$ coupling under Ag-tip. (b) An order of magnitude increase in the Fermi surface nesting function $\xi_{\mathbf{q}}$ for all $\mathbf{q}$ -vectors inside the Brillouin zone contribute to increase in $\lambda(\omega \rightarrow \infty)$. Figure reprinted from (45) by permission of IOP Publishing Ltd.

Table 3.2: Measured and calculated superconducting temperature using the Allen-Dynes modified McMillan formula, which is substantially enhanced under Ag-tip through an increase in $e - p$ coupling λ . The theoretical T_c is calculated using $\mu^*=0.18$.

	λ	T_c (K)	
		Theory	Experiment
hcp-Zr	0.52	0.51	0.57
hcp-Zr/Ag-tip	0.87	3.52	3.2

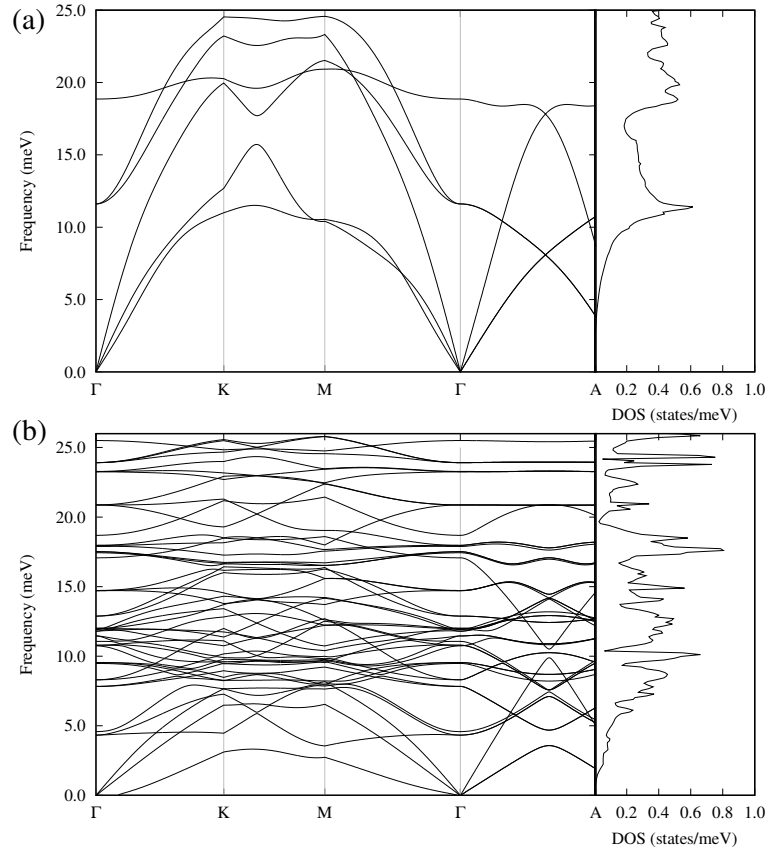


Figure 3.7: The phonon dispersion for (a) pristine hcp Zr and (b) hcp Zr under Ag tip. The superlattice model for Zr/Ag interface do not show any kinetic instability. Figure reprinted from (45) by permission of IOP Publishing Ltd.

the Zr- p contribution at the Fermi level is negligible. These two bands become doubly degenerate at A -point. The corresponding Fermi surface (FS) consists of two cylindrical hole-like sheets [Fig. 3.5(c) and (d)]. The corresponding electronic DOS at E_F is found to be 1.84 states/[eV·unit-cell] in Fig. 3.5(a). The introduction

of Ag-tip substantially perturbs the Zr band structure [Fig. 3.5(b)], which consists of three-hole pockets and one electron pocket. While the electron pocket around K -point and the hole pocket at Γ are comparable in size, the hole pockets between $A - L$ are found to be much smaller. The size of the hole pocket at Γ is larger in size [Fig. 3.5(e)] compared to pure-Zr, and the electron pockets at K are connected by a tubular network [Fig. 3.5(f)]. Due to the insertion of Ag-tip, the Zr-DOS at E_F is increased by about 62% to 2.98 states/[eV·unit-cell] in Fig. 3.5(b). In contrast, a small contribution of 0.46 states/[eV·unit-cell] is contributed from the Ag-tip. Next, we compare the phonon dispersion and DOS without and with the tip (Fig. 3.7(a) and (b)). We do not observe any kinetic instability due to Ag-tip insertion and interestingly observe softening of the acoustic modes and the additional appearance of many optical modes in the presence of tip.

In order to quantify the interaction between electrons and phonons, we calculate $\alpha^2F(\omega)$ and total $e - p$ coupling $\lambda(\omega \rightarrow \infty)$, which are shown in Fig. 3.6(a). In addition to increased spectral weight, more peaks in $\alpha^2F(\omega)$ between 5-25 meV indicate more available phonons to couple with the electrons at the Fermi level and enhance $e - p$ coupling. Further, we have calculated the Fermi surface nesting function $\xi_{\mathbf{q}} = \sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}}) \delta(\epsilon_{\mathbf{k}+\mathbf{q}})$. (211; 212) For all $\mathbf{q}$ -vectors inside the Brillouin zone, the calculated $\xi_{\mathbf{q}}$ is substantially enhanced under the influence of Ag-tip [Fig. 3.6(a)]. Thus, increased electronic DOS, phonon softening along with increased phonon DOS, and substantial increase in $\xi_{\mathbf{q}}$ together contribute to an increase in $\lambda(\omega \rightarrow \infty)$. Consequently, λ is increased by $\sim 67\%$ to 0.87 for the hcp-Zr/Ag-tip from 0.52 in pure hcp-Zr, which leads to substantial enhancement in the superconducting temperature (Table 3.2).

3.5 Conclusion

This chapter theoretically explained the absence, emergence and enhancement of superconducting transition temperature for different materials under the metallic tip. Firstly, we show that the spin polarization in the Fermi surface is approximately 12.5% for CuFeSb using the first principle calculations. However, when the Fermi velocities for the up and down spin bands are included, the ballistic transport spin polarization is found to be 46 %, which is in excellent agreement with the experimental results. Contrary to other iron-based pnictides and chalcogenides, CuFeSb has a ferromagnetic ground state which causes the absence of superconductivity in it. More significant anion height from the Fe layer, the narrow band with a high density of states, due to which Stoner instability proves the ferromagnetic order in the Fe layer. Secondly, we have studied the ZrSiS under the Ag tip for the emergence of superconductivity at the interface. Our *ab initio* calculations indicate that this emerged superconducting phase is not phonon-mediated because low electron-phonon coupling does not provide the experimental transition temperature. In the band structure, several Dirac points survive under the Ag tip, hinting toward the possible topological superconductivity in ZrSiS under the Ag tip. Last, we observed the enhancement of superconducting transition temperature in hcp-Zr under the Ag tip. Our first-principles calculations explain the improvement in electron-phonon interactions and density of states at the Fermi level under the mesoscopic metallic point contacts.

Chapter 4

First-principles study on the superconductivity of doped zirconium diborides

Recent experiments (N. Barbero, *et al.* [Phys. Rev. B 95, 094505 \(2017\)](#)) establishes that bulk superconductivity ($T_c \sim 8.3\text{-}8.7$ K) can be induced in AlB_2 -type ZrB_2 and HfB_2 , highly covalent refractory ceramics, by vanadium (V) doping. These AlB_2 -structured phases provide an alternative to earlier diamond-like or -based superconducting and superhard materials. However, the underlying mechanism for doping-induced superconductivity in these materials is yet to be addressed. In this report, we have used first-principles calculations to probe electronic structure, lattice dynamics, and electron-phonon coupling in V-doped ZrB_2 and consequently examine the origin of the superconductivity. We find that while doping-induced stress weakens the electron-phonon coupling, the concurrent induced charges strengthen it. The calculated critical transition temperature (T_c) in electron (and V) doped ZrB_2 is at least one order of magnitude lower compared to experiments, despite considering the weakest possible Coulomb repulsion between electrons in the Cooper pair, hinting at non-Bardeen-Cooper-Schrieffer (BCS) type superconductivity in it. The contents of this chapter are published in [Phys. Rev Materials 6, 044805 \(2022\)](#).

This work resulted from the collaboration with a group of researchers, Sanjay Nayak, Martin Dahlqvist, Johanna Rosen, Per Eklund and Jens Birch, from Linköping University, Sweden. The data presented in this chapter are obtained using the Swedish National Infrastructure for Computing at the National Supercomputer Centre, partially funded by the Swedish Research Council through Grant Agreement No. 2018-05973.

4.1 Introduction

Transition metal diborides (TMB_2) in AlB_2 -type crystal structure (space group: $P6/mmm$ [191]) are hard and ultrahigh-temperature ceramic materials (213–217) and have applications in, e.g., cutting tools, crucibles, wear-resistant coatings, and microelectronics (218–221). The mechanical hardness, e.g. Vickers hardness (H_v), of TMB_2 varies from 12–15 GPa to 45–50 GPa. Particularly in thin film form, the group-4 diborides such as TMB_2 (222; 223), ZrB_2 (224; 225), and HfB_2 (226; 227), are superhard with the measured indentation hardness of ≈ 45 , ≈ 45 and ≈ 43 GPa, respectively. While the measured hardness of group-5 borides [i.e. VB_2 (213), NbB_2 (228), and TaB_2 (217)] are in the range of 30 to 40 GPa, the indentation hardness of group-6 borides [i.e. CrB_2 (229; 230), MoB_2 (231; 232) and WB_2 (233)] is within 30 GPa. TMB_2 in their pristine and stoichiometric AlB_2 -type phase are typically not superconductors (234–238) but suitable doping conditions can induce superconductivity (237; 239–241). For example, ZrB_2 and HfB_2 are metals in their pristine form, but upon doping with V, they become superconducting with a critical transition temperature (T_c) < 10 K (239; 241). Similarly, Ni-doped NbB_2 becomes superconducting below 6 K (240). Along with their high hardness mechanical properties, doping-induced superconductivity in these TMB_2 make them a commercially cheap alternative to nanocomposites that contain diamond and/or c-BN. Superconducting, superhard nanocomposites are important for industrial applications in high- pressure cryogenic devices (242; 243), wear restive part of superconducting devices, superconducting micro electro-mechanical systems (MEMS) (244), superconducting radio-frequency accelerator cavities (245–247), quantum interference devices (248), photodetector (249), infrared sensors (250), and electrical contacts to nanodevices (251) etc. Despite the numerous studies to explain the origin of superconductivity in MgB_2 with AlB_2 -type structure

(11; 252–254), little is known for the doped TMB_2 family of materials (235). Consequently, from both perspectives of applications and fundamental material science, there is a need to understand the superconductivity in these doped TMB_2 phases. In view of that, we chose V-doped ZrB_2 as a representative member since it has the highest T_c reported for this family of materials.

In its pristine form, ZrB_2 is not superconducting, but doping with V or Nb as low as 1% can induce superconductivity (239; 241; 255; 256). Renesto *et al.* (241) reported that the highest T_c recorded for $\text{Zr}_{1-x}\text{V}_x\text{B}_2$ is 8.7 K for $x = 0.04$. Along with a multi-gap nature of superconducting gap (2Δ), they demonstrated that T_c increases with increasing V content in $\text{Zr}_{1-x}\text{V}_x\text{B}_2$ up to $x=0.04$, and that further increase in V doping levels causes T_c to decrease, which implies the presence of a superconducting dome. From X-ray diffraction analysis, a dopant concentration of 4 % V in ZrB_2 results in a uniaxial compressive strain of ~ 0.3 % along the c-axis. Using microscopic characterization techniques such as nuclear magnetic resonance (NMR), superconducting quantum interference device (SQUID) magnetometry, resistivity, and muon-spin rotation measurements, Barbero *et al.* (239) established the bulk superconductivity ($T_c = 8.33$ K) in $\text{Zr}_{0.96}\text{V}_{0.04}\text{B}_2$ along with an s-wave and multi-gap nature of 2Δ which was further validated by Jung *et al.* (257).

In this chapter, we investigate the electronic structure, lattice dynamics and electron-phonon coupling (EPC) in pristine and V-doped ZrB_2 using first-principles simulation to explore the origin of the superconductivity with < 4 % doping level. Our analysis reveals that upon V doping, the Fermi level (E_F) shifts towards the conduction band, making V an effectively n-type dopant to ZrB_2 . Such shifting of E_F away from the well-known pseudogap region in the electronic structure of ceramics enhances the electronic densities of states (DOS) at E_F , $[N(E_F)]$, and improve the EPC. However, at experimentally relevant doping levels, our calculated

superconducting transition temperature (T_c) is one order of magnitude lower than the reported experimental values, an indication of a complex origin of superconductivity in V-doped ZrB_2 .

4.2 Computational details

Our analysis involves uncovering the effect of (i) lattice strain, (ii) carrier doping, and (iii) alloying within the virtual crystal approximations (VCA) to the electronic, vibrational and their coupling in ZrB_2 using first-principles density functional theory (DFT) simulations as implemented in the QUANTUM ESPRESSO (206). Nonrelativistic norm-conserving pseudopotentials with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is used in our simulations (134; 258). The valence electronic configuration of Zr, V, and B are chosen as $4s^2 4p^6 5s^2 4d^2$, $3s^2 3p^6 4s^2 3d^3$, and $2s^2 2p^1$ respectively. For ground-state calculations, the Brillouin zone is sampled by a grid of $14 \times 14 \times 13$ k -points (198), and a kinetic energy cutoff for plane wave basis of ≈ 1090 eV is used. Dynamical matrices are computed over a $6 \times 6 \times 6$ q -points grid using density functional perturbation theory (DFPT). Electron-phonon coupling was computed with the Wannier interpolated scheme (142). 13 maximally localized Wannier functions (137; 259) are constructed using WANNIER90 (138) library within the EPW code (142). The electron-phonon matrix elements are calculated on a dense k -grid and q -grid of $25 \times 25 \times 25$. We have used 300 meV and 0.5 meV as electron and phonon smearing widths, respectively. Within the Migdal-Eliashberg theory (21; 22), the isotropic version of Eliashberg spectral function $\alpha^2 F(\omega)$ is defined as,

$$\alpha^2 F(\omega) = \frac{1}{N(E_F)} \sum_{mn\gamma} \int \frac{d\mathbf{k}}{\Omega_{BZ}} \int \frac{d\mathbf{q}}{\Omega_{BZ}} |g_{mn\gamma}(\mathbf{k}, \mathbf{q})|^2 \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_F) \delta(\omega - \omega_{\mathbf{q}\gamma}), \quad (4.1)$$

where $N(E_F)$ is the electronic density of states (DOS) at the Fermi level and $g_{mn\gamma}(\mathbf{k}, \mathbf{q})$ are the electron-phonon matrix elements with electronic band indices m, n and phonon band index γ . The $\sum_{mn} \int \frac{d\mathbf{k}}{\Omega_{BZ}} \delta(\varepsilon_{n\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{m\mathbf{k}+\mathbf{q}} - \varepsilon_F)$ term of above Equation is referred to nesting function (ζ_q) and is a property of the Fermi surface and hence has a pure electronic origin (142). After computing $\alpha^2 F(\omega)$, electron-phonon interaction λ is evaluated by,

$$\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega. \quad (4.2)$$

The superconducting transition temperature T_c is calculated by the McMillan-Allen-Dynes formula (23; 24):

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \quad (4.3)$$

where $\omega_{\log}$ is a logarithmically averaged phonon frequency which has replaced the Debye temperature Θ_D in the McMillan formula and is computed from the Eliashberg function ($\alpha^2 F(\omega)$) as

$$\omega_{\log} = \exp \left[\frac{2}{\lambda} \int_0^\infty \log \omega \frac{\alpha^2 F(\omega)}{\omega} d\omega \right] \quad (4.4)$$

In Eq.(1.4), μ^* is a dimensionless parameter representing the Coulomb repulsion between electrons which form the Cooper pair. This repulsive parameter is hard to compute from the *ab initio* method, and for most superconductors, its lies in the range 0.1-0.2 (16; 45; 260). However, for *d*-band metals, Bennemann and Garland (261) approximated μ^* to $N(E_F)$ as,

$$\mu^* = 0.26 \times \frac{N(E_F)}{1 + N(E_F)} \quad (4.5)$$

Our estimates of μ^* for doped ZrB_2 are in the range of 0.05-0.09 with a doping level of $0.0 e^-/\text{cell}$ to $0.2 e^-/\text{cell}$. Nevertheless, we estimate T_c for a wide range (0.0-0.1) of μ^* in our work. To model the V doping in ZrB_2 , VCA is used where Zr atomic site in ZrB_2 is replaced with a virtual atom. The pseudopotential of the virtual atom is, in turn, represented by a composition average of the Zr and V pseudopotentials, i.e. $V_{\text{virtual atom}}^x = xV_V + (1 - x)V_{\text{Zr}}$, and the atomic mass of the virtual atom is taken as the average atomic mass of Zr and V, i.e., $m_{\text{virtual atom}}^x = xm_V + (1 - x)m_{\text{Zr}}$.

4.2.1 Construction of Wannier function

We transform Bloch wave functions into the maximally localized Wannier function (MLWF) representation. MLWFs are constructed on the $12 \times 12 \times 12$ grid of the Brillouin zone. The quality of the chosen MLWF is validated by comparing electronic and phonon band structures computed by DFT and Wannier functions. In Fig.4.1, we show the electronic band structure of pristine ZrB_2 obtained with DFT and by Wannier interpolation. A clear overlapping of both data suggests the MLWFs are appropriately constructed.

We checked the spatial decay of associated physical quantities to Wannier functions, i.e., electronic Hamiltonian (H), Dipole (P) and electron-phonon matrix elements are transformed back to the Block representations at the denser k - and q -mesh of 25^3 and 25^3 , respectively. Fig.4.2 demonstrate spatial decay of this above-mentioned quantity where clear decays are seen. These decays further validate the quality of MLWF.

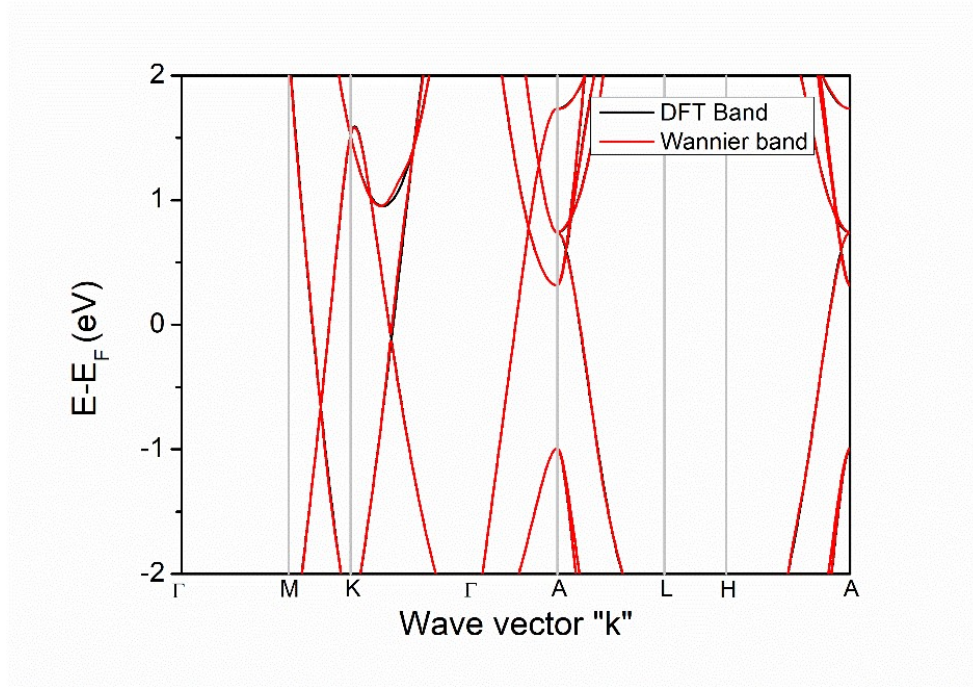


Figure 4.1: Band structure from the *ab initio* calculation matches well with Wannier interpolated band structure.

4.2.2 Determination of Debye temperature Θ_D

We compute heat capacity at constant volume (C_V) as a function of temperature by using the relation,

$$C_V = \sum_{qv} k_B \left(\frac{\hbar\omega(qv)}{k_B T} \right)^2 \frac{\exp(\hbar\omega/k_B T)}{\left[\exp\left(\frac{\hbar\omega(qv)}{k_B T} \right) - 1 \right]^2}. \quad (4.6)$$

Here q and v denote the wave vector and band index of the frequency eigenvalue (ω). Ω is computed by DFPT approach. The C_V vs T plot is shown in Fig. 4.3. To obtain the Debye temperature of ZrB_2 at low temperatures, we fitted the C_v vs T plot with the classic equation of Debye and Einstein.

$$C_V = \gamma T + \frac{12\pi^4 N k_B}{5\Theta^3} T^3 \quad (4.7)$$

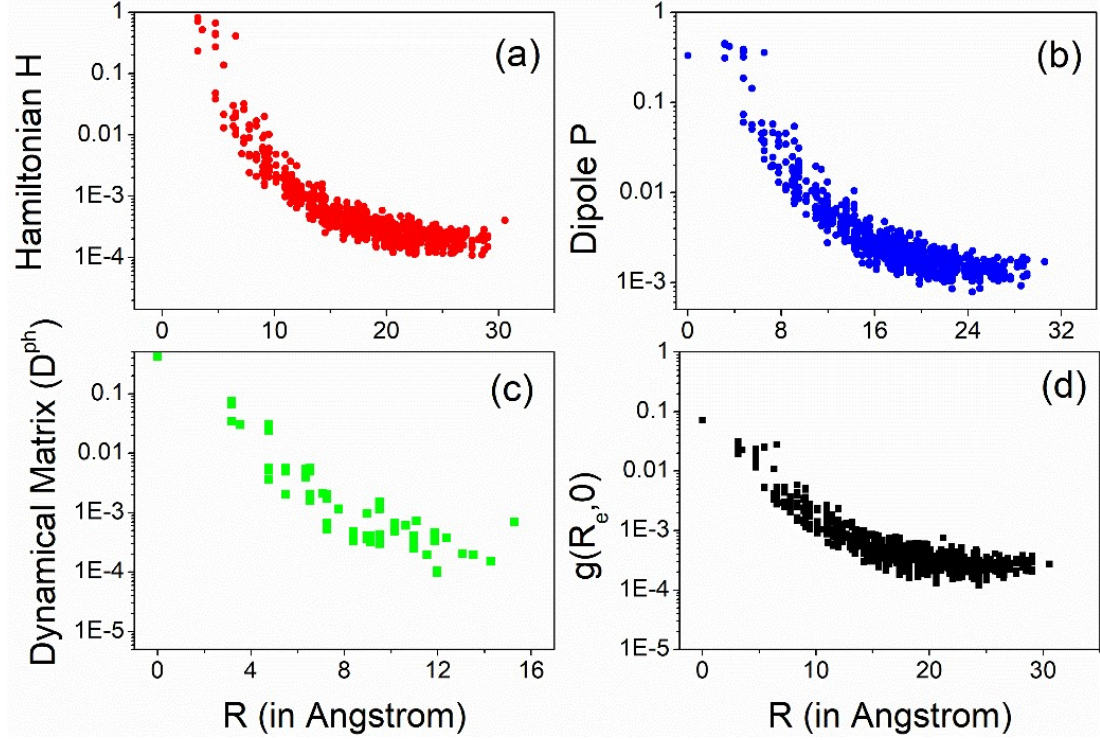


Figure 4.2: Spatial decay of the (a) electronic Hamiltonian(H), (b) Dipole (P), (c) dynamical matrix (D^{ph}) and (d) electron-phonon matrix $g(R_e, 0)$ for ZrB_2 as a function of lattice vector R of the cell. Note that Y-axes are in log scale.

4.3 Results and Discussion

Our optimized lattice parameters $a = b = 3.17 \text{ \AA}$ and $c = 3.54 \text{ \AA}$ for a unit cell (u.c.) of ZrB_2 , as well as in-plane B-B bond-length ($d_{B-B} = 1.83 \text{ \AA}$) and out-of-plane Zr-B ($d_{Zr-B} = 2.55 \text{ \AA}$) are in good agreement with previous theory and experiments (262–264). Electronic band-structure of pristine ZrB_2 shows a Dirac-like linear band dispersion along the $M - K$, $K - \Gamma$ and $\Gamma - A$ high symmetry k -path (see Fig. 4.4(a)). The linear dispersed band along the $M - K$ symmetry line is around 2 eV which is rarely observed in the Dirac materials. The features in the band structure match with previously reported ones (265; 266). The orbital projected electronic DOS shows a dominant role of Zr-4d orbital towards the conduction bands while a B-2p orbital is more dominant at valence bands along with a con-

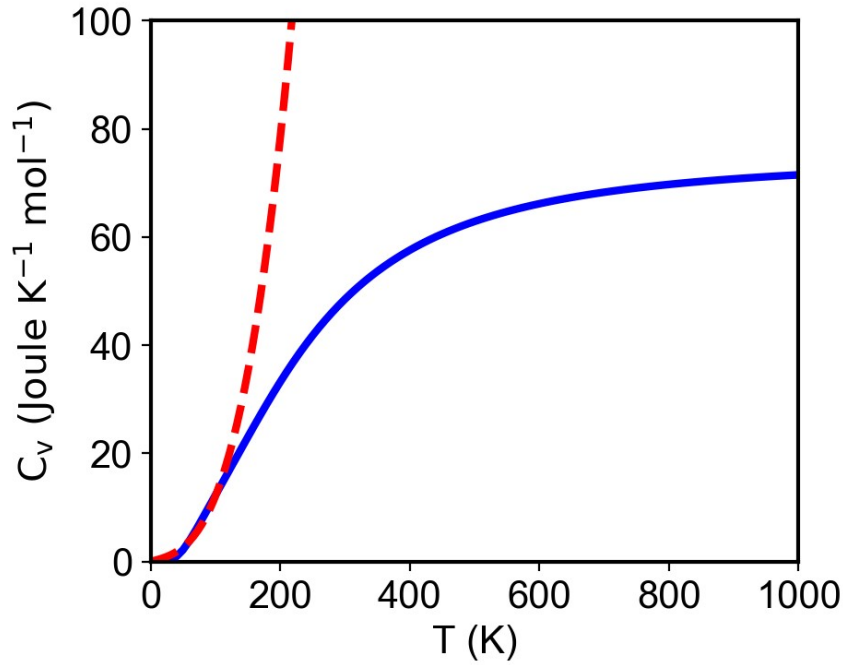


Figure 4.3: Calculated heat capacity at constant volume (C_V) as a function of temperature. The red line is the interpolated curve using the Debye-Einstein formula. Our computed Θ_D is in good agreement with that of Renosto *et al* (241)

tribution from a Zr-4d orbital (see Fig. 4.4(b)), again in good agreement with a previous report (267). The Fermi level (E_F) is located near a pseudogap region of the electronic DOS (Fig. 4.4(b)), resulting in a relatively low $N(E_F)$ [= 0.26 states $\text{eV}^{-1} \text{ cell}^{-1}$] smaller than the $N(E_F)$ of MgB_2 [= 0.72 states $\text{eV}^{-1} \text{ cell}^{-1}$] (13).

The unit cell of ZrB_2 consists of 3 atoms which result in a total of 9 phonon branches, 3 acoustic and 6 optical ($2E_{1u} + 1A_{2u} + 1B_{1g} + 2E_{2g}$), as shown in Fig. 4.4(c). The Γ -point phonon frequencies of E_{1u} , A_{2u} , B_{1g} , and E_{2g} optical modes are found at 55.61, 58.08, 68.79, and 95.02 meV, respectively (see Fig. 4.4(c) and Table 1). The phonon densities of states ($F(\omega)$) and the isotropic Eliashberg spectral functions $\alpha^2F(\omega)$ are displayed in Fig. 4.4(d) shows that spectral patterns of $\alpha^2F(\omega)$ replicate $F(\omega)$. Using Eq. 1.2, we estimate the average value of the electron-phonon

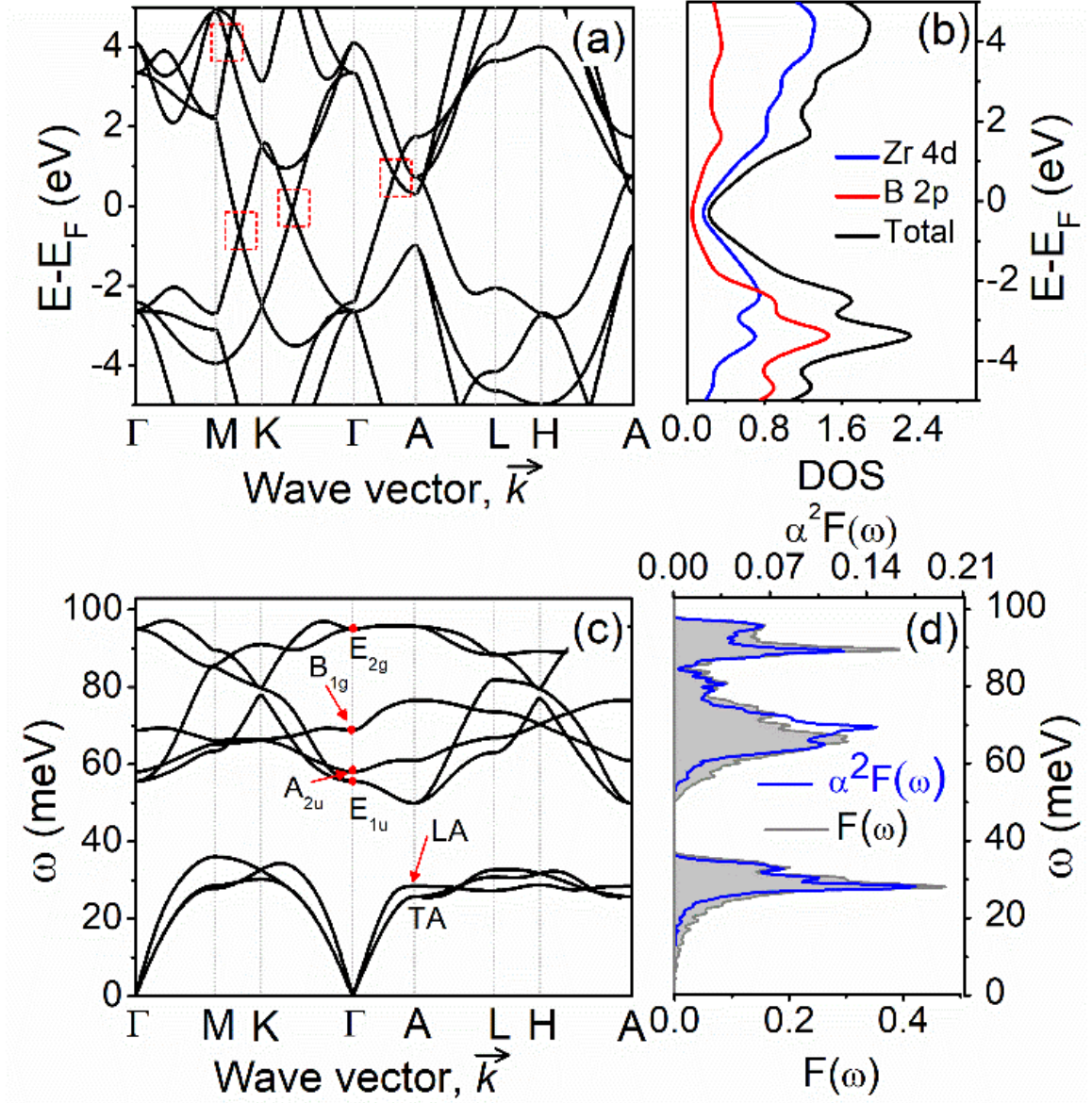


Figure 4.4: (a) Electronic band structure and (b) density of states (DOS) of pristine AlB₂-type ZrB₂. Red rectangles in (a) mark Dirac-like bands. (c) Phonon dispersion and (d) phonon DOS [$F(\omega)$]. The isotropic Eliashberg spectral functions [$\alpha^2 F(\omega)$] are overlaid in (d).

coupling constant (λ) to 0.126, in agreement with previous theoretical and experimental reports (268–270). It is noted here that, unlike in MgB₂, the E_{2g} phonon in ZrB₂ is at higher energy than the B_{1g} at Γ -point. Thus, the contribution of E_{2g} phonon modes to the $\alpha^2 F(\omega)$ of ZrB₂ is weaker than that of MgB₂ (271). Together

with low $N(E_F)$ and energetics of E_{2g} phonon modes in vibrational spectra are responsible for a weaker electron-phonon coupling strength in ZrB_2 compared to MgB_2 . This weaker electron-phonon coupling is the primary cause of the absence of superconductivity in ZrB_2 . The Debye temperature (Θ_D) is estimated to be 560 K, in agreement with the experimental value of 555.6 K by Renosto *et al* (241) (see section 4.2.2). Given that the experimental n-type carrier density in ZrB_2 is of the order of 10^{21} electrons cm^{-3} (265) is consistent with the carrier densities considered in our simulations, and that the $E_F \gg \Theta_D$ condition is satisfied suggest that the Eliashberg formalism is adequate to describe the electron-phonon interaction and consequently the superconductivity in ZrB_2 (272). The weak electron-phonon coupling in pristine ZrB_2 ($\lambda = 0.126$) results in a superconducting temperature in the mK range. With the Coulomb repulsion constant $\mu^* = [0, 0.1]$, the upper limit of the transition temperature T_c using McMillan-Allen-Dynes equation is less than 0.04 K (see Fig. 4.12), which explains the absence of the superconductivity above 1 K in pristine ZrB_2 (273).

The electronic structure of V-doped ZrB_2 is investigated using both supercell and VCA approaches. In the supercell approach, we considered two different supercells (i) $2 \times 2 \times 2$ (24 atoms) and (ii) $3 \times 3 \times 3$ (81 atoms) and substituted one V atom for Zr resulting in a V doping concentration of 12.5% ($\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$) and 3.7% ($\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$), respectively. Upon V doping in ZrB_2 , the E_F moves away from the pseudo-gap region into the conduction band (Fig. 4.5(a)) resulting in increased $N(E_F)$. The calculated $N(E_F)$ for $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$ and $\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$ are 0.34 and $0.52 \text{ eV}^{-1} \text{ cell}^{-1}$, respectively. Atom-projected DOS for shows that V-3d states are more localized than Zr-4d states near the Fermi level (Fig. 4.5(b)-(c)), with a major contribution from d_{z^2} . We also note the splitting of degenerate Zr- d_{xz} and d_{yz} orbitals upon V doping in ZrB_2 . Band structure analysis by Zhai *et al* (235)

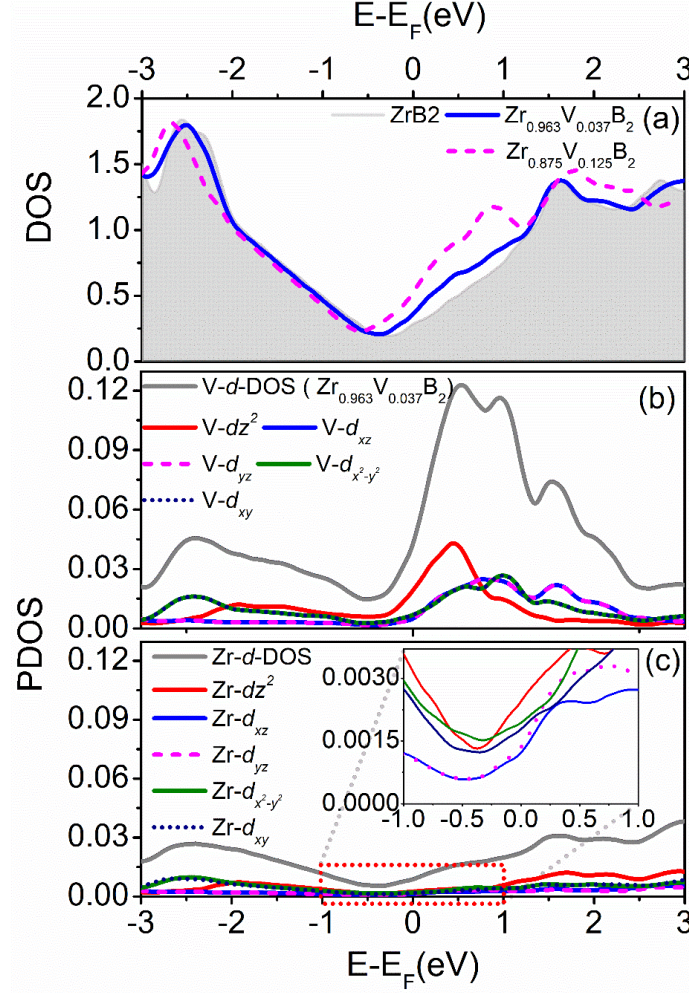


Figure 4.5: (a) Electronic density of states (DOS) per unit cell of V-doped ZrB₂ obtained with two different supercell dimensions: $3 \times 3 \times 3$ for Zr_{0.963}V_{0.037}B₂ (blue solid line) and $2 \times 2 \times 2$ for Zr_{0.875}V_{0.125}B₂ (magenta dashed line). (b) Atom and (c) orbital projected DOS of V and Zr atoms in Zr_{0.963}V_{0.037}B₂. The inset in (c) shows orbital-projected Zr states around the Fermi level (E_F).

further suggests that E_F of Zr_{0.963}V_{0.037}B₂ is very close to the $d_{xy} + d_{yz}$ band at the A high-symmetry k-point with a low dispersion width.

Full structural relaxation for supercells of Zr_{0.963}V_{0.037}B₂ and Zr_{0.875}V_{0.125}B₂ shows compressive strain along both in-plane and out-of-plane directions as compared with ZrB₂. While the change in volume ($\Delta V/V_0$), in-plane ($\Delta a/a_0$), and out-of-plane ($\Delta c/c_0$) lattice parameters of Zr_{0.963}V_{0.037}B₂ are -0.80 , -0.23 , and -0.35 ,

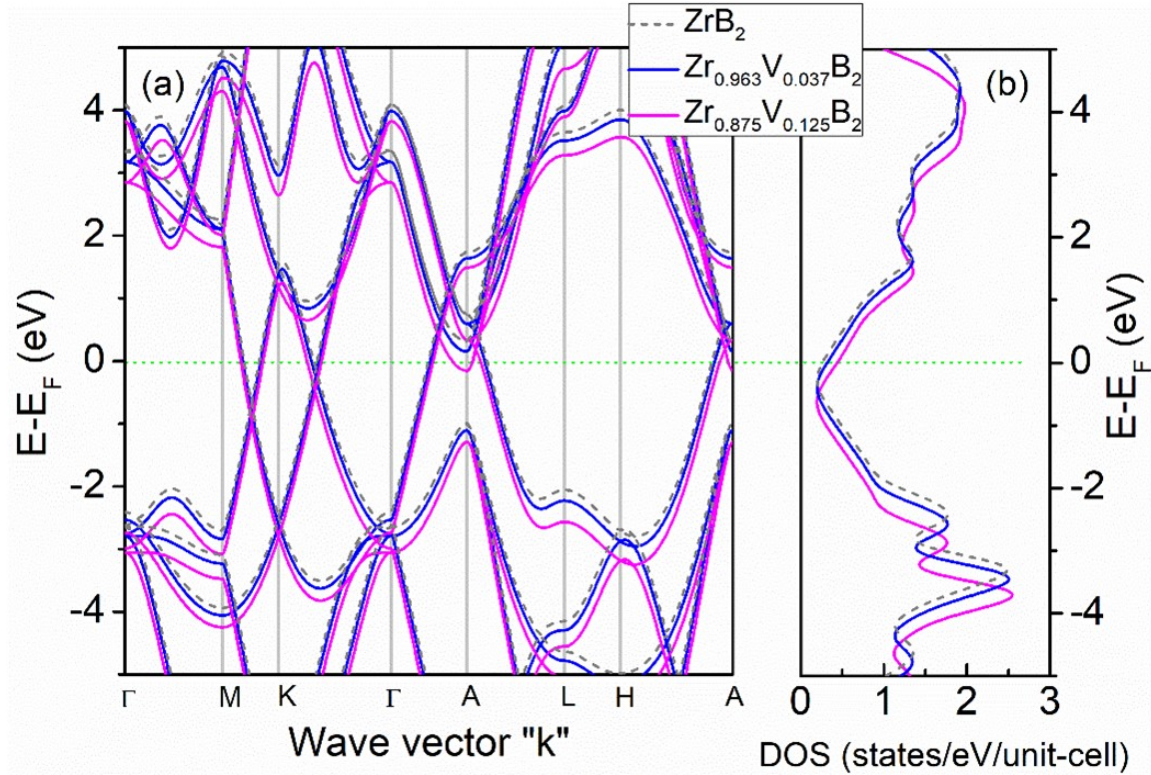


Figure 4.6: Calculate electronic (a) band structure and (b) DOS of ZrB_2 upon V-doping using the Virtual Crystal Approximation (VCA). Two different concentrations of V doping in ZrB_2 is shown; (i) 3.7 % of V in ZrB_2 [$\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$] and (ii) 12.5 % of V in ZrB_2 [$\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$].

the same for $\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$ are -2.67 , -0.72 , and -1.25 , respectively. Similar numbers are obtained when using VCA, with optimized lattice parameters a (c) of $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$ and $\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$ being 3.16 Å (3.52 Å) and 3.15 Å (3.48 Å), respectively. This corresponds to in-plane (out-of-plane) compressive strain of -0.31 (-0.56) and -0.63 (-1.7), respectively, as compared with pristine ZrB_2 . The larger compressive strain out-of-plane as compared with in-plane agrees qualitatively well with the experimental observations where strain along the c axis is well resolved, while almost no in-plane strain is noted (241). The electronic band structure and DOS analysis revealed that the E_F moves away from the pseudo-gap region into the conduction band with a corresponding increase in $N(E_F)$ for

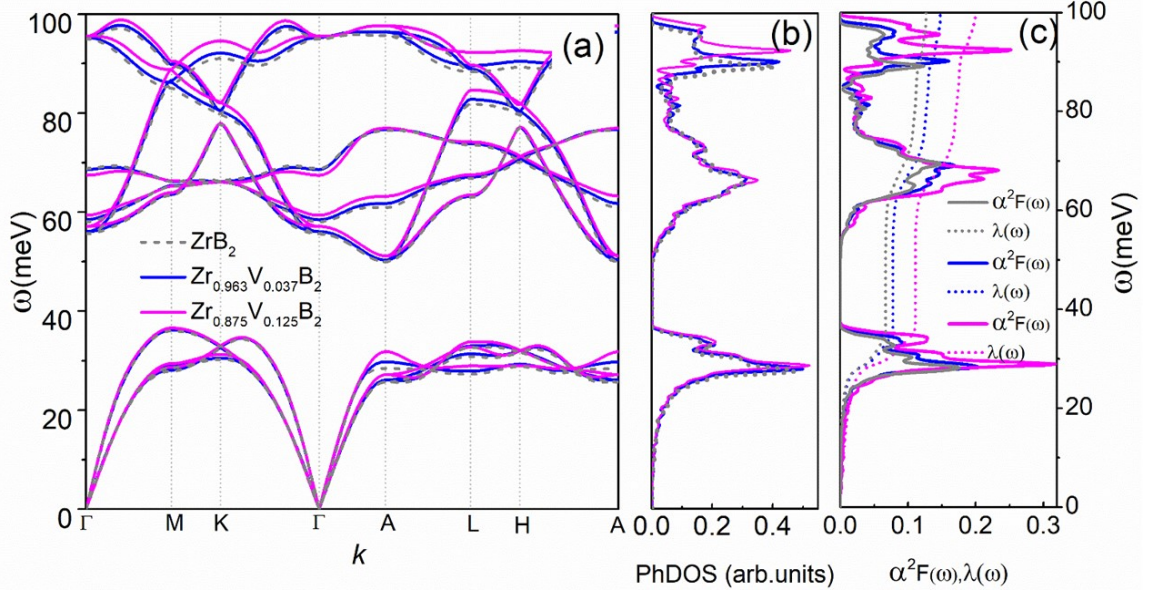


Figure 4.7: Calculated (a) phonon dispersion, (b) phonon DOS, and (c) Eliashberg spectral function ($\alpha^2F(\omega)$) of V-doped ZrB_2 . In (c), the electron-phonon coupling constant ($\lambda(\omega)$) is also shown. To obtain the phonon dispersion of V doped ZrB_2 using the VCA, we choose the atomic mass of the virtual atom to the average atomic weight of Zr and V, i.e. $m_{\text{virtual atom}}^x = xm_V + (1-x)m_{\text{Zr}}$

V-doped ZrB_2 (see Figs.4.5 and 4.6). Using VCA, $N(E_F)$ of $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$ and $\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$ 0.32 and 0.46 states $\text{eV}^{-1} \text{ cell}^{-1}$, respectively. Comparison of the electronic structure calculated at 4% of V doping using the supercell approach and VCA reveals similar results, while at 12.5% of doping levels, $N(E_F)$ from VCA calculations [$N(E_F)^{\text{VCA}} = 0.46 \text{ states eV}^{-1} \text{ cell}^{-1}$] is significantly lower than achieved with the supercell approach [$N(E_F)^{\text{SC}} = 0.52 \text{ states eV}^{-1} \text{ cell}^{-1}$].

Although at the macroscopic scale, the strain is relatively low (-0.23 to -0.35%), our bond-length distribution analysis from supercell approach ($\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$) calculations revealed that the maximum change in bond lengths of Zr-B in the supercell is as high as -1.9% . Thus, we examine the material properties of ZrB_2 over a wide range of uniaxial compressive strain $\varepsilon_{||c}$, e.g., 0.3, 0.5, 1, 3, and 5%. The electronic band structure revealed that the bands at the A symmetry k -point are be-

coming closer to E_F upon compressive stress and at $\varepsilon_{||c} = 5\%$, a new Fermi pocket appears at the A point of the Brillouin zone (see Figs. 4.8 and 4.10). We do not find any substantial changes in $N(E_F)$ upon uniaxial compressive strain along the c axis.

Phonon band and $F(\omega)$ analysis reveals that, upon compressive strain, phonon frequencies shift toward higher energy, known as phonon hardening, as seen in Figs. 4.11(a) and 4.9(a), and hence, no imaginary modes of vibrations are observed even if the strain (strain $\varepsilon_{||c}$) is relatively high ($\approx 5\%$). Recent theoretical results suggest that a thin film of layered borides like MgB_4 and InB_4 will go for structural phase transition with a relatively smaller biaxial compressive strain of -0.8 and 3% , respectively (274; 275). Similarly, layered AlB_2 can maintain structural stability from only -1.5% (compressive) to 7.5% (tensile) strain (276; 277), suggesting that bulk ZrB_2 is structurally more stable to compressive stress than the mentioned layered structure of borides.

We further notice that, while the dispersion width of acoustic phonons is increasing, optical phonons are becoming flatter, i.e., increase in $F(\omega)$, upon the compressive strain. The effect of phonon hardening is further reflected in the spectral intensity of $\alpha^2F(\omega)$ and consequently in λ and ω_{log} . The estimated λ of ZrB_2 with $\varepsilon_{||c} = 0.3, 0.5, 1, 3$ and 5% are $0.125, 0.125, 0.125, 0.124$ and 0.121 respectively, which indicates a lowering of the average EPC upon the uniaxial compressive strain. Upon compressive strain, the λ contribution from acoustic phonons ($\lambda_{aco.}$) is reduced, while the component of optical phonons ($\lambda_{opt.}$) is enhanced [see Fig. 4.11(b)]. The change in ω_{log} is linear with applied uniaxial compressive strain [see inset of Fig. 4.11(b)] and is estimated to be $506.8, 511.4, 513.4, 519.7, 546.3$ and 574.7 K for $\varepsilon_{||c} = 0.0, 0.3, 0.5, 1, 3$, and 5% respectively. The computed T_c using Eq.(1.3) is lower than for the pristine ZrB_2 (<0.04 K) when $\mu^* = [0, 0.1]$ (see Fig. 4.12). This indicates that doping-induced compressive strain is not responsi-

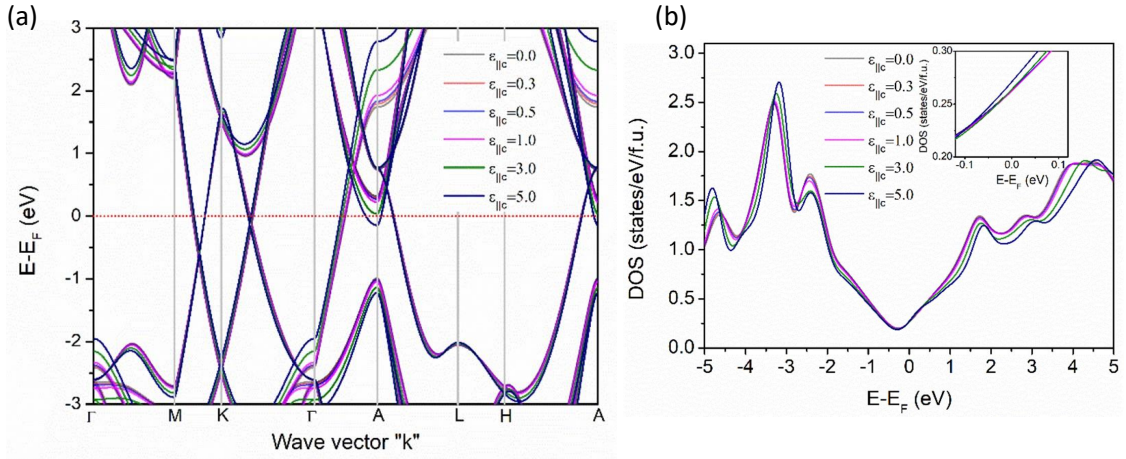


Figure 4.8: (a) Calculated electronic band-structure of ZrB₂ upon uniaxial compressive strain ($\epsilon_{||c}$). The red dotted line is the Fermi level. (b) Calculated electronic DOS of ZrB₂ upon uniaxial compressive strain ($\epsilon_{||c}$). Inset shows an enlarged view of DOS around the Fermi level. It is quite clear from the plot that no significant changes in DOS at the Fermi level upon uniaxial compressive strain in ZrB₂.

ble for the superconductivity in V-doped ZrB₂. The effect of uniaxial compressive strain on vibrational properties and T_c of ZrB₂ is opposite to that of monolayer AlB₂ and multilayered InB₄, where phonon softening and increases in T_c are estimated (274–276).

Next, we examine the effect of electron doping of ZrB₂. It is noteworthy that the highest value of T_c is observed for 4% doping of V/Nb (241), where each V or Nb atom donates one electron per atom for the conduction. This corresponds to the doping of 0.04 electrons per primitive unit cell. However, to reveal trends and clarify, the electronic and vibrational properties were computed self-consistently for a range of charge doping levels (n), i.e., 0.037, 0.1, 0.125, 0.15, 0.2 and 0.4 electrons/cell, leading to an electron doping concentration of 1.2×10^{21} to 1.2×10^{22} cm⁻³ in ZrB₂. A compensating jellium background is used to neutralize the charge in the cell. In this chapter, we simulate electron doping for two different cases: (i) full relaxation of both structural parameters and ions and (ii) only relaxation of

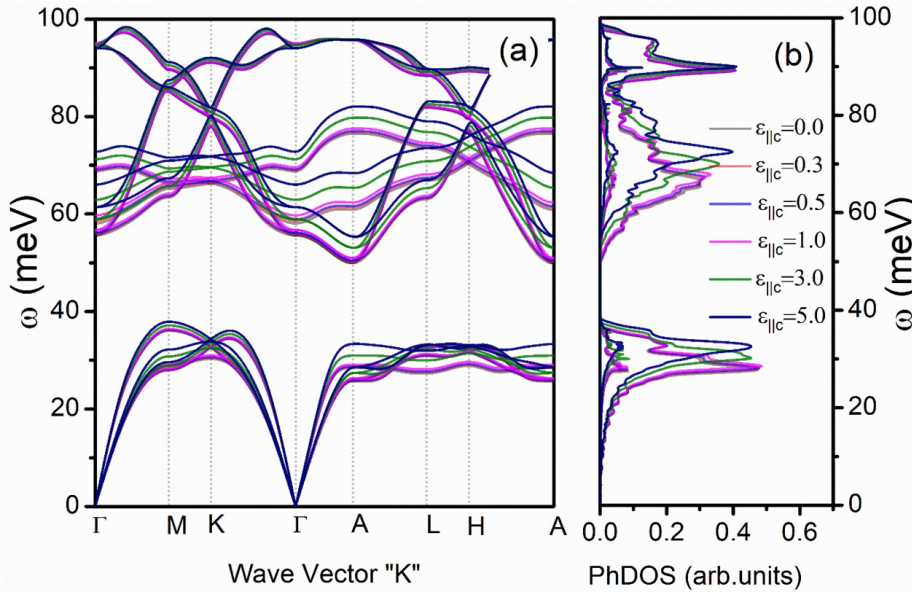


Figure 4.9: Calculated (a) phonon dispersion and (b) phonon DOS of ZrB_2 upon uniaxial compressive strain ($\epsilon_{||c} = 0.0, 0.3, 0.5, 1, 3$, and 5%). With increased compressive strain, the phonon bands are shifted towards higher vibrational frequencies.

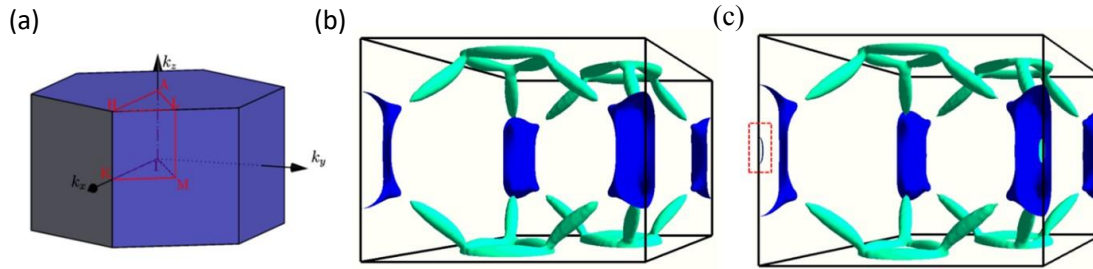


Figure 4.10: (a) The Brillouin Zone of hexagonal crystal symmetry. The Fermi surface of (b) pristine ZrB_2 and (c) ZrB_2 upon 5% of compressive strain ($\epsilon_{||c}=5.0$)

ions while keeping the unit cell static. In the former case, we find an expansion of the unit cell lattice upon carrier doping, contrary to experimental observations; hence, we present the results from the case (ii) (see Table II).

Electron doping of ZrB_2 results in E_F moving away from the pseudogap region and into the conduction band [see Fig. 4.14(a)], causing an increase in $N(E_F)$, as shown

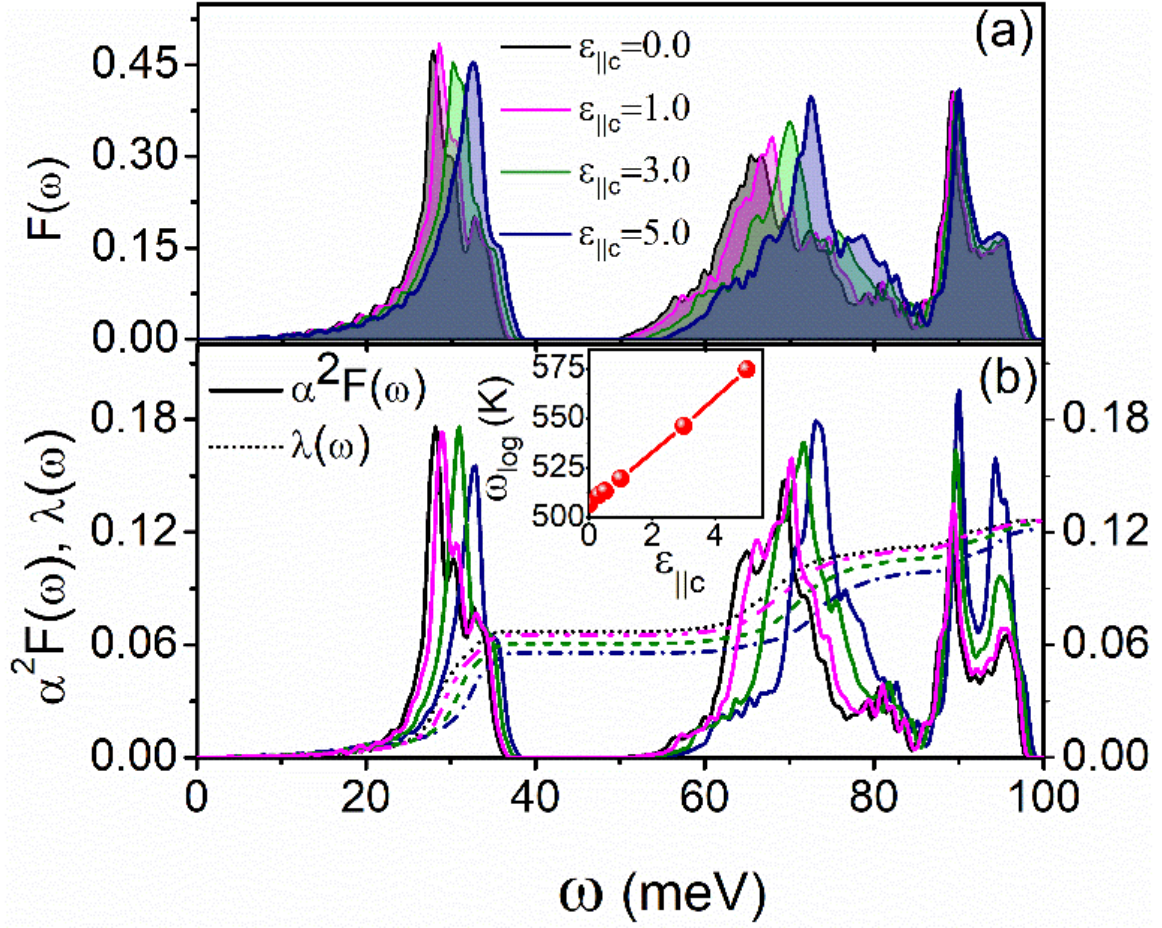


Figure 4.11: (a) Phonon density of states (DOS) $F(\omega)$ of uniaxially strained ($\epsilon_{||c}$) ZrB₂ with different strains in unit cell configurations. (b) The isotropic Eliashberg spectral function [$\alpha^2 F(\omega)$, solid lines] and electron-phonon coupling constant [$\lambda(\omega)$, dashed lines] of strained ZrB₂. Inset in (b): Logarithmic average of phonon frequencies (ω_{log}) in units of Kelvin as a function of applied strain.

in Fig. 4.17(e). At a carrier doping of $0.1 e^-/\text{cell}$, E_F is close to the d_{xz}/d_{yz} bands at the A point in the similar condition to the supercell calculation of $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$ (255) (see Fig. 4.13). Analysis of phonon bands and $F(\omega)$ in Figs. 4.11(a) and 4.15 shows both acoustic and optical phonon modes shift toward lower energy, henceforth referred to as phonon softening, upon electron doping in ZrB₂. The Γ -point phonon frequencies of optical phonon modes with different doping concentrations are tabulated in Table I and quantify the phonon softening at the point for electron-

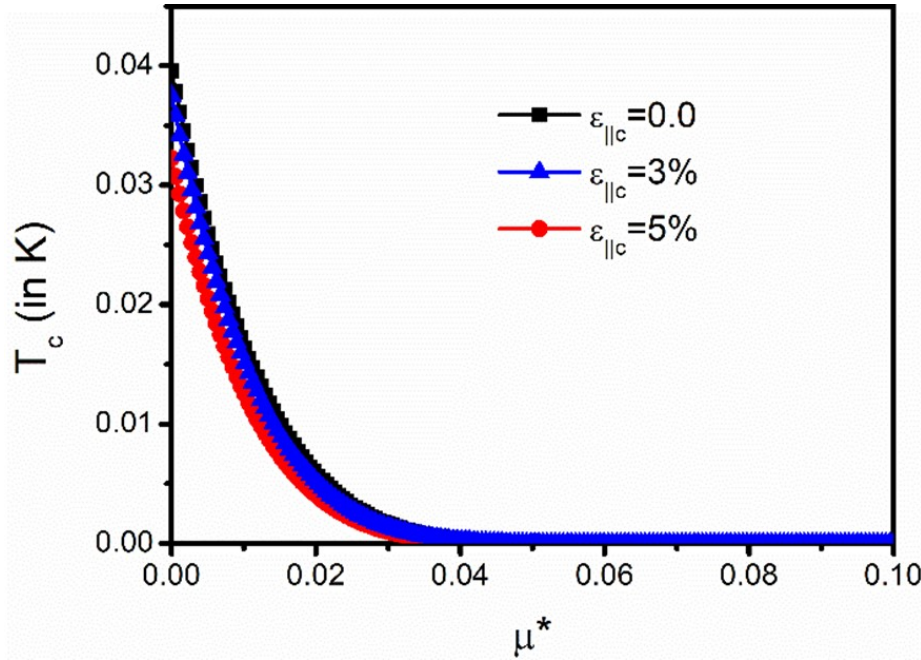


Figure 4.12: Calculated superconducting transition temperature (T_c) vs Coulomb repulsive constant (μ^*) for ZrB_2 under various compressive strain. A clear sign of suppression of T_c upon strain is concluded from the plot.

doped ZrB_2 .

With increased doping levels comes phonon softening, which, in turn, leads to the increased overall spectral weightage of $\alpha^2F(\omega)$. The spectral weight of lower frequency transverse acoustic (TA-1) phonons increases up to a doping level of $0.1e^-/\text{cell}$ and remains constant afterwards, while the contribution from high-frequency transverse acoustic (TA-2) and longitudinal acoustic (LA) modes increase continuously with increase in doping levels [see inset of Fig. 4.17(b)]. It is important to note here that a small but noticeable difference in $\alpha^2F(\omega)$ is observed between two different lattice relaxation methods (see Figs. 4.17 and 4.18(a)). While the contribution from acoustic phonons to $\alpha^2F(\omega)$ is fixed after a doping level of $0.1e^-/\text{cell}$, the contribution of optical phonons to $\alpha^2F(\omega)$ steadily increases with the doping level increment [see Fig. 4.17(b)].

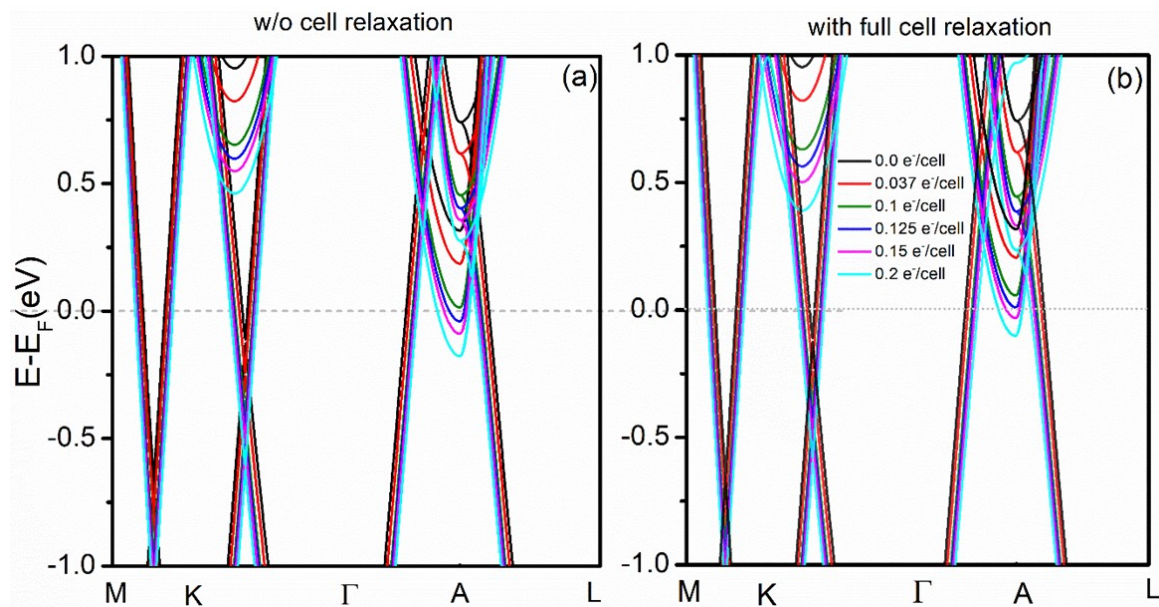


Figure 4.13: Calculated electronic band structure of electron doping in ZrB_2 for (a) only ionic relaxations while keeping the unit cell fixed and (b) complete relaxation of ions and unit cell. The dashed horizontal line marks the Fermi level.

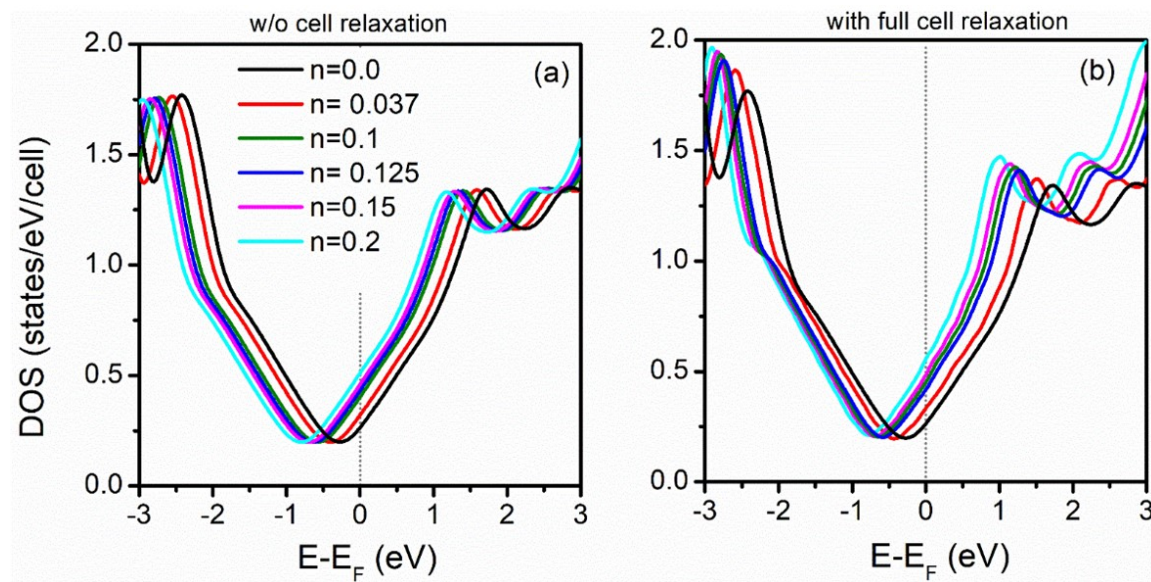


Figure 4.14: Calculated electronic DOS of electron-doped ZrB_2 for (a) only ionic relaxations while keeping the unit cell fixed and (b) complete relaxation of ions and unit cell. The dotted vertical line marks the Fermi level.

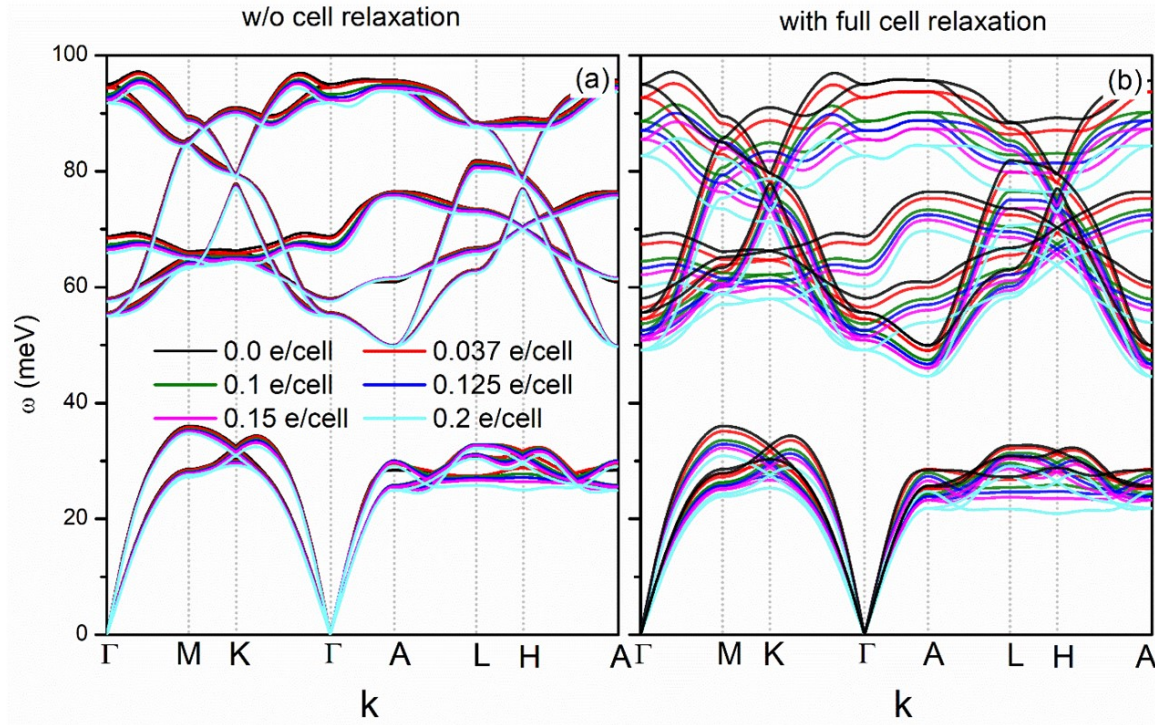


Figure 4.15: Calculated phonon dispersion of electron-doped ZrB_2 for (a) only ionic relaxations while keeping the unit cell fixed and (b) complete relaxation of ions and unit cell. Comparison of Figs. 4.14(a) and (b) shows that, for a given electron doping level, a full lattice relaxation in (b) results into larger phonon softening as compared to only ionic relaxation in (a).

The enhancement in λ is almost linear with the doping level, and it increased from 0.126 to 0.240 with an increase in the doping level from 0.0 to $0.2e^-/\text{cell}$ [see Fig. 4.17(c)]. Even though the phonon softening causes enhancement in λ , it has a detrimental effect on $\omega_{\log}$, which is lowered with increased doping levels [see Fig. 4.17(d)]. The quantitative difference in estimated λ and $\omega_{\log}$ with two different lattice relaxed configurations is clearly visible in Figs. 4.17(c) and (d). This can be attributed to a larger amplitude in phonon softening when the system is allowed for complete relaxation of both lattice parameters and ions (see Fig. 4.15).

The phonon softening in electron-doped ZrB_2 is obvious. However, the results from VCA are slightly different. We find phonon hardening in $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$

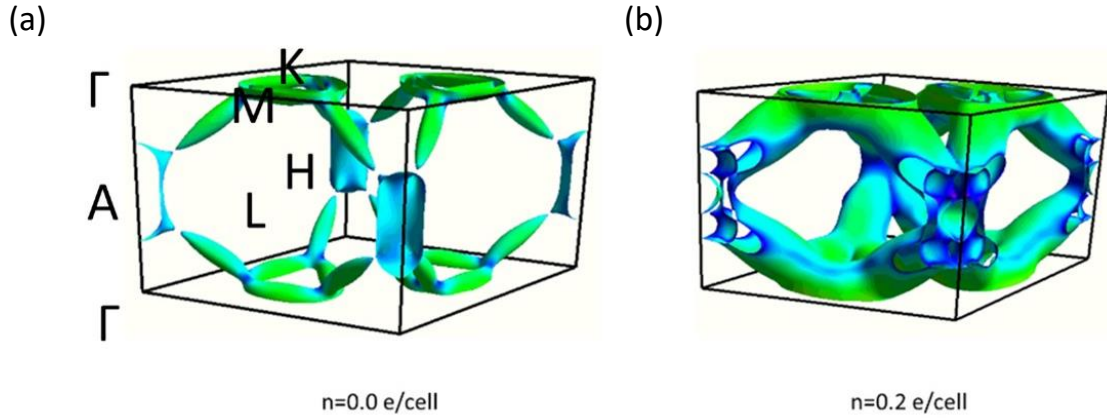


Figure 4.16: Fermi surface of undoped ($n = 0.0$ e/cell) and electron doped ($n = 0.2$ e/cell). Clearly, a 'fat' Fermi surface is observed along with new Fermi pockets at 'A' points in electron-doped ZrB_2 compared to undoped ZrB_2 .

and $\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$ as compared with ZrB_2 . The only exception is a small phonon softening of B_{1g} phonons within VCA (see Table I and Fig. 4.9(a)). Despite overall phonon hardening, we find an increase in spectral weight of $\alpha^2F(\omega)$ in $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$ and $\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$. This indicates that the electron states at the Fermi level $N(E_F)$ dictate EPC in doped ZrB_2 . To explain the enhancement in electron-phonon interaction and phonon softening for electron-doped ZrB_2 , we have calculated the Fermi nesting function ζ_q [see Fig. 4.20]. The nesting function ζ_q is the imaginary part of electronic susceptibility, responsible for the Fermi surface topology and one of the major terms in the Migdal-Eliashberg picture of electron-phonon interaction. By Eqs. (1.1) and (1.2), the increment in the nesting function can enhance the electron-phonon interaction, and this argument is supported by reported calculations (211; 278) on electron-phonon interaction.

The nesting function is one of the reasons behind the softening of the phonon modes and can be responsible for the charge density wave state (279–281). Further, the Fermi nesting function is associated with the imaginary part of electronic

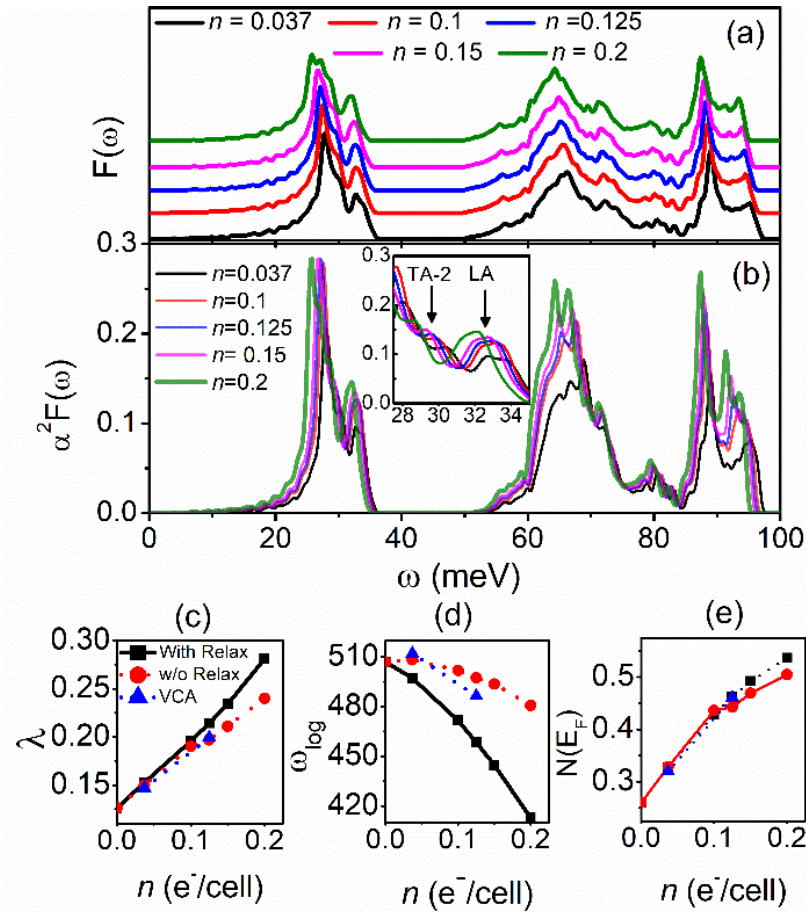


Figure 4.17: (a) Phonon density of states (DOS)[$F(\omega)$] of electron-doped ZrB_2 with different electron-doping concentrations (n in units of e^-/cell). (b) The isotropic Eliashberg spectral function [$\alpha^2 F(\omega)$] for various electron-doped levels are considered in this paper. The Inset of Figure (b) is an enlarged version of $\alpha^2 F(\omega)$ as a function of high acoustic phonon energies. Note that both (a) and (b) are obtained for the configuration at which only ionic degrees of freedom were allowed (see text for details). (c)–(e) Electron-phonon coupling constant (λ), logarithmic average of phonon frequencies ($\omega_{\log}$), and electronic DOS at the Fermi level [$N(E_F)$] as a function of doping concentrations, respectively. For virtual crystal approximation (VCA), n represents the V-doping concentration (x) in $\text{Zr}_{1-x}\text{V}_x\text{B}_2$.

susceptibility (282; 283), closely related to the Fermi surface topology (284), and strongly influences the electron-phonon interactions (285). With an increase in doping levels, we observed the appearance of electron-type Fermi pockets around the A points, with the overall Fermi surface becoming broader (see Fig. 4.16). It indicates that the Fermi surface topology has changed with electron doping, which

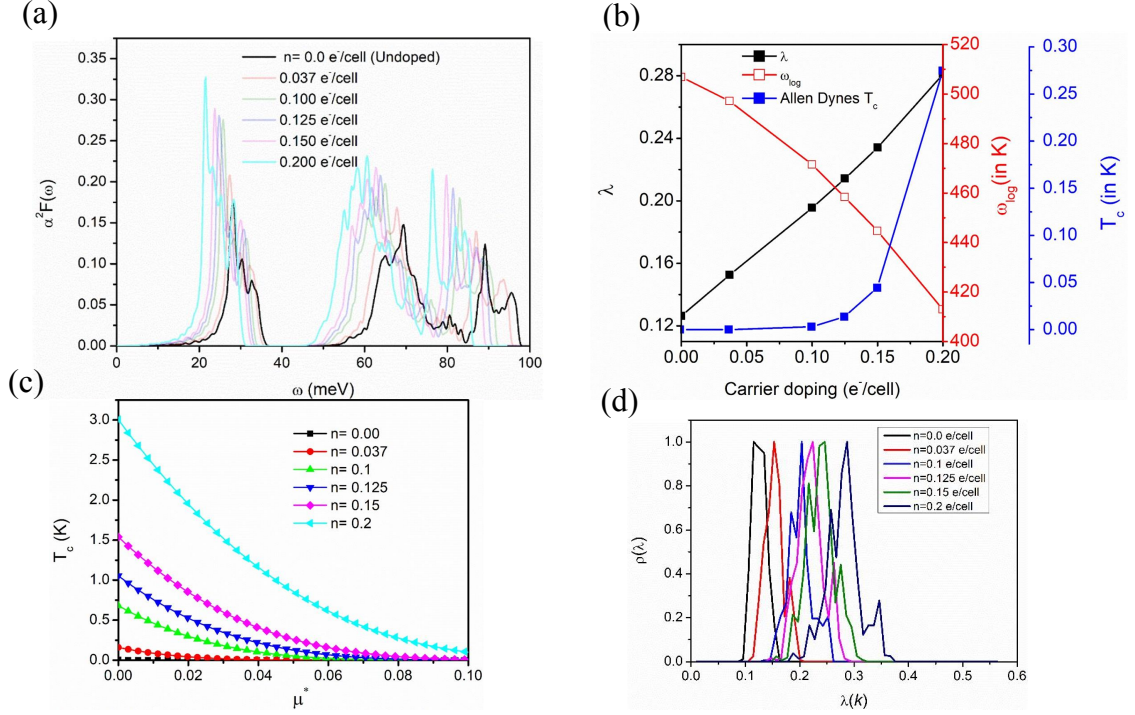


Figure 4.18: (a) Calculated isotropic Eliashberg spectra of electron-doped ZrB_2 for complete relaxation of ions and unit cell. (b) The integrated electron-phonon coupling constant (λ) (black squares), a logarithmic average of phonon frequency ($\omega_{\log}$) (red circles), and estimated superconducting transition temperature (T_c) by Allen-Dynes formula (blue triangles) for complete relaxation of ions and unit cell. We assume $\mu^* = 0.08$ when estimating T_c . (c) Estimated superconducting transition temperature (T_c) by Allen-Dynes formula vs μ^* for different doping levels. The unit of n is in e^-/cell . (d) shows the distribution of the electron-phonon coupling strength $\lambda(k)$ for ZrB_2 with and without electron doping (fixed lattice parameters).

also reflects in the broader peak in the Fermi nesting function [see Fig. 4.20]. In the electron-doped ZrB_2 case, the enhanced nesting function ζ_q further explains the phonon softening at higher doping. The estimated λ values for $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$ and $\text{Zr}_{0.875}\text{V}_{0.125}\text{B}_2$ are 0.147 and 0.199, which are close to 0.150 (0.037 e^-/cell) and 0.197 (0.125 e^-/cell) for electron-doped ZrB_2 [see Fig. 4.17(c)]. Similarly, computed $\omega_{\log}$ for the same cases are 511.9 and 486.3 K within VCA, in close agreement with values of electron-doped ZrB_2 [see Fig. 4.17(d)]. We also note that, in the case

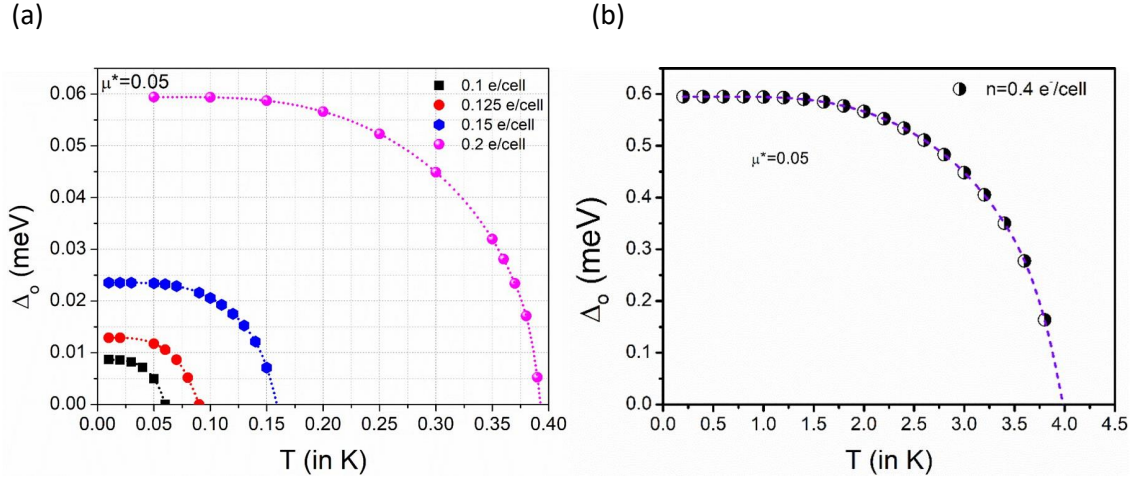


Figure 4.19: (a) Calculated superconducting gap (Δ_0) as a function of temperature for different doping levels. The dotted curves represent an extrapolation of computed data using the cubic-spline function. Note that for this given gap function, we used $\mu^* = 0.05$. (b) Calculated superconducting gap (Δ_0) as a function of temperature for the doping level of $n = 0.4$ e⁻/cell. To solve the gap equation, we used $\mu^* = 0.05$.

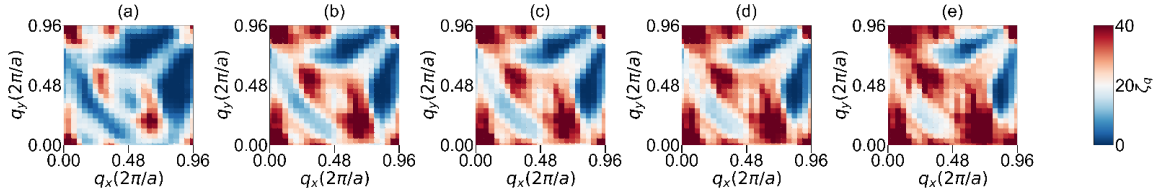


Figure 4.20: (a)-(e) q_x - q_y projected nesting function (ζ_q) computed over the irreducible wedge of the Brillouin zone of doped ZrB₂ the doping levels of 0.037, 0.1, 0.125, 0.15, and 0.2 e⁻/cell, respectively. Clearly, an enhancement in ζ_q with an increase in doping levels is observed.

where atomic configurations (i.e., cell parameters + ions) of bare electron-doped ZrB₂ could relax completely, a noticeable difference in λ and ω_{log} is found, particularly at higher doping levels [see Figs. 4.17(c) and (d)].

Now we calculate the superconducting transition temperature (T_c) using Eq.(1.3) and also estimate T_c by solving the isotropic Eliashberg gap [$\Delta(T)$] equations (16; 286). In the latter case, $\Delta(T)$ is interpolated by the cubic-spline technique, and T_c is

the temperature at which $\Delta(T) = 0$. We find that both methods provide similar values of T_c (see 4.19 and Figs. 4.21). We start by analyzing T_c with lowest extreme of μ^* . At the experimental doping level (4 of $V \leftrightarrow 0.037 e^- / \text{cell}$), the computed T_c ($\mu^* = 0.0$) is 0.14 K [see Fig. 4.21(a)]. This is much lower than the reported experimental values of 8.33 to 8.7 K. Despite an increase in the doping level to $n = 0.2e^- / \text{cell}$, T_c is estimated to be 1.8 K. It is important to note that the above mentioned T_c is the maximum extreme value, with a decrease of T_c with increasing μ^* [see Figs. 4.21(b) and (c)]. For $\mu^* = 0.05$, the computed T_c is in the range of 0.001 to 0.328 K with a doping level of 0.037-0.2 e^- / cell . Based on these results, the calculated T_c , for equal or even higher than experimental doping levels, is at least one order of magnitude lower than experimental values despite using an extremely minimal value of μ^* . The experimental value of T_c is obtained for a doping level of 0.4 Å/cell [$\approx 10^{22} \text{ cm}^{-3}$] and $\mu^* = 0.0$ [see Fig. 4.21(a)]. However, it does not appear reasonable to equate μ^* to zero at this high doping level. Using computed $N(E_F)$ for the doping level of 0.4 e^- / cell in Eq.(1.5), μ^* is estimated to be 0.11. These high values of μ^* result in a $T_c \approx 0.8$ K, one order of magnitude smaller than the experimental value of 8.3–8.7 K.

To find a possible explanation for this severe underestimation of T_c by the isotropic Eliashberg theory, we have calculated momentum-resolved electron-phonon interactions for various doping levels (see Fig. 4.18(d)). In all doping levels, the distribution of electron-phonon interaction has only a single peak for which spreading increases with doping. The maximally doped ZrB_2 has a shorter spread, reflecting its lesser anisotropic nature than MgB_2 (16). Unlike MgB_2 , doped ZrB_2 does not have isolated multiple sheets of the Fermi surface and is quite small, resulting in being more isotropic with lesser electron-phonon strength. These features of doped ZrB_2 provide a McMillan-Allen-Dynes T_c one order lower than that of MgB_2 using the isotropic Eliashberg theory (16). With more isotropic electron-phonon in-

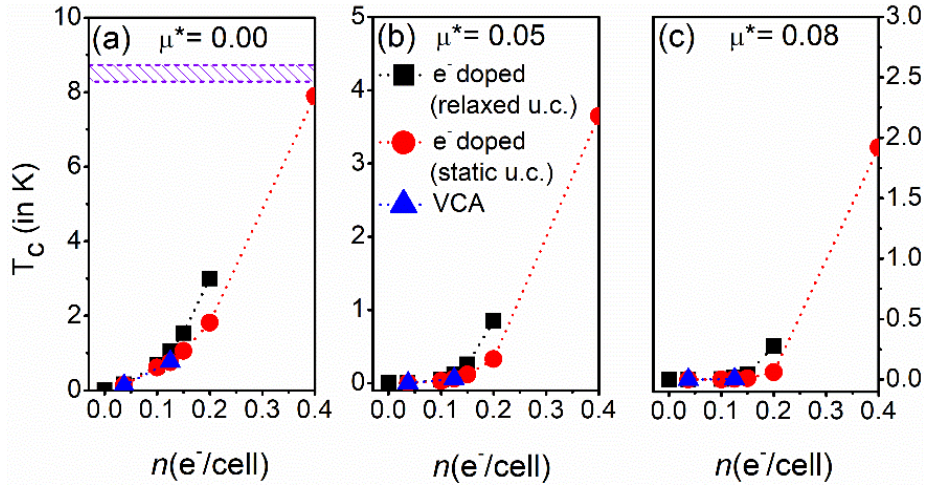


Figure 4.21: Calculated superconducting transition temperature (T_c) as a function of electron doping in a unit cell (u.c.) for three different values of effective screened Coulomb repulsion constant (a) $\mu^* = 0.0$, (b) $\mu^* = 0.05$, and (c) $\mu^* = 0.08$ in Eq.(1.3). For virtual crystal approximation (VCA), n represents the V-doping concentration (x) in $\text{Zr}_{1-x}\text{V}_x\text{B}_2$. The shaded region in (a) indicates the range of experimentally reported values (i.e., 8.3–8.7 K).

teraction, the nearly continuous Fermi surface and lower isotropic transition temperature indicate that the solution of the anisotropic Eliashberg equations will not result in the increase in the theoretical estimation of superconducting transition temperature for doped ZrB_2 as they do in pristine MgB_2 (16; 141; 287). It is important to note that V doping in ZrB_2 creates localized d -band defect states near the Fermi level (see Fig. 4.5), which could not be completely replicated in the electronic structure of electron-doped ZrB_2 nor within the VCA. Often, localized defect states enhance the average EPC strength (λ) in materials (288; 289). The formation of a VB_2 -like local region in $\text{Zr}_{1-x}\text{V}_x\text{B}_2$ may further enhance the average EPC strength as VB_2 has a relatively larger EPC strength ($\lambda_{\text{VB}_2} = 0.28$) and almost the same logarithmic average of phonon frequencies ($\omega_{\log}$) as ZrB_2 (290; 291). Also, the effect of local inhomogeneity of V in $\text{Zr}_{1-x}\text{V}_x\text{B}_2$ cannot be completely ignored, as it can play a non-trivial role in enhancing the superconducting transition temperature as observed in Cu-doped Bi_2Se_3 (292; 293). All these phenomena together

or individually may influence the average EPC strength (λ) and consequently the determination of the superconducting transition temperature (T_c). Thus, we suggest a mechanism beyond those investigated earlier is responsible for the observed superconductivity.

Experiments suggest that superconductivity in V-doped ZrB_2 has bulk nature. To eliminate the role of compositional fluctuations in V-doped ZrB_2 , Renosto *et al.* (241) carried out temperature (T)-dependence measurements of the specific heat (C_p) at zero applied magnetic field. A clear jump in C_p/T vs T^2 is observed, which was consistent with their magnetization (M) vs T and resistivity (ρ) vs T measurements. Similar observations were found for Nb-doped ZrB_2 (255). Both Renosto *et al.* (241) and Marques *et al.* (255) found that, at low temperature, the electronic contribution to specific heat at log scale [$\ln(C_e/\gamma T_c)$] as a function of T_c/T shows a clear deviation from typical Bardeen-Cooper-Schrieffer (BCS)-type behavior. The change in $\Delta C/\gamma T_c$ from non-superconducting to superconducting phase was determined to be 0.42 (241) and 0.15 (255), values that are considerably smaller than the weak-coupling BCS theory value (~ 1.43). The superconducting gap [$\Delta(0)$]-to-temperature (T) ratio in $\text{Zr}_{0.963}\text{V}_{0.037}\text{B}_2$, being $2\Delta(0)/k_B T_c \approx 8.95$, is much higher than the BCS theory of ≈ 3.5 (256). Along with the experiments discussed above, our theoretical results hint that superconductivity in V-doped ZrB_2 is of complex origin.

4.4 Conclusion

In summary, we have examined the origin of superconductivity in electron-doped AlB_2 -type ZrB_2 within Migdal-Eliashberg formalism using various approaches. We found that doping-induced uniaxial compressive strain along the c direction causes a weakening of the EPC owing to acoustic and low-frequency phonon hard-

ening, which suppresses superconductivity. Contrary to compressive strain, electron-doping-induced carriers strengthen the EPC due to the enhancement of densities of electronic states at the Fermi level as well as softening of both acoustic and optical phonons. Even though the calculated EPC constant in ZrB_2 is enhanced upon carrier doping, it is not sufficiently large to explain the superconducting transition temperature of 8.3–8.7 K within standard phonon-mediated superconductivity theory. The highest value of calculated superconducting temperature is one order of magnitude lower with respect to reported experimental transition temperatures, which indicates a complex origin of the superconductivity in ZrB_2 . The results indicate that further theoretical and experimental studies are required to understand the origin of this superconductivity. Electron doping in V-doped ZrB_2 can be related to a relatively localized V-4*d* orbital, whose role in the superconductivity warrants further investigation. The non-trivial topological-like bands appearing near the Fermi level of ZrB_2 , which are robust upon doping, may be important for this superconductivity.

Chapter 5

Long-range anisotropic Heisenberg ferromagnets and electrically tunable ordering

Recent realizations of intrinsic magnetic order in truly two-dimensional materials have opened new avenues in fundamental knowledge and spintronic applications. Here we develop an anisotropic Heisenberg model with relativistic exchange interactions that are obtained from the first-principles calculations. We demonstrate the crucial importance of magnetic interactions beyond the first-neighbour to qualitatively and quantitatively reproduce the experimental results. Once we ascertain the predictive capacity of the model for chromium trihalides and CrGeTe_3 , we investigate the feasibility of tuning the magnetic ordering by electrical means in these materials. A remarkable five-fold increase in the ferromagnetic Curie temperature is predicted in monolayer CrI_3 within experimentally obtainable hole density. The elusive microscopic mechanism behind the doping-dependent Curie temperature is illustrated. Further, in the present context, the effects of induced biaxial strain and chemical doping are also addressed. The results should trigger further experimental attention to test the present conclusions. The results of this chapter is reported in [Phys. Rev. B 103, 214411 \(2021\)](#).

5.1 Introduction

The magnetic anisotropy arising from the intrinsic spin-orbit coupling breaks the continuous rotational symmetry of spins on a lattice. Consequently, and in apparent contradiction to the Hohenberg-Mermin-Wagner theorem, (63; 64) the magnetic phase transition in two-dimension (2D) becomes susceptible at a finite temperature. (60–62; 294) Both single-ion and exchange anisotropies play decisive roles for the appearance of long-range magnetic order in 2D, and the long-wavelength excitation becomes gaped. Ising model description of magnetism is adequate only when the single-ion anisotropy is very strong, and an ordered phase emerges at a finite temperature as predicted by Onsager. (55) In contrast, the case with weak single-ion anisotropy is somewhat complicated, and an anisotropic Heisenberg model is required, where the spins can freely rotate in the three-dimensional space. (77; 295; 296) Accordingly, the ordering temperature is considerably suppressed due to spin fluctuations. In contrast, for a system with strong in-plane single-ion anisotropy, the magnetism is described by the XY model, and a quasi-long-range magnetic order is established by the Berezinskii-Kosterlitz-Thouless mechanism of topological defect formation. (297; 298)

Historically the search for magnetism in reduced dimension remained confined in the ultrathin films (299; 300) and layered magnetic materials with weak interlayer interactions. (301) While the ultrathin films of conventional bulk magnets retain magnetic ordering, their ordering temperature plunges much below the room-temperature in the quasi-2D limit. (299; 300) Further, their application becomes limited owing to the uncontrollable interaction with substrates and difficulties in producing uniform ultrathin layers. To circumvent these drawbacks, the search for van der Waals 2D magnets becomes imperative. However, it was only recently, in 2016; the existence of magnetic orderings was discovered in truly 2D

materials. Monolayer FePS₃ exhibited antiferromagnetic ordering, (60) while ferromagnetism was observed in atomically thin CrGeTe₃ and CrI₃ in the bilayer and monolayer limits, respectively. (61; 62) These seminal experimental results triggered a new field of research involving 2D magnets and attracted enormous attention due to fundamental physics interest as well as applications in emergent technologies. Thereafter, a few other insulating and itinerant 2D ferromagnets have been discovered such as CrCl₃, CrBr₃, VI₃, VSe₂, and Fe₃GeTe₂. (69–76) Several other 2D magnets, including the Cr-based ones, have been theoretically predicted via high-throughput computational screening. (302–306) Since the strength of magnetic anisotropies and the corresponding symmetry together dictate the underlying magnetic model, these 2D crystals with diverse anisotropy offer an opportunity to investigate the physics of different spin models and test their applicability in real materials. Further, integration of these 2D ferromagnets in van der Waals heterostructures may trigger emergent phenomena originating from the exchange proximity effects that could be utilized in disruptive technologies. (307–311)

Here, we particularly focus on the Cr-based ferromagnets, chromium trihalides and CrGeTe₃. (61; 62; 69–73) It was observed that the Curie temperature T_C increases with increasing perpendicular external magnetic field. (61; 62) This phenomenon, which is unprecedented in three-dimensional materials, indicates the significance of single-ion anisotropy in magnetic ordering on a 2D lattice. However, the magnitude of anisotropy is expected to be small from the minute Kerr rotation and less than 1 T spin reorientation field. This feature is also anticipated from the qualitative theoretical analysis. In all these materials, the Cr³⁺ ions form an in-plane honeycomb lattice and are subjected to an octahedral crystal field. From Hund's rules, we expect $S = 3/2$ state owing to $t_{2g}^3 e_g^0$ electronic structure with a completely quenched orbital moment. (70; 312; 313) Therefore, the single-ion anisotropy is expected to be very small below 1 meV and only originate from

the quantum fluctuation of the orbital moment in a distorted environment. (77) The magnetic interactions between Cr^{3+} ($S = 3/2$) spins arise due to the superexchange interaction via the non-magnetic ligands proposed by Anderson. (81) According to the Goodenough-Kanamori rules, (82; 83) the magnetic ordering depends both on the filling of d -levels and the cation-anion-cation angle φ . Following these rules, ferromagnetic interaction emerges between the half-filled t_{2g}^3 spins, since $\varphi(\text{Cr}-\text{X}-\text{Cr}) \sim 90^\circ$. Moreover, the corresponding theoretical description of T_C is strongly influenced by the presumed spin model, which is highly debated, and a complete picture is lacking. (77; 296; 314–318) Regardless of the expected inadequacy of single-ion anisotropy, CrI_3 was initially argued to have Ising behaviour. The exact solution for the Ising model on the honeycomb lattice provides $k_B T_C = 1.519 J S^2$, where J is the exchange interaction between the classical spins S . Thus, the Ising picture yields a considerably higher T_C of 90 - 130 K, (77; 296) which is much greater than the experimental value of 45 K. (62) Strong renormalization in T_C is due to the spin fluctuations owing to inadequate single-ion anisotropy and thus, spins in CrI_3 should be treated within anisotropic Heisenberg model. (77) A combination of various anisotropic interactions such as single-ion anisotropy, anisotropic exchange, Kitaev exchange and Dzialoshinskii-Moriya interaction has been considered with some success. (77; 296; 314–320) Although, the magnetic interactions beyond the first neighbour and their implications in 2D magnets are generally neglected in the literature.

Here, we develop a predictive yet straightforward spin model based on the first-principles calculations. We show that the long-range magnetic exchanges beyond the first-neighbour, along with the single-ion anisotropy, provide a better description of magnetic ordering and also render the correct spin excitations in a honeycomb lattice. In the context of elusive room-temperature ferromagnetism, we predict a five-fold increase in T_C for the CrI_3 monolayer under experimentally

attainable hole density. Further, the present model reproduces the experimentally observed trends in magnetism under carrier doping, and we provide a detailed microscopic mechanism. Moreover, we describe the effects of biaxial strain and chemical doping in the context of T_C manipulation. We also show that the present anisotropic Heisenberg model also characterizes other similar materials such as CrCl_3 , CrBr_3 and CrGeTe_3 .

5.2 Spin-Hamiltonian

To describe magnetism in these 2D materials, we propose a classical XYZ Heisenberg model Hamiltonian for the Cr^{3+} ($S = 3/2$) spins on a honeycomb lattice,

$$\mathcal{H} = -\frac{1}{2} \sum_{ij} \left[J_x S_i^x S_j^x + J_y S_i^y S_j^y + J_z S_i^z S_j^z \right] - \sum_i \mathcal{A}_z S_i^z S_i^z.$$

With $J_x = J_y = \mathcal{J}$ as the isotropic exchange coupling and $\Lambda = J_z - \mathcal{J}$ as the anisotropic exchange, the above Hamiltonian reduces to the XXZ Heisenberg Hamiltonian,

$$\mathcal{H} = -\frac{1}{2} \sum_{ij} \left(\mathcal{J} \mathbf{S}_i \cdot \mathbf{S}_j + \Lambda S_i^z S_j^z \right) - \sum_i \mathcal{A}_z S_i^z S_i^z.$$

The isotropic exchange coupling $\mathcal{J}$ between the neighbouring $\mathbf{S}_i$ and $\mathbf{S}_j$ spins favour either ferromagnetic $\mathcal{J} > 0$ or antiferromagnetic $\mathcal{J} < 0$ order. The symmetric term Λ in the anisotropic superexchange interaction originates from the spin-orbit coupling of the anion. In contrast, the antisymmetric Dzyaloshinski-Moriya (DM) interaction, $-\mathcal{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$ for the nearest-neighbor spins is zero due to the presence of inversion symmetry. Here, $\mathcal{D}_{ij}$ is the DM vector. However, it has been shown that in a hexagonal lattice structure and in the presence of inversion symmetry, a finite intrinsic $\mathcal{D}_{ij}$ perpendicular to the plane arises from the next-nearest-neighbor spin-orbit coupling. While such DM interaction may lead

to interesting topological properties, (321–324) the next-nearest-neighbor DM interaction is at least an order of magnitude smaller than the magnetic anisotropies that are the lowest energy scales in the Hamiltonian. (318) Therefore, it will be safe to ignore the DM interaction entirely in the present context of predicting magnetic phase transition. The $\mathcal{A}_z$ is the single-ion anisotropy and calculated for the ferromagnetic ground state. $\mathcal{A}_z > 0$ and $\mathcal{A}_z < 0$ indicate easy-axis and easy-plane magnetism, respectively. Since magnetic anisotropies are proportional to the spin-orbit coupling, we expect both Λ and $\mathcal{A}_z$ to be considerable in CrI_3 and CrGeTe_3 , while these should be much smaller in CrBr_3 and CrCl_3 . The other anisotropic terms such as the off-diagonal Kitaev interactions are not considered, since they are typically an order of magnitude smaller than the isotropic interaction. (315)

The above anisotropic Heisenberg Hamiltonian solely involving the nearest-neighbour exchange interactions have been used earlier. (77; 296; 314–320) While such a description provides a qualitative account, it typically underestimates the ordering temperature, and also fails to predict the correct experimental trends in magnetism under charge doping. (326) Moreover, such a nearest-neighbour consideration is not able to accommodate the complex spin excitations on the honeycomb lattice. These compel a spin model beyond the nearest-neighbour and consider the critical second- and third-neighbour interactions that can additionally describe the zigzag and stripy antiferromagnetic orders. Therefore, we extend the Hamiltonian to include the long-range isotropic and anisotropic exchange interactions,

$$\mathcal{H}_\ell = -\frac{1}{2} \sum_{k=1}^3 \sum_{\langle ij \rangle_k} \left(\mathcal{J}_k \mathbf{S}_i \cdot \mathbf{S}_j + \Lambda_k S_i^z S_j^z \right) - \sum_i \mathcal{A}_z S_i^z S_i^z,$$

where $\langle ij \rangle_k$ with $k = 1, 2, 3$ represents the first, second and third neighbours in the honeycomb magnetic lattice; $\mathcal{J}_k$ and Λ_k are the corresponding isotropic and anisotropic exchange interactions. Within the first-principles calculations, we will later show that the long-range isotropic and anisotropic interactions are con-

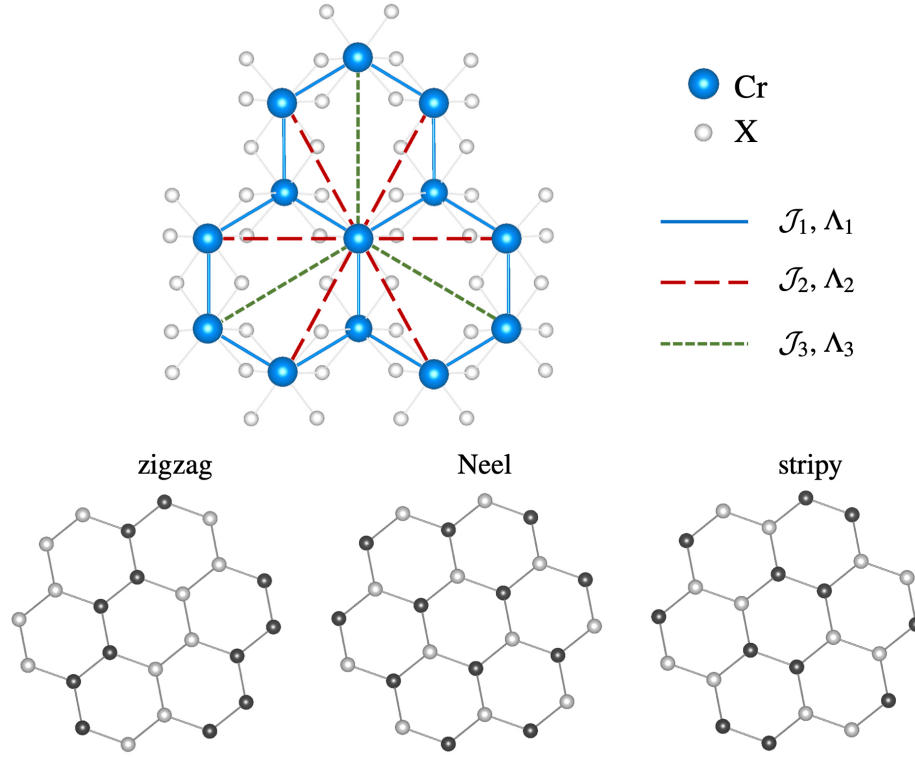


Figure 5.1: In the monolayers of CrX_3 ($X = \text{I, Br, Cl}$), the Cr^{3+} ions are arranged in a honeycomb lattice of edge-sharing $\text{Cr}^{3+} \text{X}_6^-$ octahedra. The magnetic interactions $\mathcal{J}_k$ and Λ_k till the third-neighbour are marked, which are crucial to describe the magnetic ordering. The bottom panel schematically represents three different antiferromagnetic structures with zigzag, Néel and stripy spin orders in the honeycomb lattice. Dark and light-coloured balls characterise antiparallel Cr-spins. Figure reprinted from (325) by permission of American Physical Society.

siderably large and comparable with the corresponding first-neighbour interactions. Further, these interactions become necessary to reproduce the correct experimental trend in the ordering temperature under carrier pumping.

The parameters of the above spin Hamiltonian $\mathcal{H}_\ell$ are calculated within the density functional theory-based calculations as implemented in the Vienna *ab initio* simulation package. (182; 183). Energies of the various magnetic configurations (Fig. 5.1) are fitted to the Heisenberg Hamiltonian $\mathcal{H}_\ell$. Additionally, different crystallographic orientations of the Cr-spins are also analyzed, by considering the relativistic spin-orbit coupling, to calculate various types of anisotropy energies. The wave functions within the spin-polarized density functional theory are described

within the projector augmented formalism with the plane-wave basis of 600 eV for the kinetic energy cutoff. (184) The exchange-correlation energy is expressed by the local density approximation (LDA) that is supplemented with the Hubbard-like on-site Coulomb interaction U for the localized Cr-3d electrons. We choose U_{Cr} to be 0.5 eV for CrI_3 and CrGeTe_3 throughout the calculations using the rotationally invariant Dudarev's method. (327) Relatively small value of U_{Cr} has been argued earlier, (315) which results from the strong hybridization of Cr-3d electrons with the shallow p -orbitals of the heavy ligands. In contrast, for CrBr_3 and CrCl_3 , we use a slightly higher U_{Cr} of 1 and 1.5 eV, respectively. While the right set of exchange-correlation functional and U_{Cr} are required for better quantitative agreements with the experimental results, a different choice of exchange-correlation functional and U_{Cr} exhibit the same qualitative results. A $2 \times 2 \times 1$ supercell with a vacuum space of 20 Å perpendicular to the surface is adopted, which ensures negligible interactions between the periodic images. The structures are completely optimized until all the force components are below the 5×10^{-3} eV/Å, along with a 10^{-8} eV threshold for the total energy convergence. The first Brillouin zone is sampled by a Γ centred $17 \times 11 \times 1$ Monkhorst-Pack $\mathbf{k}$ -grid. (198)

To study the phase transition and obtain the T_C , we implement Monte Carlo simulation on the 2D honeycomb lattice with the Hamiltonian $\mathcal{H}_\ell$. We consider a periodic 50×50 lattice consisting of 10^4 spins that minimize the finite-size effects. The Metropolis algorithm is employed with a single-site update scheme. (328) At every Monte Carlo step, a random spin $\mathbf{S}_i = (S^x, S^y, S^z)$ is selected, which is followed by an attempt to assign a new random direction in the three-dimensional space, $\mathbf{S}_i \rightarrow \mathbf{S}'_i$, using the Marsaglia procedure. (329) At every temperature, we run 2×10^8 Monte Carlo steps to ensure thermal equilibrium, and 192 independent simulations are used to reduce the statistical fluctuation. The ordering temperature T_C is calculated by fitting the magnetic order parameter, $m(T) = m_0(1 - T/T_C)^\beta$,

where β is the corresponding critical exponent.

5.3 Results and Discussion

First, we examine the magnetic ordering in chromium trihalides and CrGeTe_3 with honeycomb magnetic lattice and extensively analyze the results in the context of the available experimental data. Once we establish the applicability of the present model to describe magnetism in these 2D materials, we will continue to discuss the electrical tunability of the corresponding magnetic ordering.

5.3.1 Magnetic ordering in two-dimension

Calculations indicate that CrI_3 is a ferromagnetic insulator, and the magnetic moment is localized mostly at the Cr-sites on the honeycomb lattice. Various antiferromagnetic excited states persist within 7-16 meV/ CrI_3 energy, and the zigzag antiferromagnetic order is found to be the first excited state independent of exchange-correlation functional and on-site Coulomb interaction (Table 5.2). Such zigzag ground state is found in honeycomb antiferromagnets such as FePS_3 , (60) NiPS_3 , (330; 331) and quantum spin liquid candidates RuCl_3 (332) and Na_2IrO_3 . (333) In contrast, the previous calculations do not consider such spin excitation and the exchange interactions were extracted by considering the excited Néel order. (77; 296) The Cr-spins preferentially align perpendicular to the lattice plane, and the corresponding single-ion anisotropy $\mathcal{A}_z$ is 0.29 meV indicating easy-axis anisotropy (Table 5.1), which is in agreement with experiments. (62) Such a small $\mathcal{A}_z$ is indicative of quenched orbital moment at Cr with $t_{2g}^3 e_g^0$ electronic configuration and is consistent with the previous calculations. (77; 296; 315)

Table 5.1: Magnetic interaction parameters, in the anisotropic Heisenberg Hamiltonian $\mathcal{H}_\ell$, are obtained from the first-principles calculations including the spin-orbit coupling. The isotropic exchange $\mathcal{J}_k$ beyond the first-neighbour has a crucial contribution. In the undoped systems, the single-ion and exchange anisotropies, $\mathcal{A}_z$ and Λ_k , respectively, systematically increases with the spin-orbit coupling strength of the anion. The Curie temperatures T_C are calculated using the Monte Carlo simulations, and the results are in good agreement with available experimental data. The critical exponent β deviates from the two-dimensional Ising model, and the values agree with the experimental predictions.

	Isotropic exchange (meV)			Exchange anisotropy (μ eV)			A_z (meV)	Present	T_C (K)		β
	$\mathcal{J}_1$	$\mathcal{J}_2$	$\mathcal{J}_3$	Λ_1	Λ_2	Λ_3			Expt.		
CrI ₃	2.358	0.640	−0.636	−55.6	−55.6	155.5	0.289	42.5	45 (62)	0.215	
CrBr ₃	1.933	0.361	−0.322	9.7	−5.0	21.2	0.082	30.5	27- 34 (70; 71)	0.226	
CrCl ₃	1.142	0.165	−0.234	0	0	3.7	0.007	13	13 (69)	0.287	
CrGeTe ₃	5.522	−0.642	0.356	112.2	19.4	81.5	0.178	53	30 ± 5 (2L) (61)	0.213	
Mo _{0.25} Cr _{0.75} I ₃	2.392	0.551	−0.866	−38.9	−63.9	135.2	0.433	33	—	0.182	
W _{0.25} Cr _{0.75} I ₃	3.186	0.596	−0.731	−38.9	−75.0	101.9	0.778	50.5	—	0.205	

Moreover, the calculated $\mathcal{A}_z$ is in good quantitative agreement with the experimental estimate of 0.27 meV from the acoustic magnon energy shift interpolated to zero field. (334) The isotropic and anisotropic exchange interactions, $\mathcal{J}_k$ and Λ_k , are calculated by mapping the energies of the ferromagnetic ground state along with the zigzag, Néel and stripy antiferromagnetic orders with the anisotropic Heisenberg Hamiltonian $\mathcal{H}_\ell$ (Table 5.1). Both the in-plane and out-of-plane spin orientations are explicitly considered in this regard.

The exchange interactions beyond the first-neighbour are substantial, $|\frac{\mathcal{J}_3}{\mathcal{J}_1}| = 0.27$ and $|\frac{\mathcal{J}_2}{\mathcal{J}_1}| = 1$, for CrI_3 that can not be neglected (Table 5.1). Moreover, while the first- and second-neighbour interactions are ferromagnetic, $\mathcal{J}_3$ is antiferromagnetic. The anisotropic exchange interactions $\Lambda_k S_i^z S_j^z$ appear due to the strong spin-orbit coupling at the halide site. With these first-principles parameters $\mathcal{J}_k$, Λ_k , and $\mathcal{A}_z$ in the anisotropic XXZ Heisenberg Hamiltonian $\mathcal{H}_\ell$ (Table 5.1), we calculate the T_C using the Metropolis Monte Carlo method. We predict that the ferromagnetic ordering emerges at 42.5 K, which is in excellent agreement with the experimental T_C of 45 K. (62) It would be interesting to further decipher the quantitative importance of the second- and third-neighbour interactions in $\mathcal{H}_\ell$. We notice that the ordering temperature is severely underestimated to 28 K, while only the first-neighbour interactions, $\mathcal{J}_1$ - Λ_1 - $\mathcal{A}_z$, are considered. The inclusion of ferromagnetic $\mathcal{J}_2$ increases the ordering temperature and the corresponding $\mathcal{J}_1$ - Λ_1 - $\mathcal{J}_2$ - Λ_2 - $\mathcal{A}_z$ model overestimates the T_C to 55 K. Therefore, for a better quantitative description of magnetic ordering, the inclusion of interactions till the third-neighbour is essential. However, the long-range exchange interactions are largely neglected in the context of 2D magnetism. (77; 296; 314–320) To understand the critical behaviour of the system, we calculate β by fitting $m(T) = (1 - T/T_C)^\beta$ power-law near the phase transition and we estimate β to be 0.215 ± 0.002 . While there is no experimental estimation for the monolayer, consistent with the expected $\beta_{2D} < \beta_{3D}$

feature, the present result is slightly lower than the bulk CrI_3 , $\beta_{3\text{D}} = 0.249 \pm 0.014$ estimated via inelastic neutron scattering experiments. (317; 335)

We observe that while a different set of exchange-correlation functional and on-site Coulomb interaction provides a similar qualitative result, the ordering temperature is crucially dependent on the choice of U_{Cr} (Fig. 5.3). In this regard, we investigate CrI_3 with LDA and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals and varied the on-site Hubbard interaction within 0–2 eV range (Table 5.2 and Fig. 5.3). Independent of the functional and U_{Cr} , the qualitative results such as the ferromagnetic ground state and the signs of $\mathcal{J}_k$, Λ_k , and $\mathcal{A}_z$, remain unaltered. However, their magnitudes are greatly affected. Regardless the exchange-correlation description, the ferromagnetic $\mathcal{J}_1$ increases monotonically with U_{Cr} , $\mathcal{J}_2$ remains unaffected, and the magnitude of antiferromagnetic $\mathcal{J}_3$ decreases slowly (Fig. 5.2). In contrast, the anisotropic interactions are not significantly affected by U_{Cr} . Combined variations in the interaction parameters are reflected in the calculated T_{C} that increases with the on-site Hubbard interaction (Fig. 5.3). Further, we notice that the PBE functional systematically overestimates the T_{C} due to a much stronger first-neighbour isotropic $\mathcal{J}_1$.

The present results can be discussed in comparison with the Ising model. Note that, in the limit of $\mathcal{A}_z \rightarrow \infty$, the in-plane spin components are quenched, and all excitations will have spins aligned along the out-of-plane easy-axis. Consequently, the present spin model in $\mathcal{H}_\ell$ becomes asymptotically equivalent to the Ising model with $J_k^{\text{Ising}} = \mathcal{J}_k + \Lambda_k$. Assuming the first-neighbour interaction only, we estimate $T_{\text{C}}^{\text{Ising}} = 1.519(\mathcal{J}_1 + \Lambda_1)S^2/k_B \sim 91 \text{ K}$, which is also consistent with the Ising Monte Carlo simulations. However, $T_{\text{C}}^{\text{Ising}}$ is much higher than the experimental ordering temperature of 45 K, and the present prediction of 42.5 K within the anisotropic Heisenberg model. Further inclusion of the long-range interactions aggravates the situation, and through the Monte Carlo simulations, we obtain $T_{\text{C}}^{\text{Ising}}$ as 132 K,

Table 5.2: The lattice parameter of the monolayer CrI_3 and the relative energies of the various antiferromagnetic solutions with reference to the FM ground state crucially depends on the exchange-correlation functional E_{XC} and the supplemented on-site Coulomb interaction U_{Cr} . Spin-orbit interaction is included, and the relative energies are calculated when Cr-spins align along the $\langle 001 \rangle$ direction. Regardless the choice of E_{XC} and U_{Cr} , the ground state remains FM and the zigzag AFM order remains the first excited state.

	E_{XC}	U_{Cr} (eV)	a (Å)	Relative energy (meV/ CrI_3)			
				$\Delta_{\text{FM}}^{\text{FM}}$	$\Delta_{\text{Neel}}^{\text{FM}}$	$\Delta_{\text{Stripy}}^{\text{FM}}$	$\Delta_{\text{Zigzag}}^{\text{FM}}$
CrI_3	LDA	0.0	6.762	0	9.0	13.2	4.9
		0.5	6.774	0	12.3	15.6	7.2
		1.0	6.785	0	14.8	17.2	8.9
		1.5	6.799	0	16.7	18.1	10.5
		2.0	6.816	0	18.1	18.6	11.4
CrI_3	PBE	0.0	6.981	0	18.2	18.8	11.2
		0.5	6.995	0	20.3	19.9	11.7
		1.0	7.015	0	22.4	21.4	12.9
		1.5	7.026	0	24.3	22.8	13.8
		2.0	7.048	0	26.6	23.9	14.8

within the J_1 - J_2 - J_3 Ising model. In contrast, the rapid spin fluctuation owing to the small $\mathcal{A}_z$ is responsible for the strong renormalization of ordering temperature in CrI_3 .

Beyond the classical approximation, the Cr-spins can be treated by quantum mechanical $S = 3/2$ operators. Within the linear spin-wave approximation, the spin operators are expressed in terms of Holstein-Primakoff transformation. (336) At low temperature $S^z \simeq S$, and the spin excitations become gapped due to the magnetic anisotropy that is responsible for magnetic ordering in 2D. Within this formalism, the zero-temperature spin wave gap can be expressed as, (77; 296) $\Delta_0 = (2S - 1)\mathcal{A}_z + \sum_k N_k S \Lambda_k$, where N_k is the number of k -th nearest-neighbours; $N_k = 3, 6, 3$ for the first, second and third nearest-neighbours, respectively, for the honeycomb lattice. The calculated spin gap of $\Delta_0 = 0.54$ meV is in good agreement

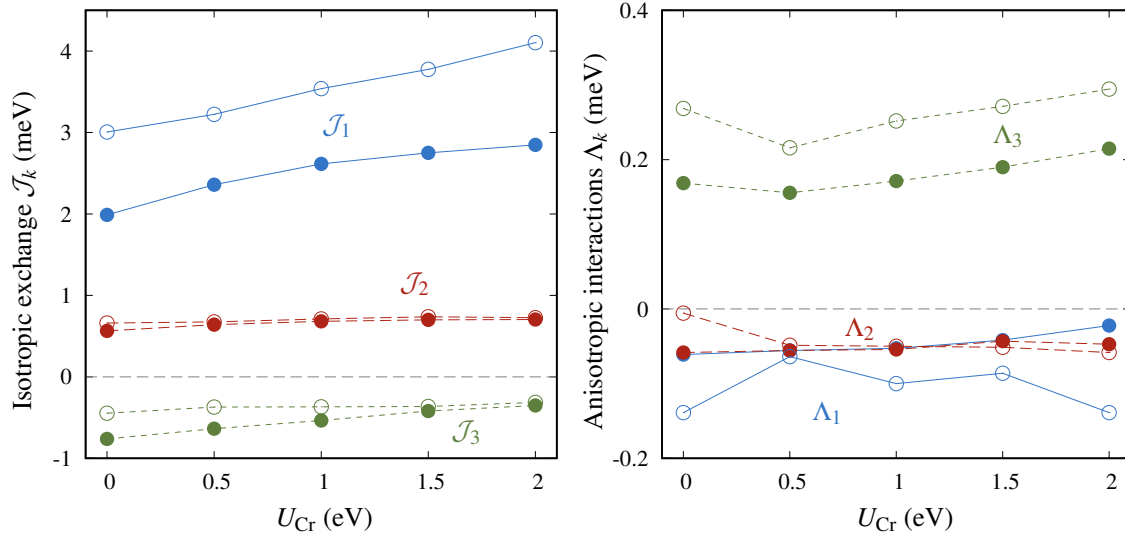


Figure 5.2: Both isotropic and anisotropic exchange interactions vary with on-site Coulomb interaction U_{Cr} . The LDA + U + SOC data is presented with the filled circles $\bullet$ and the same for the PBE + U + SOC is represented with the open circles $\circ$. Notice, that the first-neighbour J_1 has a dramatic effect over the choice of the exchange-correlation functional, and is responsible for higher T_C , predicted with PBE functional. In all cases $\mathcal{A}_z > 0$. Figure reprinted from (325) by permission of American Physical Society.

with the most recent experimental data such as the ferromagnetic resonance (0.3 meV), (316) inelastic neutron scattering experiment (0.37 meV), (317) and magneto-Raman spectroscopy. (334)

Having discussed the case of CrI_3 in details, it would be straightforward to describe the magnetic phase transitions in the other similar materials of interest, CrBr_3 , CrCl_3 and CrGeTe_3 . While CrBr_3 and CrCl_3 are isostructural to CrI_3 , the magnetic lattice of CrGeTe_3 also has honeycomb symmetry. Similar to CrI_3 , in all these materials, the ferromagnetic ordering emerges between the $\text{Cr}^{3+}(S = 3/2)$ spins according to the Anderson-Goodenough-Kanamori rules. The corresponding ordering temperature depends on their respective interaction parameters in the Hamiltonian $\mathcal{H}_\ell$. While Cr-ions in these materials have the same $t_{2g}^3 e_g^0$ electronic configuration, due to a reduction in the spin-orbit coupling strength at the halide

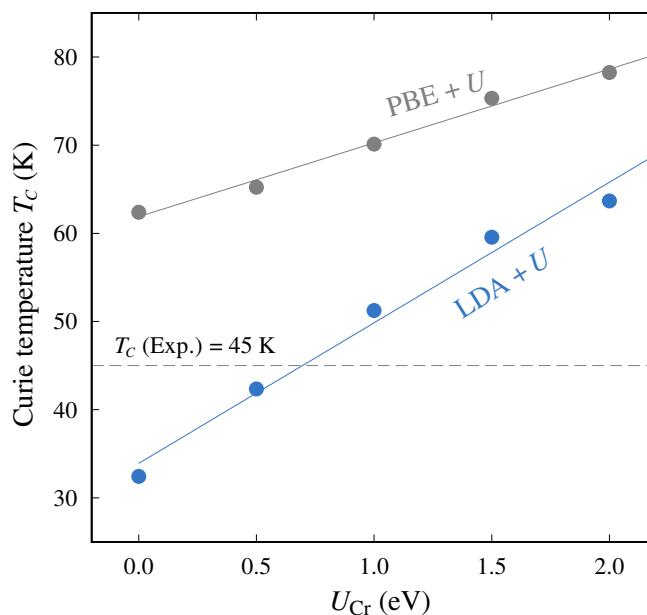


Figure 5.3: Magnetic interactions and therefore the T_C , crucially depend on the type of exchange-correlation functional and the on-site Coulomb interaction U_{Cr} . Magnetism in CrI_3 is better described by the LDA + U formalism. The calculated T_C of 42.5 K with the first-principles parameters and $U_{Cr} = 0.5$ eV is in excellent agreement with the experiment. (62) The spin-orbit coupling is considered for all the calculations. Figure reprinted from (325) by permission of American Physical Society.

side along $\text{I} \rightarrow \text{Br} \rightarrow \text{Cl}$ row, the magnitudes of both $\mathcal{A}_z$ and Λ_k are expected to decrease accordingly (Table 5.1), indicating a reduced preference to the out-of-plane orientation of the Cr moments. This trend has been experimentally demonstrated in mixed-halide $\text{CrCl}_{3-x}\text{Br}_x$ compounds. (337) The present results that includes the relativistic interactions are in qualitative agreement with earlier theoretical efforts, although different exchange-correlation functionals were used. (314; 319; 320)

Compared to CrI_3 , the lowering of spin-orbit coupling at the halide site results in smaller anisotropic magnetic interaction parameters Λ and $\mathcal{A}_z$ for CrBr_3 (Table 5.1). However, the nature of the isotropic interactions $\mathcal{J}_k$ remain unchanged. The Monte Carlo simulation reveal a ferromagnetic ordering temperature of 30 K, which is in good agreement with the experimental estimates of 27-34 K de-

terminated using the magneto-optical (70; 71) and micro-magnetometry measurements. (338) Since the bulk CrBr_3 orders at 37 K, (339) the relatively small decrease in T_C in monolayer suggest that the interlayer interaction in bulk and few-layer flakes is weak. The magnetization $m(T)$ follows $(1 - T/T_C)^\beta$ power-law and the best fit near the T_C yields $\beta = 0.226$, which is consistent with the monolayer CrI_3 (Table 5.1).

While layered antiferromagnetism persists till the bilayer CrCl_3 , (70; 72) the magnetism in monolayer remained elusive until recently. (69) The ordering temperature is recognised to be almost thickness independent, (70; 72) and CrCl_3 has been regarded as a two-dimensional easy-plane spin system with weak anisotropy, which is in contrast to both CrI_3 and CrBr_3 . However, theoretical calculations, including the earlier attempts, (314; 319; 320) are in contradiction, and we predict a weak easy-axis anisotropy (Table 5.1). It was argued that magnetic anisotropy is comparable to the magnetic shape anisotropy in CrCl_3 , which ultimately dictates the overall anisotropy to be in-plane. (340) Moreover, the present results on the free-standing monolayer may not be immediately compared to the recent experiment since CrCl_3 was deposited on graphene/6H-SiC(0001), resulting in substrate-induced trigonal distortions. (69) Such distortion may induce a stronger magnetic anisotropy compared to the present calculation. The nature of $\mathcal{J}_k$ follows similar trend, and second and third neighbour interactions are still significant (Table 5.1). However, the exchange anisotropies are found to be almost zero due to very weak halide spin-orbit coupling. Regardless the contradiction in $\mathcal{A}_z$, the calculated Cr-moment of $2.87 \mu_B$, T_C and β are in good agreement with the experimental data. (69) Using the magnetic interaction parameters in Table 5.1, we estimate the ferromagnetic T_C to be 13 K, which is in good agreement with 13 K determined by the element-specific X-ray magnetic dichroism. (69) Near the magnetic transition, the exponent β (0.287 ± 0.021) in CrCl_3 is larger than CrI_3 and

CrBr₃ monolayers.

The case of CrGeTe₃ is interesting, which in bulk orders around 65 K (341–344) that is slightly higher than the CrI₃ counterpart. (312) While a layer-dependent T_C is demonstrated, experimental observation of ordering has remained absent in the monolayer. (61) We notice that the monolayer CrGeTe₃ has easy-axis anisotropy in agreement with the bulk and few-layer samples. (341–344) Expectedly the $\mathcal{A}_z$ is weaker than that of CrI₃ (Table 5.1). The nature of exchange coupling is slightly different from the chromium trihalides; $\mathcal{J}_1$ remains ferromagnetic but with $\mathcal{J}_2 < 0$ and $\mathcal{J}_3 > 0$. The magnetic parameters from the first-principles calculations (Table 5.1) indicate expected ordering, which contrasts the experimental data to date. Within the anisotropic Heisenberg Monte Carlo, we determine the T_C to be 53 K, which is somewhat higher than the bilayer (30 ± 5 K) but comparable to the few-layer flakes, 52 ± 5 K for 5-layer CrGeTe₃. (61) In the bulk crystal, the Cr-moment decreases rapidly with increasing temperature, from $2.8 \mu_B$ (2 K) to $2.3 \mu_B$ at 60 K. (343) Considering this fact, we have recalculated the T_C using a smaller Cr-moment of $2.3 \mu_B$ along with the exchange parameters in the Table 5.1, which produces a lower T_C of 30.5 K ($\beta = 0.191$), which is in better agreement with the experiment. The calculated β for the monolayer is 0.213, which is in agreement with the bulk values of 0.177–0.242 that are experimentally determined. (341; 342) While we anticipate a ferromagnetic ordering in the monolayer according to the present results and also expect the same from the experimental trends in few-layer flakes, (61) it has remained practically elusive till date. Moreover, we will discuss later that accidental chemical contamination or passivation leading to small charge doping may destroy ordering in the monolayer limit. Therefore, in this regard, monolayer CrGeTe₃ should draw further theoretical and experimental attention.

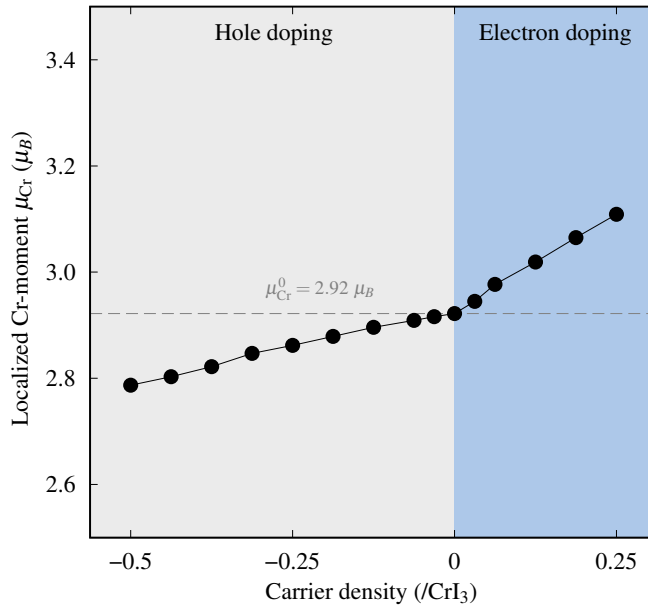


Figure 5.4: Variation of localized Cr-moment with charge doping. The magnetism is still described by the localized Cr-moment, which is barely perturbed ($< 5\%$). Therefore, the Heisenberg model provides a good description of magnetic phase transition under charge doping. Figure reprinted from (325) by permission of American Physical Society.

5.3.2 Manipulation of magnetism

Electric control of magnetism is of fundamental interest in nanoscale magnetic devices. (346) Interlayer magnetic coupling in bilayer CrI_3 and the strength of magnetic order in three-layer Fe_3GeTe_2 have been altered by inducing charge via electrostatic gating. (76; 345; 347) A three-fold increase in the ferromagnetic ordering temperature is reported in three-layer itinerant Fe_3GeTe_2 flakes. Therefore, it would be worthwhile to explore the effects of electrostatic gating in these 2D materials. It should be noted here that despite an insulator to metal transition under charge doping, the magnetism is nevertheless described by the localized Cr-moments. Therefore, the present Heisenberg model is univocally applicable under charge doping (Fig. 5.4).

We observe contrasting consequences of hole and electron doping on the or-

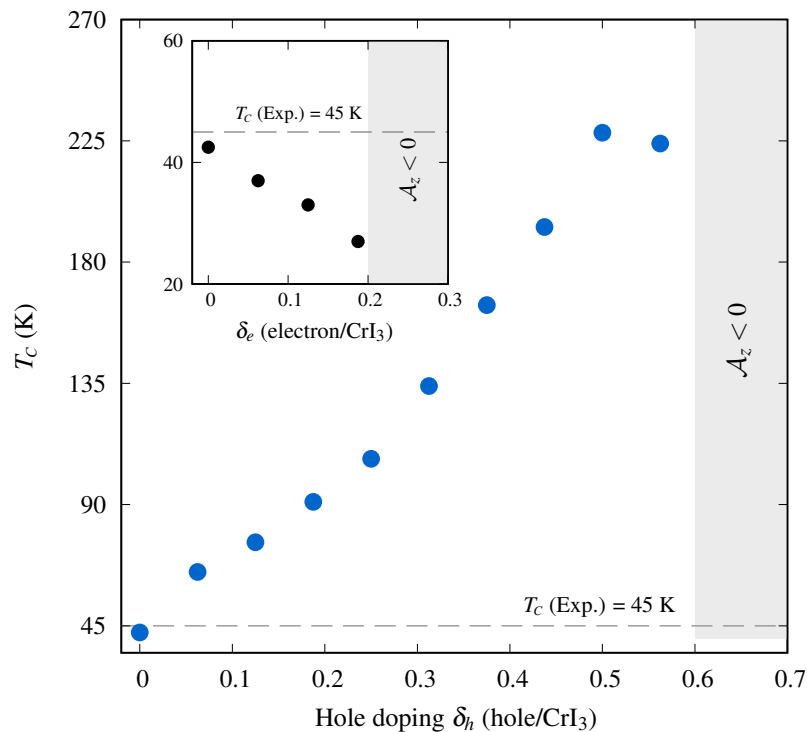


Figure 5.5: The Curie temperature T_C of single-layer CrI₃ is critically affected by the carrier doping, which could be electrically exploited. The experimental T_C of 45 K for the neutral monolayer CrI₃ (62) is well reproduced within the present long-range and anisotropic Heisenberg model. The hole and electron (inset) doping has contrasting effects. Calculated T_C gradually increases with hole doping, and the increase is as much as five-fold for $\delta_h = 0.5$ hole/CrI₃, which is equivalent to $2.66 \times 10^{14} \text{ cm}^{-2}$ hole density. Such a level of doping could be achieved through ionic gating or femtosecond laser pulse. In contrast, the electron doping, shown in the inset, has a detrimental effect, since the T_C gradually decreases with increasing doping level δ_e . The overall trends are in agreement with the experimental observations. (345) Beyond certain doping densities, the Cr-moments prefer in-plane orientations with $A_z < 0$. Figure reprinted from (325) by permission of American Physical Society.

dering temperature (Fig. 5.5), and the present results also corroborate the experimental observations under electrostatic gating. Hole doping strengthens the ferromagnetic order in monolayer CrI₃, while electron doping weakens magnetism (Fig. 5.5). Calculated Curie temperature T_C increases monotonically upon hole injection, and rises as much as five-fold to 228 K at an experimentally achievable hole density of $\delta_h = 0.5 \text{ hole/CrI}_3 \sim 2.66 \times 10^{14} \text{ cm}^{-2}$. In contrast, electron dop-

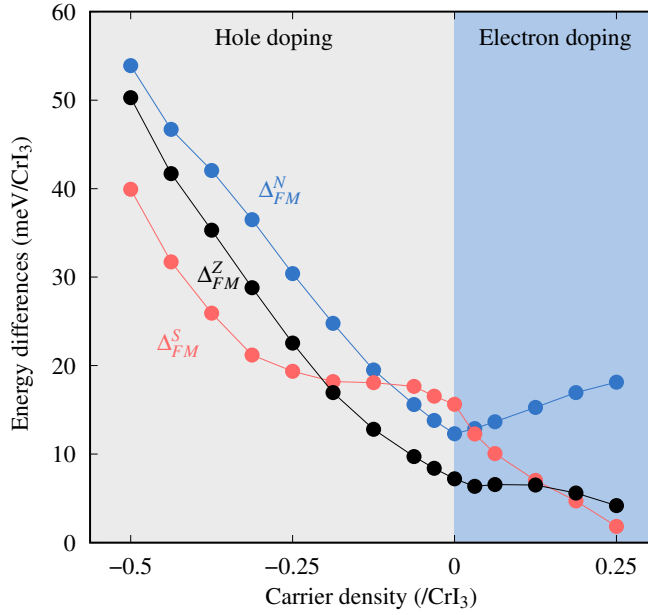


Figure 5.6: Relative energies of the various antiferromagnetic states as a function of carrier density. Relative energies are calculated with respect to the ferromagnetic ground state; $\Delta_{\text{FM}}^{\text{N}} = E(\text{Neel}) - E(\text{FM})$, $\Delta_{\text{FM}}^{\text{S}} = E(\text{stripy}) - E(\text{FM})$, and $\Delta_{\text{FM}}^{\text{Z}} = E(\text{zigzag}) - E(\text{FM})$. Note that for both electron and hole doping, the Néel structure becomes more and more unfavourable with increase in charge density as $\Delta_{\text{FM}}^{\text{N}}$ increases. Figure reprinted from (325) by permission of American Physical Society.

ing shows deleterious influence, as T_{C} consistently decreases to 27 K at a density $\delta_{\text{e}} = 0.2$ electron/ CrI_3 (Fig. 5.5). We also observe that at a critical electron and hole densities the magnetism in monolayer CrI_3 switches to in-plane orientation, $\mathcal{A}_{\text{z}} < 0$. Interestingly, another phase transition is observed at high density above 0.4 electron/ CrI_3 , and a stripy AFM ($\mathcal{A}_{\text{z}} > 0$) emerges as the ground state. The present results correspond well with the experimental trends, where differing impacts were discerned upon electron and hole doping. (345) At a low doping level of about $\delta \sim 2.5 \times 10^{13} \text{ cm}^{-2}$, a 10% rise or reduction in T_{C} was realised via hole and electron doping, respectively. (345) While a charge density below $3 \times 10^{13} \text{ cm}^{-2}$ has been experimentally realised, (345) a much higher density beyond 10^{14} cm^{-2} should be feasible through ionic gating or femtosecond laser pulse in CrI_3 . For example, very high electrostatic doping of $4 \times 10^{14} \text{ cm}^{-2}$ has been obtained in

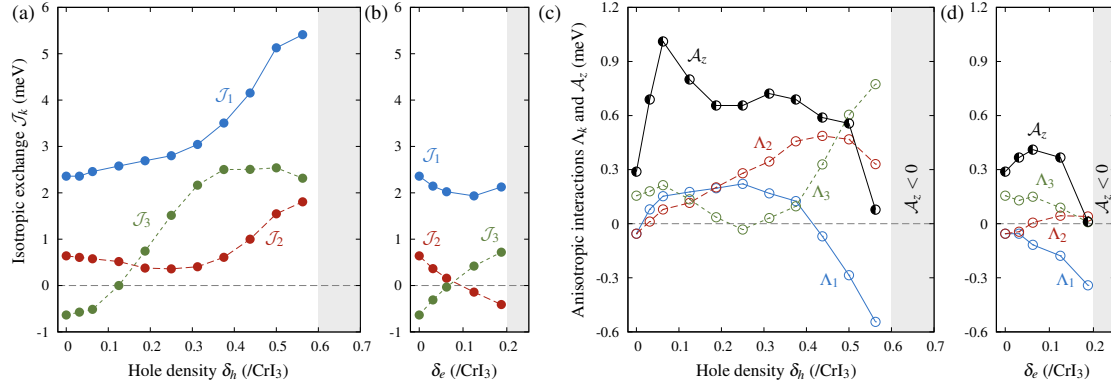


Figure 5.7: For the monolayer CrI₃, the microscopic dependence of the various magnetic interactions on carrier doping that can be electrically controlled. (a) and (b) show the variations in the isotropic exchange interactions $\mathcal{J}_k$ with hole and electron doping, respectively. $\mathcal{J}_k$ are severely affected by carrier doping. (c) and (d) represent the variations in the anisotropic magnetic interactions Λ_k and $\mathcal{A}_z$ with δ_h and δ_e , respectively, which are mostly non-monotonous. The complex interdependence of orbital occupancies, the local and orbital moments, and the resulting on-site spin-orbit coupling drive the intricate doping dependence. Beyond the critical hole and electron density, the magnetism switches, and the Cr-moments prefers in-plane orientation, $\mathcal{A}_z < 0$, which is represented by the shaded region. These variations in $\mathcal{J}_k$, Λ_k and $\mathcal{A}_z$ dictate the discussed doping-dependent ordering temperature T_C (Fig. 6.10), and qualitatively corroborates the experimental observations. (345) Figure reprinted from (325) by permission of American Physical Society.

monolayer MoS₂ via ionic liquid gating. (348; 349) Further, a very high density of carriers $\sim 3.2 \times 10^{14} \text{ cm}^{-2}$ were injected via femtosecond pulse laser in a few-layer ferromagnetic Fe₃GeTe₃. (350)

The present trends described in Fig. 5.5 are in contradiction with the earlier theoretical predictions, where an increase in ordering temperature was perceived in both electron and hole-doped monolayers. (326) We argue this disagreement to correlate with an inadequate description of magnetism considered earlier. In this context, it is intriguing to understand the situation if we only considered the first-neighbour interaction, and calculate $\mathcal{J}_1$ and Λ_1 using the energy difference, $\Delta_{\text{FM}}^{\text{N}} = E_{\text{Neel}} - E_{\text{FM}}$ (Fig. 5.6); similar to that in Ref. (326). Qualitative analysis indicates that under such incomplete magnetic description, both electron and hole

doping contributes to the increase in ordering temperature. However, the minimalistic picture of only first-neighbour interaction fails to reproduce the correct experimental dependence, (345) along with the present results (Fig. 5.5). This analysis further establishes the importance of long-range exchange interactions in predicting the ordering temperature under electrostatic doping.

Although an observation similar to that described in Fig. 5.5 has been made experimentally, the microscopic mechanism of doping dependent T_C remains unclear. (345) The present results reveal that the fundamental interdependence of various magnetic interactions with doping (Fig. 5.7) is responsible for the observed trend. We find that charge doping severely alters the isotropic exchange couplings $\mathcal{J}_k$ as well as both types of anisotropic interactions Λ_k and $\mathcal{A}_z$ (Fig. 5.7). The isotropic $\mathcal{J}_1$ and $\mathcal{J}_2$ remains ferromagnetic upon hole doping and follow a similar behaviour [Fig. 5.7(a)]. Below a critical hole density of $\delta_h < 0.4$ hole/CrI₃, $\mathcal{J}_1$ and $\mathcal{J}_2$ are only slightly affected, and beyond this density these exchange interactions increase very rapidly. In contrast, the antiferromagnetic $\mathcal{J}_3$ is critically affected by the hole doping with $\delta_h < 0.4$ hole/CrI₃, but remains unaltered with further increase in doping level [Fig. 5.7(a)]. At low doping, the antiferromagnetic $\mathcal{J}_3$ monotonically increases with hole density and changes sign to become ferromagnetic. In the case of electron doping, $\mathcal{J}_1$ decreases with increasing doping, while $\mathcal{J}_2$ and $\mathcal{J}_3$ show opposite trends [Fig. 5.7(b)]. The isotropic $\mathcal{J}_2$ ($\mathcal{J}_3$) decreases (increases) monotonically with δ_e and consequently changes the nature of magnetic coupling at a particular density.

Charge doping perturbs the orbital occupancies that are reflected in the calculated moments localized at the Cr-sites. The $|\mu_{Cr}|$ decreases gradually with hole doping, and the trend is reversed for the electron doping. However, the change is only about $\pm 5\%$ within the entire doping range considered in Fig. 5.5. In analogy with an earlier experiment, a similar trend is witnessed in the saturation magne-

tization. (345) Compared to μ_{Cr} , the induced $|\mu_I|$ moment is severely affected by the charge doping but shows a trend opposite to the μ_{Cr} . The $|\mu_I|$ is $0.04 \mu_B$ for the neutral case, which increases to $0.06 \mu_B$ at 0.5 hole/CrI_3 , and decreases to 0.03 at $0.25 \text{ electron/CrI}_3$. The orbital moments μ_{orb}^{Cr} and μ_{orb}^I are also affected by the charge doping. The μ_{orb}^{Cr} (μ_{orb}^I) decreases (increases) to $0.047 \mu_B$ ($0.017 \mu_B$) at $\delta_h = 0.5 \text{ hole/CrI}_3$ from $0.091 \mu_B$ ($0.008 \mu_B$) for the neutral CrI_3 monolayer. In contrast, the orbital moments are not affected significantly upon electron doping.

Therefore, orbital occupancies, local and orbital moments together perturb the on-site spin-orbit coupling energies that eventually trigger modifications in various anisotropic magnetic interactions [Fig. 5.7(c) and 5.7(d)]. Overall, the variations in Λ_k and $\mathcal{A}_z$ are non-monotonous. The anisotropic exchange interactions Λ_1 and Λ_2 are negative for the neutral CrI_3 , which change sign with hole doping and remain positive except $\Lambda_1 < 0$ beyond 0.4 hole/CrI_3 [Fig. 5.7(c)]. In contrast, Λ_3 remains positive and raises sharply for $\delta_h > 0.4 \text{ hole/CrI}_3$. The single-ion anisotropy $\mathcal{A}_z$ increases sharply with hole doping at low density, which then gradually falls with a further increase in δ_h . Finally, the nature of magnetism changes completely at very high hole density $\delta_h > 0.6 \text{ hole/CrI}_3$ and the Cr-spins prefer in-plane orientation with $\mathcal{A}_z < 0$ [Fig. 5.7(c)]. Electron doping, on the other hand, has contrasting behaviour. While Λ_1 and Λ_3 decreases with increasing doping, the Λ_2 increases in comparison and changes sign at a density [Fig. 5.7(d)]. Compared to the hole doping, $\mathcal{A}_z$ shows a similar trend due to electron doping. However, the XY-type spin preference is observed at a much lower density δ_e [Fig. 5.5(d)]. The combinatorial doping dependencies of $\mathcal{J}_k$, Λ_k and $\mathcal{A}_z$ result in contrasting doping-dependant T_C for the hole and electron doping (Fig. 5.5), and also corroborate the microscopic mechanisms behind the similar experimental observations. (345)

The multiorbital picture of superexchange interactions can also corroborate the doping-dependent T_C in Fig. 5.5. The Cr^{3+} -ions with $t_{2g}^3 e_g^0$ electronic configura-

tions interact via $t_{2g}^3 - t_{2g}^3$ and $t_{2g}^3 - e_g^0$ orbital channels. According to the Kugel-Khomskii mechanism, (351) the half-filled $t_{2g}^3 - t_{2g}^3$ exchange interaction is antiferromagnetic, whereas the interaction between the t_{2g}^3 and the empty e_g^0 is ferromagnetic. In the monolayer CrI_3 , the competing $t_{2g}^3 - e_g^0$ superexchange dominates ensuring a ferromagnetic state for the system. Such multiorbital superexchange is complex, and the orbital occupancies play a critical role, which is affected by the charge doping. At a finite hole density δ_h , a partial hole δ_o is introduced at the t_{2g}^3 orbital, which destabilises the antiferromagnetic $t_{2g} - t_{2g}$ interactions. Therefore, a stronger ferromagnetism emerges with hole doping. Qualitatively, the δ_o further increases with hole doping, and the overall ferromagnetic exchange coupling gradually increases [Fig. 5.7(a)], which consequently leads to a gradual increase in the ferromagnetic ordering temperature (Fig. 5.5). The description for the electron doping follows a similar argument, and a partial charge δ_e is introduced at the empty e_g^0 orbital at a finite δ_e . This δ_e destabilises the ferromagnetic $t_{2g} - e_g$ interaction, and the ferromagnetic ground state becomes weaker upon electron doping. Since δ_e increases with electron doping, the resultant ferromagnetic exchange interaction decreases monotonically [Fig. 5.7(b)] and the ferromagnetic T_C gradually decreases (Fig. 5.5).

It would be relevant to address the effects of strain while explaining the electrostatic doping dependent magnetism in CrI_3 . The lattice constants are modified under charge doping, and a biaxial tensile (compressive) strain is produced due to electron (hole) injection (Fig. 5.8). While maintaining an external in-plane compressive strain in two-dimension is not practical, (352) we investigate its effect to disentangle the contribution on T_C . The intrinsic strain induced by the charge doping ultimately perturbs the magnetic interactions in $\mathcal{H}_\ell$, and consequently affects the ordering temperature. Therefore, it would be appealing to decouple the contribution from the induced lattice strain itself. For the undoped CrI_3 monolayer,

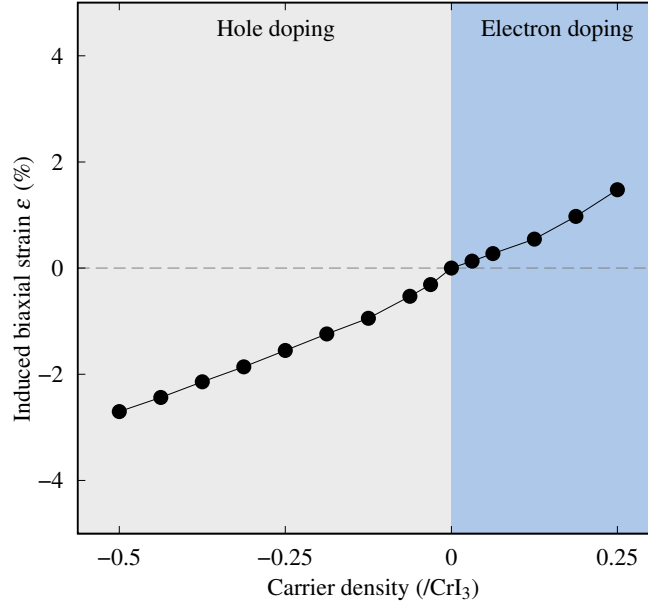


Figure 5.8: Biaxial tensile (compressive) strain is produced due to electron (hole) doping. Figure reprinted from (325) by permission of American Physical Society.

the ferromagnetic $\mathcal{J}_1$ is strongly affected under the biaxial strain and monotonically decreases with both compressive $\varepsilon < 0$ and tensile $\varepsilon > 0$ strains [Fig. 5.9(a)]. While the ferromagnetic $\mathcal{J}_2$ and antiferromagnetic $\mathcal{J}_3$ exhibit a weaker dependence with increasing or decreasing lattice parameters. We also note that under a sizeable compressive strain beyond -3% , the monolayer CrI_3 undergoes a magnetic phase transition and becomes antiferromagnetic with Néel order [Fig. 5.9(a)]. Further, the Cr-spins rearranges from out-of-plane to in-plane orientation with $\mathcal{A}_z < 0$ [Fig. 5.9(b)]. Consolidating the microscopic variations of the magnetic interactions described in Fig. 5.9(a)-(b), we predict that T_C decreases under both compressive and tensile strains [Fig. 5.9(c)]. However, note that at a small strain range $-1\% < \varepsilon < 1\%$, the T_C remains unaltered. Present results are consistent with the earlier efforts. (314) It was also experimentally found that the hydrostatic pressure alters the interlayer magnetic coupling in thin CrI_3 flakes, and the T_C in bulk. (353; 354) However, in contrast to the monolayer, the bulk CrI_3 behaves differently since the T_C was observed to increase with the hydrostatic pressure, and was explained to

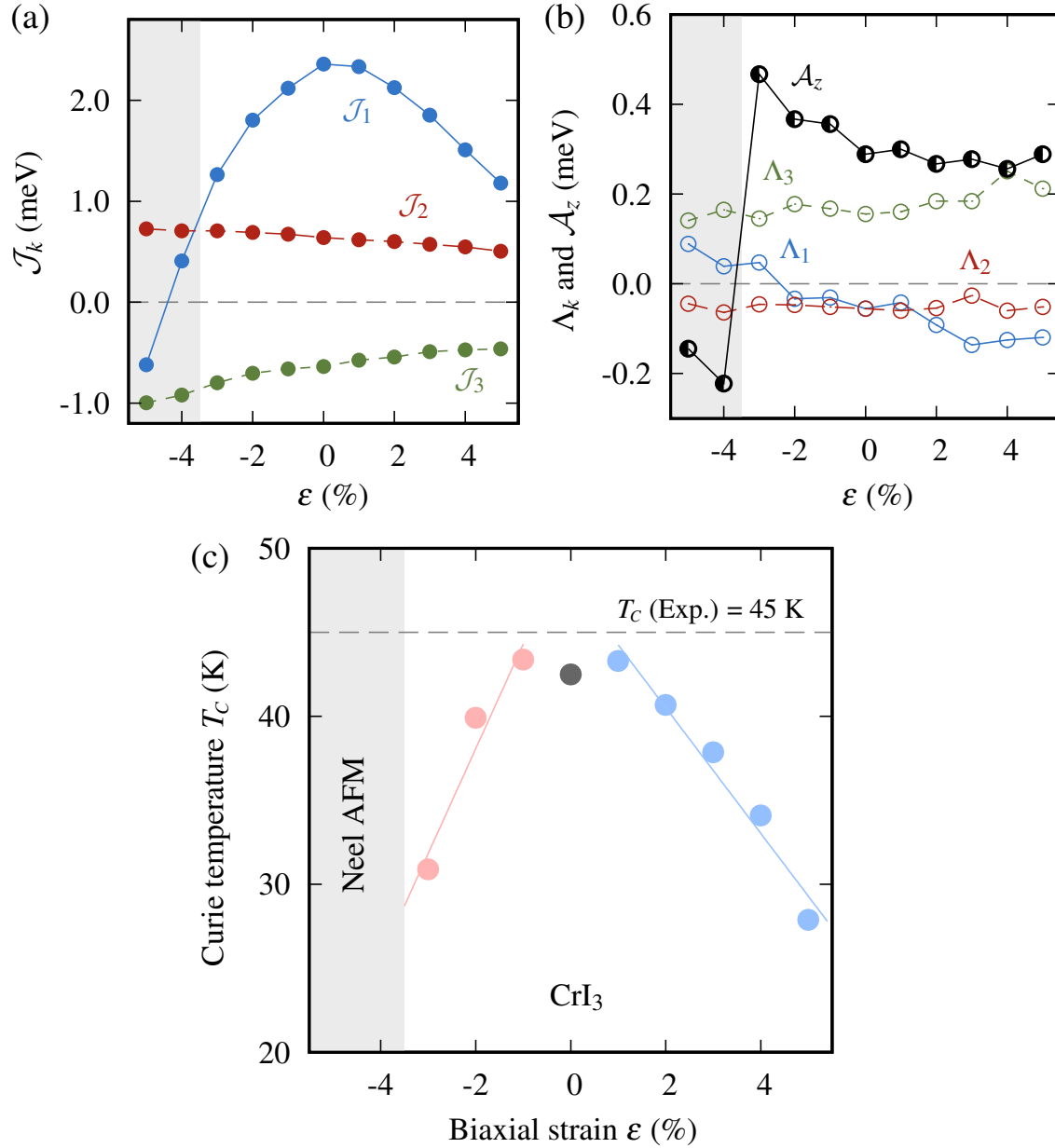


Figure 5.9: Bi-axial strain ϵ in the CrI_3 honeycomb lattice modifies the magnetic interactions and thus the ferromagnetic T_C . (a)-(b) Variations of $\mathcal{J}_k$, Λ_k and $\mathcal{A}_z$ on the compressive ($\epsilon < 0$) and tensile ($\epsilon > 0$) strains. While at a moderate strain the monolayer remains ferromagnetic, for a large compressive strain above -3% , CrI_3 becomes antiferromagnetic with in-plane Néel order. (c) Calculated T_C gradually decreases under the influence of both compressive and tensile strains. Figure reprinted from (325) by permission of American Physical Society.

the modulation in interlayer exchange coupling. (355)

Now we analyse the above results in the context of the strain induced by charge

doping. A 2.7% biaxial compressive strain is induced by 0.5 hole/CrI₃, and the corresponding T_C decreases to 33 K for the updoped monolayer with this value of strain. This observation is in contrast to the finding in Fig. 5.5, which indicates that the hole-induced increase in ordering temperature is entirely of electronic origin. A similar qualitative conclusion can be drawn for the tensile strain produced by electron doping. A maximum of 1% tensile strain is induced with δ_e studied in Fig. 5.5, and at this strain level T_C remains unaffected [Fig. 5.9(c)].

Inspired by the present results on monolayer CrI₃ (Fig. 5.5), we investigate the effects of charge doping in CrGeTe₃. However, and to our surprise, we notice that the results are contrary to CrI₃. The out-of-plane magnetism in the neutral CrGeTe₃ switches easily upon charge doping, and the Cr-moments prefer in-plane orientation ($\mathcal{A}_z < 0$). Unlike CrI₃, the critical density is order-of-magnitude lower, which is less than $0.025/\text{CrGeTe}_3 \sim 1.27 \times 10^{13} \text{ cm}^{-2}$. The results indicate that the magnetism in monolayer CrGeTe₃ could be easily perturbed and becomes a 2D-XY system, resulting in suppressing ordering, which might explain the non-observation of magnetic ordering in the monolayer. We also conclude that a charge-induced increase in ordering temperature is not a generic feature in 2D ferromagnets, but chemical constituents are crucial.

Similar to charge doping, chemical doping may also tune the anisotropic magnetic couplings. We have previously discussed that since spin-orbit coupling strength at the anion-site drops from CrI₃ to CrCl₃; the magnetic anisotropies decline monotonically (I $\rightarrow$ Br $\rightarrow$ Cl), resulting in decreasing ordering temperature (Table 5.1). This fact has also been experimentally confirmed in mixed halide compounds such as CrCl_{3-x}Br_x. (337) Similarly, anisotropies can be modulated by doping at the cation-site. In this regard, we investigated Mo_{0.25}Cr_{0.75}I₃ and W_{0.25}Cr_{0.75}I₃ (Table 5.1), where both Mo and W are isoelectronic to Cr and assumes identical oxidation and spin states. Indeed the single-ion anisotropy $\mathcal{A}_z$ increases considerably

in these materials (Table 5.1). Compared to the pristine CrI_3 monolayer, the nature of the magnetic interactions are qualitatively the same in these materials, but the magnitudes of $\mathcal{J}_k$ and Λ_k are altered due to doping-dependent lattice parameters. Compiling all the interactions in Table 5.1 into the Monte Carlo simulations reveal that while the T_C increases to 50.5 K in $\text{W}_{0.25}\text{Cr}_{0.75}\text{I}_3$, it decreases to 33 K for $\text{Mo}_{0.25}\text{Cr}_{0.75}\text{I}_3$. Therefore, we argue that chemical doping is not a promising route toward achieving the elusive room-temperature ferromagnetism in 2D.

5.4 Summary and outlook

To describe magnetism in 2D materials, we develop an anisotropic Heisenberg model with exchange interactions beyond the first-neighbour, which has been primarily neglected earlier.^(77; 296; 314–320) The parameters of the model, single-ion anisotropy, isotropic and anisotropic exchange interactions, are calculated from the relativistic first-principles calculations. We demonstrate that the second and third neighbouring magnetic interactions on a honeycomb lattice are critical to qualitatively and quantitatively explain the existing experimental results and trends. The model incorporates various spin excitations on a honeycomb lattice and quantitatively reproduces the experimental T_C for the monolayer ferromagnetic insulators such as CrI_3 , ⁽⁶²⁾ CrBr_3 , ^(70; 71) and CrCl_3 . ⁽⁶⁹⁾ For CrGeTe_3 , while we predict a magnetic ordering in the monolayer, the experimental demonstration remains elusive. However, the layer-dependent T_C ⁽⁶¹⁾ and the present results indicate that a long-range ordering in the monolayer should exist, and therefore, further experimental and theoretical investigations are necessary. Small on-site magnetic anisotropy in these materials triggers finite-temperature spin fluctuations, and therefore the corresponding critical temperatures are much lower than the corresponding Ising picture. The magnetic critical exponent β ranges between

0.21 to 0.29 for the monolayers, which are expectedly but only slightly lower than their bulk analogues. (317; 335; 338; 341; 342; 356) This fact signifies a weaker interlayer magnetic coupling in the bulk and few-layer flakes; and the nature of magnetism grossly remains thickness-independent. Moreover, the calculated β for the monolayers lie between the values corresponding to the 2D Ising ($\beta = 0.125$) and 3D Heisenberg ($\beta = 0.365$) models. Due to the presence of various magnetic anisotropies, the spin excitation becomes gapped, and the zero-temperature spin-wave gaps are in agreement with a range of measurements such as ferromagnetic resonance, (316) inelastic neutron scattering experiment, (317) and magnetoraman spectroscopy. (334) While the present model has been adopted for the honeycomb lattice, it is readily applicable to materials with different lattice symmetries.

The predictive model described here can be further employed to investigate the impacts of various external perturbations and chemical doping. We illustrate that charge doping critically affects the isotropic and anisotropic magnetic interactions that modify the ordering temperature. Moreover, hole doping considerably enhances the T_C and a five-fold increase to 228 K is witnessed at $2.66 \times 10^{-14} \text{ cm}^{-2}$ hole density. Such a high carrier density is experimentally realizable in the 2D materials through electrostatic gating (348; 349) or femtosecond laser pulse. (350) In contrast, electron doping has a detrimental effect on the ordering as T_C gradually decreases. We notice that below a critical carrier density, the magnetism remains out-of-plane and beyond which it switches to the in-plane orientation as $\mathcal{A}_z$ changes sign. While a similar qualitative trend is followed experimentally at a lower carrier density, (345) here we also render the elusive microscopic mechanism for carrier tuneable magnetism (Fig. 5.5). We further describe the effects of induced biaxial strain in the honeycomb lattice and find that the compressive and tensile strains modify the magnetic interaction parameters such that in both cases,

the ordering temperature decreases monotonically. Considering the trend of T_C in neutral CrI_3 under the biaxial strain, we conclude that carrier tuneable magnetism is entirely of electronic origin. Overall, while we argue that electrical manipulation of ordering temperature is a promising route to achieve room-temperature ferromagnetism in the 2D van der Waals materials, chemical doping seems not so encouraging. The present results should motivate further experimental studies in this regard.

Chapter 6

Electrical tunable room temperature ferromagnetism in CrBr_3

High-temperature ferromagnetism and its control in ultrathin materials are of critical interest in disruptive quantum technologies. However, intrinsic ferromagnetic ordering in recently discovered two-dimensional materials is limited to cryogenic temperatures due to fundamental spin fluctuation in reduced dimensions. While chromium trihalides order below 45 K, we report a dramatic manipulation of long-range ferromagnetic order above room-temperature in CrBr_3 monolayer predicted within the first-principles long-range Heisenberg XXZ model. Gate-induced charge carrier doping externally modulates various magnetic interactions in the Mott insulating monolayer, and a nontrivial magnetic phase diagram emerges. Under varied hole density, the monolayer remains ferromagnetic with Curie temperature increasing monotonically, while electron doping triggers a complex evolution of magnetic phases. The microscopic details are investigated, and the high-temperature ferromagnetism is attributed to the substantial increase in effective ferromagnetic exchange and magnetic anisotropies under an experimentally attainable hole density. Such electrically controlled ferromagnetism in CrBr_3 stands for experimental verification and presents enormous new possibilities for spintronic and magnetoelectric quantum devices based on atomically thin crystals. The findings of the current chapter is appeared in [Phys. Rev. Materials 6, 084407 \(2022\)](#).

6.1 Introduction

Relativistic magnetic anisotropy is indispensable for a finite-temperature phase transition in two dimensions. The continuous rotational symmetry of the spin, which is the fundamental assumption of the Hohenberg-Mermin-Wagner theorem, (63; 64) is broken by the magnetic anisotropy originating from the relativistic spin-orbit coupling in natural materials. The long-wavelength spin excitation becomes gapped for finite anisotropy, and a long-range magnetic ordering emerges at a non-zero temperature. (61; 62; 294) Moreover, different anisotropic magnetic interactions determine the magnitude of the spin gap, which in turn dictates the ordering temperature. (77) In natural materials, the on-site single-ion anisotropy is significantly small owing to weak spin-orbit coupling strength. Therefore, the celebrated Ising or XY models cannot predictably describe magnetism. Instead, an anisotropic Heisenberg model is a suitable descriptor that accounts for the spin fluctuations and, thus, significantly renormalises the ordering temperature. To date, the discovered two-dimensional magnetic materials function at cryogenic temperatures, (61; 62; 70–77; 294) hindering their potential utilisation in disruptive technologies.

Since the intrinsic ferromagnetism has been experimentally witnessed in two-dimensional van der Waals crystals of CrGeTe₃ (61) and CrI₃, (62) a few other ferromagnetic materials have been identified. Nevertheless, the Curie temperature in all these materials persisted much below the room-temperature. (70–76) The insulating monolayer of chromium trihalides ferromagnetically orders below the liquid-nitrogen temperature, with a maximum of 45 K in CrI₃. (62; 70–72) The Curie temperature of bilayer CrGeTe₃ and monolayer Fe₃GeTe₂ is also much below the ambient temperature, at 30 and 130 K, respectively. (61; 357) While manganese selenides are antiferromagnetic in bulk, the room-temperature ferromagnetism is

observed in single-layer MnSe₂. (358) Yet it is not clear if the ferromagnetism is intrinsic or results from the defects and interfacial effects in samples grown by molecular beam epitaxy on vdW substrates. Similarly, the high-temperature ferromagnetism in 1T-VSe₂ remains doubtful, despite considerable attention. (75; 359; 360) Contradictory results of room-temperature ferromagnetism and high-temperature charge density wave phase that suppresses any magnetism have been reported. Consequently, intrinsic ferromagnetism above room-temperature remains elusive, and the fundamental question of Curie temperature manipulation arises naturally.

Intrinsic magnetism may be controlled by coupling to external perturbations such as strain, (314) nanoscale patterning, (361) gating, (76; 325; 345; 347) chemical doping (362) and intense light. (350) Moreover, the electric control of magnetism has colossal importance in nanoscale magnetic devices and has already proven effective in vdW materials. For instance, the nature and strength of exchange interactions in Fe₃GeTe₂ and CrI₃ have been altered by injecting charge carriers through electrostatic gating. (76; 325; 345; 347) The gate voltage controls the ordering temperature, saturation magnetization, coercivity, and interlayer magnetic coupling in insulating CrI₃. (325; 345; 347) Further, ordering in itinerant Fe₃GeTe₂ thin flakes shows a three-fold increase reaching beyond room-temperature. (76) Interactions with the femtosecond laser pulse can also drive the ferromagnetic ordering to a higher temperature, as demonstrated recently in few-layer Fe₃GeTe₂. (350) While some experimental success has been reported in controlling the long-range ordering, the underlying microscopic mechanism down to the various magnetic interactions remains unexplored.

Charge doping in two-dimensional materials has intriguing consequences, and new physics may emerge. In Mott insulators, carrier density away from the half-filling may nontrivially modify the underlying quantum magnetism. Indeed, we electrically manipulate the magnetism in Mott insulating CrBr₃ monolayer, and the

room-temperature ferromagnetism emerges in the hole-doped regime of the phase diagram. Predictions are made within a long-range anisotropic XXZ Heisenberg model, where the parameters are obtained from the relativistic first-principles calculations. While monolayer CrBr₃ orders below 30 K, (70; 71; 310; 338) the phase transition is pushed beyond 300 K under hole doping with experimentally feasible density. In contrast, electron doping has an insignificant effect on the ordering temperature, but it triggers a complex evolution of magnetic phases. We further elaborate on the microscopic origin of the electrically controllable magnetic phase diagram and disentangle the concurrent effects of induced strain. The present results indicate that CrBr₃ warrants further experimental attention to test the present predictions.

6.2 Spin Hamiltonian and density functional methods

We consider the anisotropic XXZ Heisenberg model Hamiltonian with interactions beyond the first neighbour, (325)

$$\mathcal{H} = -\frac{1}{2} \sum_{k=1}^3 \sum_{\langle ij \rangle_k} \left(\mathcal{J}_k \mathbf{S}_i \cdot \mathbf{S}_j + \Lambda_k S_i^z S_j^z \right) - \sum_i \mathcal{A}_z S_i^z S_i^z,$$

where $\langle ij \rangle_k$ with $k = 1, 2, 3$ represents the first, second and third neighbours in the honeycomb magnetic Cr³⁺ ($S = 3/2$) lattice. The second and third neighbour interactions are critical to characterize magnetism in two-dimensional magnets. (325) $\mathcal{J}_k$ and Λ_k are the corresponding isotropic and anisotropic exchange interactions. The neighbouring spins $\mathbf{S}_i$ and $\mathbf{S}_j$ are coupled ferromagnetically $\mathcal{J}_k > 0$ or antiferromagnetically $\mathcal{J}_k < 0$. The spin-orbit coupling at the anion produces symmetric anisotropic superexchange Λ_k , which is fundamentally crucial for magnetic ordering. $\mathcal{A}_z$ represents the on-site single-ion anisotropy, and $\mathcal{A}_z > 0$ ($\mathcal{A}_z < 0$) indicates

easy-axis (easy-plane) magnetism. We demonstrated earlier that such a spin model provides a quantitative description of the experimental results. (325)

The parameters of the anisotropic Heisenberg spin model are extracted from the relativistic first-principles calculations by fitting the energies of the ordered magnetic phases. We use the configurations in FM and collinear AFM states, such as Néel, zigzag and stripe, where the Cr-spins are oriented either along the in-plane or out-of-plane directions. Wave functions in the density functional theory are expressed within the projector augmented formalism (184) as implemented in the Vienna *ab initio* simulation package. (182; 183). A plane-wave basis of 600 eV for the kinetic energy cut-off is used, and the spin-orbit coupling is considered. Local density approximation is used to represent the exchange-correlation energy, which is supplemented with the Hubbard-like on-site Coulomb interaction U_{Cr} (1 eV) for the localized 3d-electrons. (327) A $\pm 20\%$ change in U_{Cr} retains the qualitative and quantitative physics intact (Figure 6.3). To describe all possible magnetic structures, we consider a $2 \times 2 \times 1$ supercell, and the first Brillouin zone is sampled with a Γ -centred $17 \times 11 \times 1$ Monkhorst-Pack k -grid. (198) A vacuum space of 20 Å is assumed to minimize the interactions between the periodic images. The structures are optimized until all the force components are below the 5×10^{-3} eV/Å threshold. A uniform background of compensating counter charge is considered for the charge-doped systems. The lattice parameter, ionic positions, and charge density are then self-consistently optimized. The magnetic phase transition is studied using the Heisenberg Monte Carlo method on a periodic 50×50 lattices consisting of 10^4 spins that minimize the finite-size effects. A random direction to a random three-dimensional spin $\mathbf{S}_i \rightarrow \mathbf{S}'_i$ is considered using the Marsaglia procedure, (329) followed by an update within the Metropolis algorithm. (328) To ensure thermal equilibrium, 2×10^8 Monte Carlo steps are employed at every temperature, and 192 independent simulations are used to reduce the statistical

fluctuation. The Curie temperature T_C is calculated by fitting the magnetic order parameter, $m(T) = m_0(1 - T/T_C)^\beta$, where β is the critical exponent.

The free-standing layers are an excellent model system to investigate magnetism in two-dimensional materials. While bare flakes may be chemically reactive in ambient conditions, the ultrathin magnetic materials are exfoliated in a glove box under an inert atmosphere and encapsulated in graphite, graphene, and hBN layers to minimize the environmental effects. (62; 70; 345; 347) Moreover, the CrBr₃ flakes are much more air-stable in an ambient environment than CrI₃. (71) Furthermore, the explicit consideration of substrate is also unwarranted since the dielectric screening from the non-magnetic substrate does not influence intrinsic magnetism. (62; 70; 345; 347) While the substrate can cause lattice strain and thereby indirectly influence the exchange interactions, it has been shown that such an effect is negligible. (325) It should also be noted that the gate-induced charge will be uniformly distributed in atomically thin 2D materials as discussed, in the context of structural phase transition in monolayer MoTe₂. (363) Further, any possible charge inhomogeneity with the thickness is inadequate in few-layer samples to disrupt the doping-induced phase transitions. (345; 349; 357)

6.3 Results and discussion

Before investigating the charge carrier-induced magnetic phase diagram, we discuss the intrinsic magnetism in the monolayer and compare the results with the available experimental data. Subsequently, we demonstrate how hole doping pushes the ferromagnetic ordering temperature beyond room-temperature.

6.3.1 Intrinsic magnetism in the monolayer

The magnetic Cr-atoms in CrBr₃ are arranged in a honeycomb lattice, surrounded by edge-sharing Br-octahedra. The calculated in-plane lattice parameter of 6.25 Å is consistent with the single-layer and bulk crystals. (301; 364) Electronically CrBr₃ is a Mott insulator, and the half-filled t_{2g}^3 states are separated by 1.68 eV from the empty e_g^0 states, consistent with experimental data. (71) Similar to CrI₃, the monolayer CrBr₃ is a ferromagnetic (FM) insulator following Anderson-Goodenough-Kanamori rules. (81–83) Ligand mediated superexchange interactions between the half-filled Cr- t_{2g}^3 levels with Cr–Br–Cr angle of 94° trigger FM interaction. Magnetic moments are primarily localized at the Cr-sites (2.93 μ_B), which is compatible with the experimental data. (339) The magnetism in the neutral CrBr₃ monolayer can be described by the localized moment at the Cr-site. The calculated Cr-moment of 2.93 μ_B is consistent with Cr³⁺ ($t_{2g}^3 e_g^0$)-state, and in agreement with the experimental results. (339) The Cr-moments increase (decrease) only slightly with electron (hole) doping (Figure 6.1), and thus the magnetism in carrier-doped monolayer can still be described by the localized moments. Complex antiferromagnetic (AFM) phases are possible on a hexagonal magnetic lattice, and the zigzag AFM solution is the first excited state, $\Delta_Z^{\text{FM}} = 5.5$ meV/CrBr₃. The corresponding Néel and stripe AFM are $\Delta_N^{\text{FM}} = 11.1$ and $\Delta_S^{\text{FM}} = 11.9$ meV/CrBr₃ higher in energy. We calculate the relative energies of the collinear AFM states as, $\Delta_{N/S/Z}^{\text{FM}} = E_{N/S/Z} - E_{\text{FM}}$, where $E_{N/S/Z/\text{FM}}$ are the energies of the Néel, stripe, zigzag AFM and FM states (Table 6.1). For the neutral monolayer, we find $E_{\text{FM}} < E_Z < E_N < E_S$ energy ordering. With increasing δ_h , stripe and zigzag AFM switch energy ordering, and stripe AFM becomes the first excited state for $\delta > 0.1$ hole [Figure 6.2(a)]. Electron doped side of the phase diagram is rich [Figure 6.2(b)], and the FM state with out-of-plane spin orientation ($\mathcal{A}_z > 0$) exists only with a narrow region of electron doping. With

further increase in δ_e , the FM ($\mathcal{A}_z > 0$) $\rightarrow$ FM ($\mathcal{A}_z < 0$) $\rightarrow$ stripe AFM FM ($\mathcal{A}_z > 0$) transition is observed.

Table 6.1: Energies of various AFM configurations relative to the corresponding FM state are shown. Spin-orbit interaction is incorporated, and each configuration is investigated with Cr-spins oriented along the [001] and [100] directions. $\Delta_{[100]}^{[001]} = E_{\text{FM}}^{[100]} - E_{\text{FM}}^{[001]}$. All the energies are quoted in meV/Cr. Two representative densities are compared with the neutral monolayer.

ML CrBr ₃ carrier density	Spin direction	$\Delta_{\text{N}}^{\text{FM}}$	$\Delta_{\text{S}}^{\text{FM}}$	$\Delta_{\text{Z}}^{\text{FM}}$	$\Delta_{[100]}^{[001]}$
Electron doped $\delta_e = 7.3 \times 10^{13} \text{ cm}^{-2}$	[001]	10.37	2.45	3.25	-0.58
	[100]	11.40	3.20	3.98	
Neutral	[001]	11.07	11.94	5.54	0.18
	[100]	10.88	11.96	5.43	
Hole doped $\delta_h = 3.1 \times 10^{14} \text{ cm}^{-2}$	[001]	76.62	38.32	73.87	4.58
	[100]	71.05	32.00	68.18	

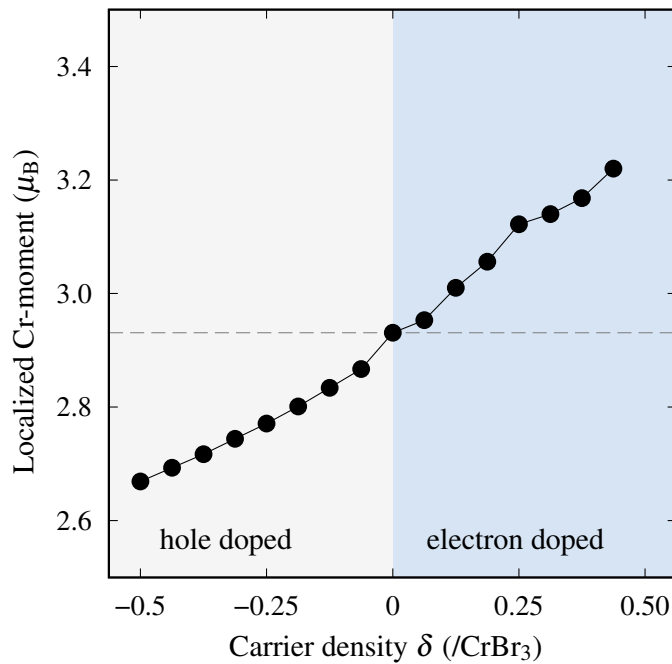


Figure 6.1: The localized Cr-moment varies only slightly with carrier doping and describes the magnetism. Figure reprinted from (365) by permission of American Physical Society.

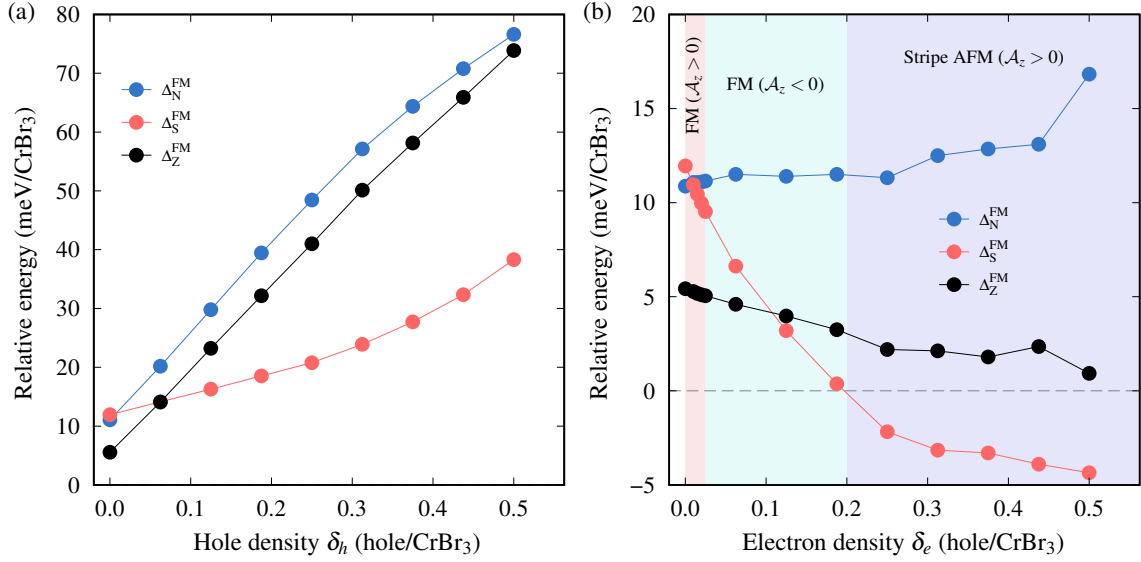


Figure 6.2: Relative energies of various AFM configurations with respect to the FM state, for (a) hole and (b) electron doping. Figure reprinted from (365) by permission of American Physical Society.

Monte Carlo simulations using the long-range Heisenberg XXZ Hamiltonian $\mathcal{H}$ reveal an FM phase transition at 30.5 K ($\beta = 0.226$), consistent with several experimental measurements of 27–34 K, such as magnetic circular dichroism, (70) helicity resolved photoluminescence, (71; 310) magneto-optical Kerr effect, (310) and micromagnetometry. (338) In contrast, a relatively lower T_C is estimated for the hBN encapsulated monolayer and bulk samples. (366) Note that the calculated β resides midway between the respective values for the 3D Heisenberg ($\beta = 0.365$) and 2D Ising ($\beta = 0.125$) models.

Since the on-site Coulomb interaction U_{Cr} acts as a parameter, it may influence the ordering and, therefore, should be carefully decided. The on-site Coulomb interaction influences the exchange couplings; thus, the magnetic ordering temperature is also impacted (Figure 6.3). As expected, the T_C monotonically increases with U_{Cr} and varies in the range of 12–38 K for U_{Cr} between 0–2 eV. We notice that U_{Cr} in the range 0.8–1.2 eV reproduces the experimental T_C between 27–34

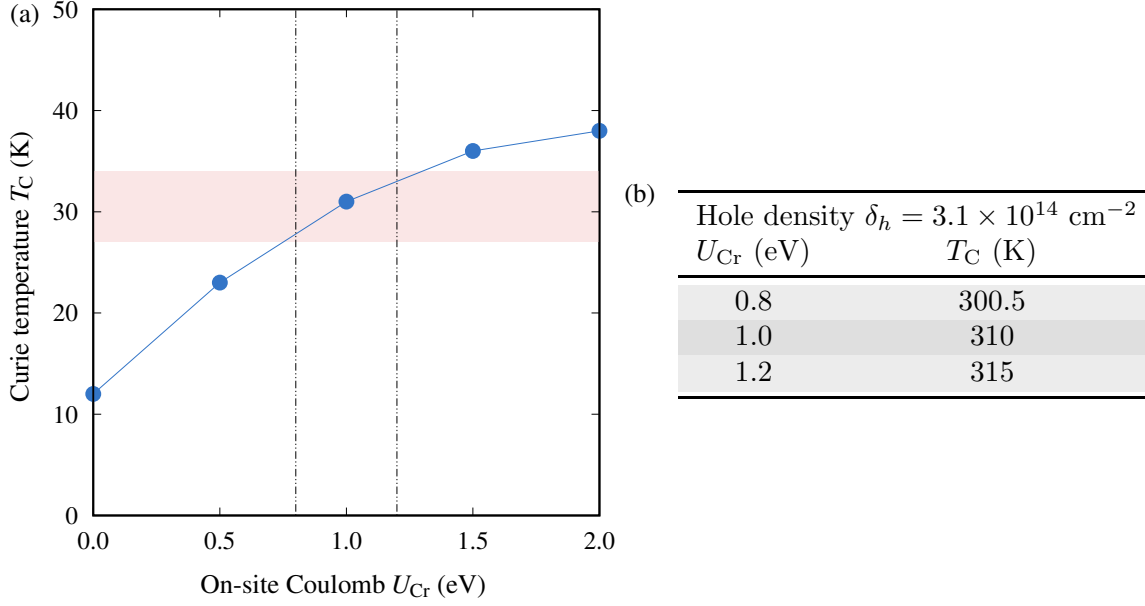


Figure 6.3: (a) Calculated Curie temperature T_C as a function of on-site Coulomb interaction U_{Cr} for neutral CrBr₃ monolayer. The horizontal shaded area represents the experimentally measured range of T_C (27–34 K). The trend remains unaltered in carrier doped CrBr₃ shown in the table. (b) The calculated T_C weakly varies (300–315 K) for the hole-doped case for a variation in U_{Cr} in the 0.8–1.2 eV range. Figure reprinted from (365) by permission of American Physical Society.

K. (70; 71; 310; 310; 338) Following these calculations, we fixed U_{Cr} at 1 eV for the rest of the charged-doped calculations. Further, we observe that a $\pm 20\%$ deviation in $U_{Cr} = 1$ eV does not alter the T_C significantly for the hole-doped monolayer. The sluggish dependence of T_C on layer thickness with $T_C^{\text{bulk}} = 37$ K indicates the two-dimensional nature of magnetism and weaker interlayer magnetic coupling. (338; 339) Exchange interactions beyond the first-neighbour with significant $\mathcal{J}_2/\mathcal{J}_1 \sim 0.2$ and $\mathcal{J}_3/\mathcal{J}_2 \sim -0.8$ cannot be neglected to explain phase transition. While the spin model with $\mathcal{J}_1$ alone underestimates the T_C (22.5 K, $\beta = 0.244$), the inclusion of $\mathcal{J}_2$ overestimates it to 37 K ($\beta = 0.247$). In concurrence with X-ray magnetic circular dichroism data, (367) the anisotropic interactions, Λ and $\mathcal{A}_z$ (0.08 meV), are considerably smaller in CrBr₃ than CrI₃ due to lower spin-orbit coupling strength at the halide site. Therefore, the overall magnetism in CrBr₃ re-

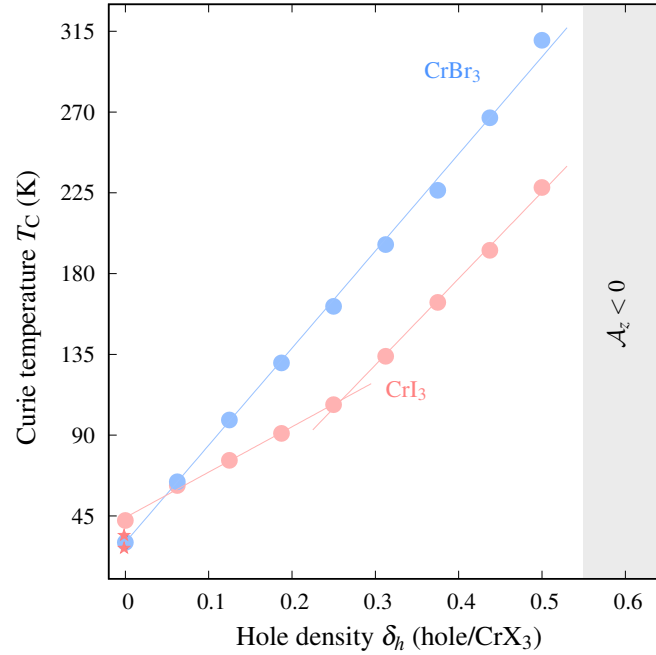


Figure 6.4: The magnetic ordering in monolayer CrX₃ is electrically manipulated, and the critical impact of hole doping is illustrated. Results for the neutral monolayers are in quantitative agreement with the experimental T_C , (62; 70; 71; 310; 338) stars designate the experimental data for the CrBr₃ monolayer. The evolution of T_C in CrBr₃ is compared with CrI₃. Calculated T_C linearly varies with hole density δ_h , and surprisingly, the room-temperature ferromagnetism is predicted in monolayer in CrBr₃ at $\delta_h = 0.5$ hole/CrBr₃ $\sim 3.1 \times 10^{14}$ cm⁻². Ionic-gating or femtosecond laser pulse could realise such high carrier density experimentally. (348–350) Figure reprinted from (365) by permission of American Physical Society.

sides far away from the Ising model ($A_z \rightarrow \infty$) description. Owing to severe finite temperature spin-fluctuations, the T_C is renormalized from T_C^{Ising} of 102 K, which is erroneously much higher than the experimental and current predictions of 27-34 K.

6.3.2 Controlling magnetism with charge doping

Driving a Mott-insulator away from the half-filling may establish a rich magnetic phase diagram in charge doped ultrathin layers. Further, the electrical manipulation of magnetism has drawn much attention due to its promise in spintronic devices with low power consumption. (346; 368–370) The change in carrier density

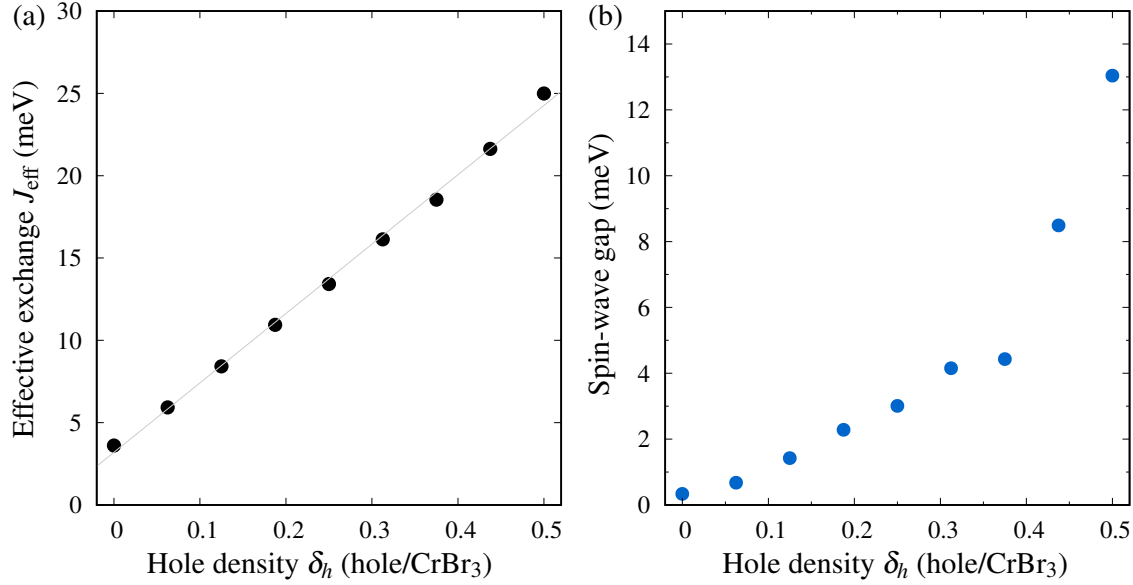


Figure 6.5: (a) Effective exchange coupling linearly grows with δ_h . (b) Spin-gap rapidly increases with the hole density. Figure reprinted from (365) by permission of American Physical Society.

influences the exchange interactions and magnetic anisotropy. Despite the insulator to metal transition under charge doping, the Heisenberg spin model remains univocally appropriate as the localized Cr-moments describe the magnetism (Figure 6.1).

We observe that the hole-doped monolayer CrBr₃ remains FM with easy-axis anisotropy ($\mathcal{A}_z > 0$), and the ordering temperature monotonically increases above room-temperature at a sufficient hole density (Figure 6.4). The Curie temperature goes linearly with the exchange interaction at the mean-field level. (319; 371) In the present model, we can calculate an effective exchange interaction, $J_{\text{eff}} = \frac{n_1}{2}(\mathcal{J}_1 + \Lambda_1) + \frac{n_2}{2}(\mathcal{J}_2 + \Lambda_2) + \frac{n_3}{2}(\mathcal{J}_3 + \Lambda_3) + \mathcal{A}_z$, which varies linearly with the hole density [Figure 6.5(a)], although the individual parameters have non-linear dependence. This illustrates the linear dependence of T_C with hole density in Figure 6.4. The spin excitation gap, which is responsible for the finite-temperature phase transition in the two-dimension, is calculated within the linear spin-wave formalism

of Holstein-Primakoff. The calculated spin-wave gap rapidly increases with hole density δ_h [Figure 6.5(b)], indicating a concurrent rise in the Curie temperature. A remarkable ten-fold increase in $T_C \sim 310$ K is observed at a hole density, $\delta_h \sim 0.5$ hole/CrBr₃ $\sim 3.1 \times 10^{14}$ cm⁻², which is experimentally achievable. The qualitative trend in T_C remains intact for a $\pm 20\%$ change in U_{Cr} , and the highest attainable T_C varies only between 300-315 K (Figure 6.3). Such high carrier density can be experimentally achieved in two-dimensional materials via ionic-liquid gating or femtosecond laser pulse. (348–350; 372) In comparison, the other chromium trihalide, CrI₃, shows a similar qualitative trend but with a few critical quantitative differences (Figure 6.4). First, the maximum attainable T_C in CrI₃ is 225 K, but surprisingly the ordering is elevated above 300 K in CrBr₃ at the same hole density (Figure 6.4). Further, the doping-dependent T_C is non-monotonous in CrI₃ and could be divided into two distinct regimes. At densities $\delta_h < 0.25$ hole/CrI₃, the dependency is slower, $\frac{dT_C}{d\delta_h} \sim 250$ K/hole, as the growth in T_C is predominantly dictated only by the increasing $\mathcal{J}_3$, while the change in $\mathcal{J}_1$ and $\mathcal{J}_2$ is insignificant. Instead, the $\mathcal{J}_3$ barely changes at higher densities above 0.25 hole/CrI₃, while the FM $\mathcal{J}_1$ and $\mathcal{J}_2$ increase rapidly with δ_h . Therefore, the corresponding Curie temperature grows at a higher rate, $\frac{dT_C}{d\delta_h} \sim 480$ K/hole. In contrast, for monolayer CrBr₃, computed T_C varies linearly with δ_h for the entire doping range, $\frac{dT_C}{d\delta_h} \sim 540$ K/hole (Figure 6.4). The nature of magnetism changes at $\delta_h > 0.56$ hole/CrBr₃, where the Cr-spins switch to the in-plane orientation, $\mathcal{A}_z < 0$, and the corresponding T_C is envisioned to be suppressed in the XY-spin system. The energy ordering of the excited AFM structures is also altered upon hole doping [Figure 6.2(a)]. Instead of zigzag AFM in the undoped case, the stripe AFM becomes the first excited state at $\delta_h > 0.1$ hole/CrBr₃.

The microscopic nature of magnetism is unveiled through the critical exponent β , which, for the undoped CrBr₃ monolayer ($\beta = 0.226$), is in between the values

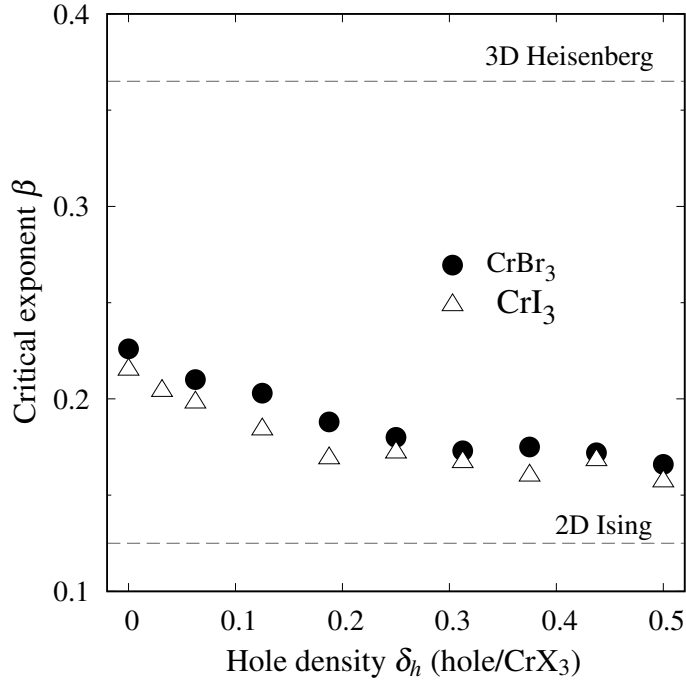


Figure 6.6: The critical exponent β indicates the nature of the underlying magnetic phase transition. The calculated β for monolayer CrBr₃ and CrI₃ is between the values characterising the 2D Ising and 2D Heisenberg spin systems, which agrees with numerous experimental measurements. However, as the magnetic anisotropies increase with δ_h , the exponent β decreases toward the Ising value. Figure reprinted from (365) by permission of American Physical Society.

for 3D Heisenberg and 2D Ising models (Figure 6.6). Due to the spin fluctuations, such a departure from the Ising spin description is observed in many van der Waals magnets. (317; 335; 338; 341; 342; 356; 373) We observe that hole doping critically influences the phase transition (Figure 6.6). As the overall magnetic anisotropy becomes more robust with increasing δ_h (Figure 6.8), the magnetic exponent β decreases though it remains far away from the 2D Ising limit. For example, β becomes 0.166 at a density $\delta_h = 3.1 \times 10^{14} \text{ cm}^{-2}$. Expectedly, the CrI₃ monolayer also exhibits a similar qualitative trend (Figure 6.6).

Contrary to hole doping, electron doping is not supportive in the present context of boosting T_C . Nevertheless, it renders a rich magnetic phase diagram in the Mott insulating monolayers. Multiple phase transitions, FM ($\mathcal{A}_z > 0$) $\rightarrow$ FM

($\mathcal{A}_z < 0$) $\rightarrow$ stripe AFM ($\mathcal{A}_z > 0$) are observed with increasing δ_e , and will be discussed later in Figure 6.10.

We note that a biaxial tensile and compressive strain is induced in the hexagonal spin-lattice under electron and hole doping, $\varepsilon = \pm 2\%$ at the highest carrier densities studied [Figure 6.7(a)]. Thus, it becomes crucial to understand how the induced strain influences the exchange coupling, and T_C . The strain-dependent variation in $\mathcal{J}_2$ and $\mathcal{J}_3$ is insignificant, and the nature of FM $\mathcal{J}_2$ and AFM $\mathcal{J}_3$ remains unaltered. However, FM $\mathcal{J}_1$ shows a significant variation with strain, which becomes AFM at a high compressive strain beyond 3%. Consequently, a Néel AFM ground state emerges [Figure 6.7(b)]. The corresponding T_C indicates a relatively weaker but non-monotonous variation predominantly dictated by the qualitative trend in $\mathcal{J}_1$ [Figure 6.7(c)]. Biaxial tensile strain alone increases the T_C slightly to 34 K at $\varepsilon = 2\%$ in the neutral monolayer before it decreases with a further increase in ε . On the contrary, the T_C is rapidly pushed to a lower value of 15 K at $\varepsilon = -2\%$. Therefore, it is evident that the hole-dependent increase in ordering temperature described in Figure 6.4 is exclusively of electronic origin.

The microscopic interpretation of carrier-induced enhancement in ordering temperature (Figure 6.4) is intriguing. Charge doping severely modifies all the magnetic interactions that drive the phase transition. The dependence is shown in Figure 6.8 for varied hole density. All the isotropic exchanges remain ferromagnetic for the entire range of δ_h studied. Compared to $\mathcal{J}_1$ and $\mathcal{J}_2$, the variation of the third-neighbour $\mathcal{J}_3$ is significant [Figure 6.8(a)], which sharply increases with δ_h , demonstrating the importance of long-range interactions to describe magnetism. Further, the anisotropic interactions, Λ_1 , Λ_2 and on-site $\mathcal{A}_z$, increase significantly with δ_h [Figure 6.8(b)] and influence the ordering. Using gate-induced coercivity data in few-layer Fe₃GeTe₂ such carrier induced modulation in magnetic anisotropy has been discussed earlier. (76) At high density, $\delta_h > 0.6$ hole/CrBr₃, Cr-spins switch

direction and prefer an in-plane orientation, $\mathcal{A}_z < 0$. The weak XY model describes the corresponding magnetism, and the concurrent FM T_C is expected to be renormalized.

Calculated isotropic $\mathcal{J}$, anisotropic Λ and on-site $\mathcal{A}_z$ are shown in the Figure 6.9

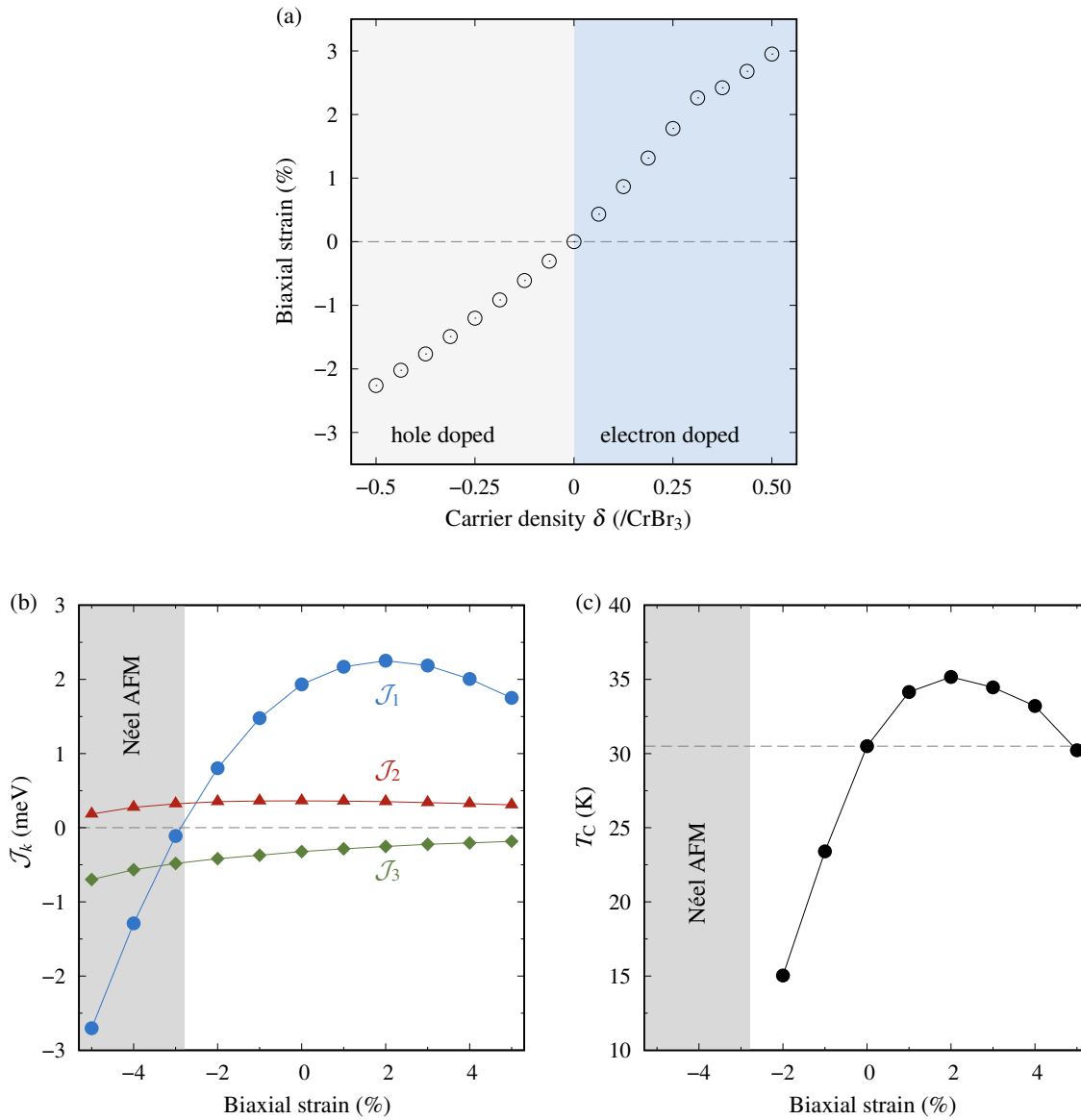


Figure 6.7: (a) Biaxial tensile and compressive strain is generated in monolayer CrBr₃ due to electron and hole doping, respectively. (b) Variation in the isotropic exchange couplings caused by the stain. (c) FM ordering temperature T_C shows a relatively weak but nonmonotonous dependence. Figure reprinted from (365) by permission of American Physical Society.

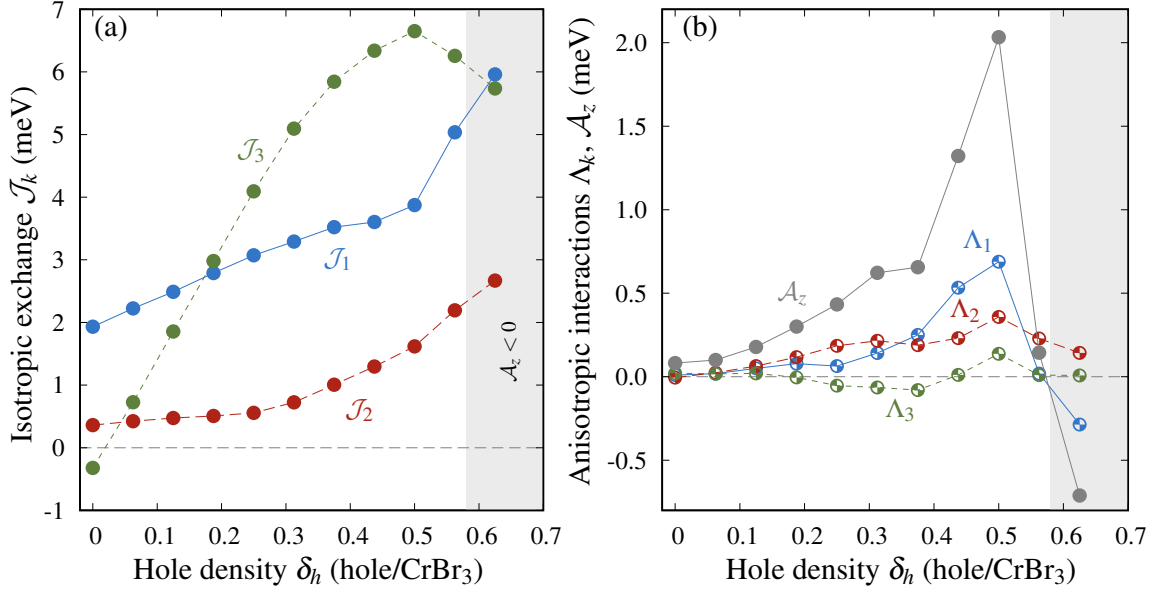


Figure 6.8: Charge carrier doping alters the exchange J_k and anisotropic interactions Λ_k and A_z that dictate the phase transition. (a) All the isotropic exchanges remain ferromagnetic for the entire hole density δ_h . Compared to J_1 and J_2 , variation in the third-neighbour J_3 is significant, sharply increasing with δ_h , which demonstrates the importance of long-range interaction to describe magnetism. (b) Anisotropic interactions, especially Λ_1 , Λ_2 and A_z strongly depend on δ_h and influence the ordering temperature. However, the Cr-spins switch direction at a high density, $\delta_h > 0.6$ hole/CrBr₃ (shaded area), and prefer an in-plane orientation $A_z < 0$, and the magnetism becomes weak XY-type. Figure reprinted from (365) by permission of American Physical Society.

for electron density. The J_1 evolves weakly, decreasing with increasing δ_e and then increasing again. With increasing δ_e , FM J_2 and AFM J_3 alter their nature to become AFM and FM, respectively, and their magnitudes monotonically grow with further increase in density. The anisotropic interactions Λ remain very small, below 0.1 meV throughout the density considered. Most notably, beyond a very low density, the easy axis switches from out-of-plane ($A_z > 0$) to in-plane ($A_z < 0$) direction, which remains the case throughout the density.

Exchange interactions under electron doping behave in an entirely distinct manner than for the varied δ_h (Figure 6.9). Both J_1 and J_2 decrease with δ_e , and J_2 further changes the sign and becomes AFM. In contrast, with increasing δ_e , J_3 be-

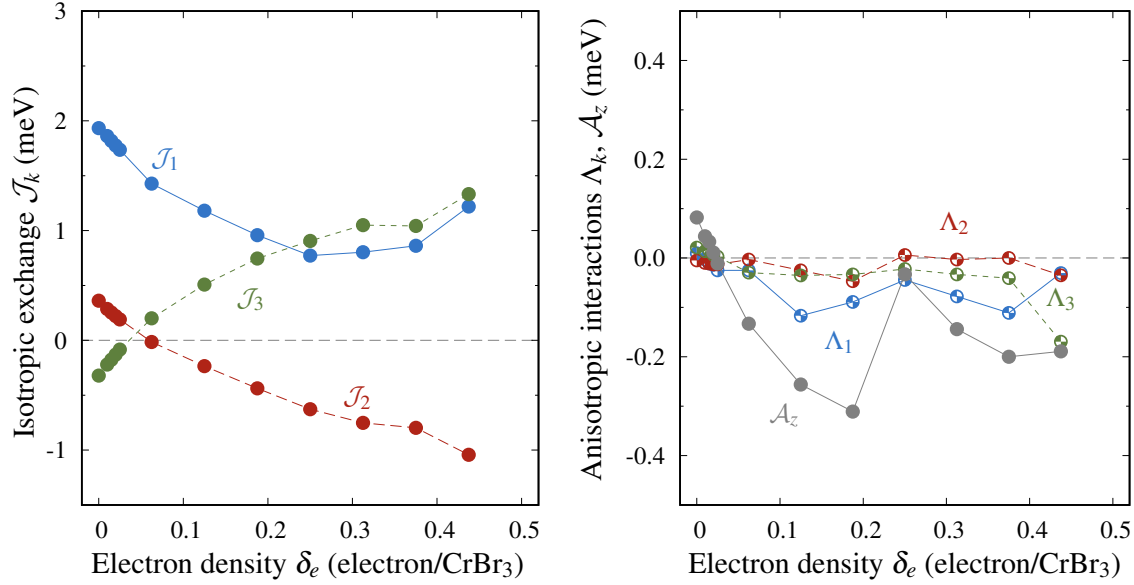


Figure 6.9: The dependence of isotropic and anisotropic magnetic interactions upon electron doping. Figure reprinted from (365) by permission of American Physical Society.

comes FM, which is otherwise AFM for the neutral monolayer.

Since the localized Cr-moments still describe the magnetism (Figure 6.1), and the multiorbital Kugel-Khomskii mechanism of superexchange can corroborate the carrier induced ferromagnetism. (351) The FM $t_{2g}^3 - e_g^0$ interaction in the undoped monolayer dominates over the AFM $t_{2g}^3 - t_{2g}^3$ exchange. With increasing δ_h , the partial hole δ_0 in the $t_{2g}^{3-\delta_0}$ destabilizes the AFM $t_{2g} - t_{2g}$ interaction and a stronger FM state emerge. The spin-wave analysis provides further understanding in this regard since the spin excitation becomes gapped due to anisotropic magnetic interactions. The Heisenberg XXZ Hamiltonian can be rewritten in Holstein-Primakoff bosons and transform the spin operators with the magnon annihilation a and creation $a^\dagger$ operators. (336) At low-temperature ($k_B T \ll \mathcal{J}_k$ and $S^z \simeq S$), we use linear approximation, $S^x + iS^y = \sqrt{2S}a$, $S^x - iS^y = \sqrt{2S}a^\dagger$, and $S^z = S - a^\dagger a$. Here, S^α ($\alpha = x, y, z$) are the components of the spin operator, and $S^\pm = S^x \pm iS^y$ are the ladder operators. The corresponding spin-wave Hamiltonian describes magnon

excitation with energy, $\epsilon_0 = 2S\mathcal{A}_z + \sum_k n_k \mathcal{J}_k S + \sum_k n_k \Lambda_k S$, where n_k is the number of first, second and third nearest-neighbours on the honeycomb lattice, $\mathcal{J}_k$ and Λ_k are the isotropic and anisotropic exchange interactions, and $\mathcal{A}_z$ is the on-site anisotropy. The calculated zero-temperature magnon gap at Γ point depends only on the anisotropic parameters, $\Delta_0 = 2S\mathcal{A}_z + 3S(\Lambda_1 + 2\Lambda_2 + \Lambda_3)$, and yields 0.34 meV for the undoped CrBr₃. Computed Δ_0 can be compared with the inelastic neutron scattering data but is unavailable for CrBr₃. The magnon gap Δ_0 rapidly increases with δ_h (Figure 6.5(b)) due to increased anisotropies (Figure 6.8), resulting in magnetic ordering at elevated temperatures.

6.3.3 The magnetic phase diagram

To gain a microscopic understanding, we calculate the carrier induced phase diagram projected onto the classical honeycomb $\mathcal{J}_1$ - $\mathcal{J}_2$ - $\mathcal{J}_3$ XXZ Heisenberg model with FM $\mathcal{J}_1$. (374–376) Due to the long-range interactions, the classical phase diagram consists of FM, collinear AFM (Néel, zigzag and stripe) ground states and supports coplanar helical phases. In good agreement with this phase diagram, carrier doping scans through a large part of the phase diagram as the exchange interactions are modulated (Figure 6.10). The undoped FM CrBr₃ ($\mathcal{J}_2/\mathcal{J}_1 = 0.19$ and $\mathcal{J}_3/\mathcal{J}_1 = -0.17$) resides near the helical and zigzag AFM phase boundary. Charge doping pushes the neutral Mott insulating monolayer away from the half-filling, and a complex phase evolution emerges (Figure 6.10) as exchange interactions are modified (Figure 6.8). While both $\mathcal{J}_1$ and $\mathcal{J}_2$ increase with hole density δ_h [Figure 6.8(a)], the ratio $\mathcal{J}_2/\mathcal{J}_1$ remains unaltered. In contrast, $\mathcal{J}_3$ increases much more rapidly than $\mathcal{J}_1$ with δ_h [Figure 6.8(a)], resulting in a monotonous increase in $\mathcal{J}_3/\mathcal{J}_1$ in the range $-0.2 < \mathcal{J}_3/\mathcal{J}_1 < 1.75$ (Figure 6.10). Consequently, CrBr₃ remains FM at any hole density consistent with the classical XXZ phase diagram. The corresponding T_C increases with δ_h (Figure 6.10) due to the rapid increase in effective

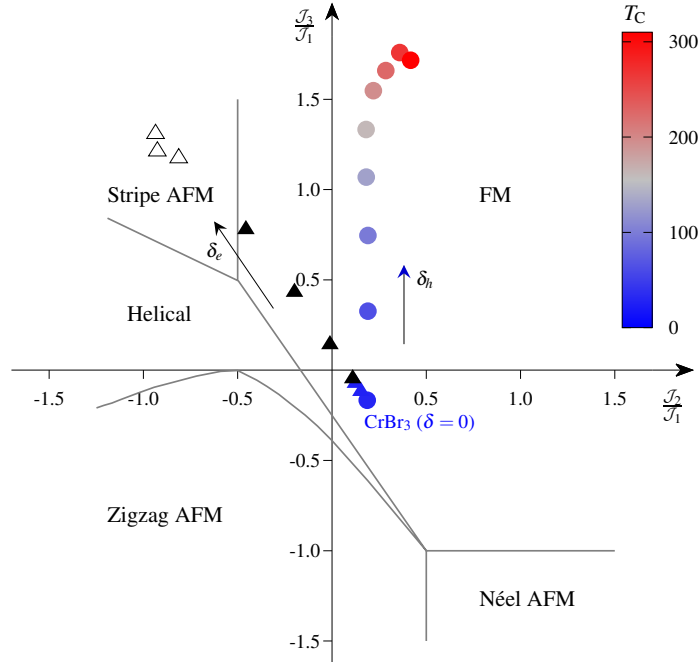


Figure 6.10: Isotropic exchange interactions $\frac{J_2}{J_1}$, $\frac{J_3}{J_1}$; and the corresponding T_C obtained from the first-principles calculations are plotted on the classical J_1 - J_2 - J_3 XXZ Heisenberg phase diagram with ferromagnetic J_1 for the honeycomb lattice (adopted from the Ref. (375)). The CrBr₃ monolayer remains FM under any hole density δ_h (circle), and a continuous increase in Curie temperature is traced with color palette. In contrast, with increasing electron density δ_e (triangle), multiple phase transitions, FM ($\mathcal{A}_z > 0$; blue $\blacktriangle$) $\rightarrow$ FM ($\mathcal{A}_z < 0$; black $\blacktriangle$) $\rightarrow$ stripe AFM ($\mathcal{A}_z > 0$; black $\triangle$) are observed. Figure reprinted from (365) by permission of American Physical Society.

ferromagnetic exchange along with an increase in magnetic anisotropies.

In comparison, the phase evolution upon electron doping is complex (Figure 6.10). As discussed earlier that J_1 and J_2 are FM for the neutral monolayer, while the J_3 is AFM. As electron density δ_e increases, J_1 stays FM throughout but evolves weakly. In contrast, the nature of exchanges beyond the first-neighbour is altered due to electron doping beyond a critical density, $\delta_e > 0.05$ electron/CrBr₃ (Figure 6.9). The FM J_2 (AFM J_3) exchange interaction decreases (increases) with density and becomes AFM (FM). Consequently, J_2/J_1 decreases and changes the sign to become negative above this density. In contrast, the ratio J_3/J_1 increases monotonically from -0.17 to 1.3 with increasing density δ_e . Such intricate variations in

$\mathcal{J}_2/\mathcal{J}_1$ and $\mathcal{J}_3/\mathcal{J}_1$ trigger a rich magnetic phase diagram, and FM ($\mathcal{A}_z > 0$) $\rightarrow$ FM ($\mathcal{A}_z < 0$) $\rightarrow$ stripe AFM ($\mathcal{A}_z > 0$) evolution is predicted. (i) At low electron density $\delta_e < 0.02$ electron/CrBr₃, the monolayer remains ferromagnetic, and the T_C shows a weaker dependence as it monotonically decreases to 25 K. Such a decrease in T_C upon electron doping has been observed experimentally in CrI₃. (345) (ii) For $0.02 < \delta_e < 0.2$ electron/CrBr₃, the monolayer remains FM, but the Cr-spins switch to the in-plane direction ($\mathcal{A}_z < 0$). Here, a weak XY-system represents the magnetism, and the corresponding T_C is anticipated to be renormalised. (377; 378) Therefore, regardless of the sign of $\mathcal{A}_z$, an FM solution emerges in this doping range with $0.1 > \mathcal{J}_2/\mathcal{J}_1 > -0.5$ and $-0.05 < \mathcal{J}_3/\mathcal{J}_1 < 0.8$. (iii) At higher densities, $\delta_e > 0.2$ electron/CrBr₃, another phase transition is observed when a stripe AFM with $\mathcal{A}_z > 0$ emerges and remains the ground state with a further increase in δ_e described by $\mathcal{J}_2/\mathcal{J}_1 < -0.5$ and $\mathcal{J}_3/\mathcal{J}_1 > 1$. The phase diagram of the mono-

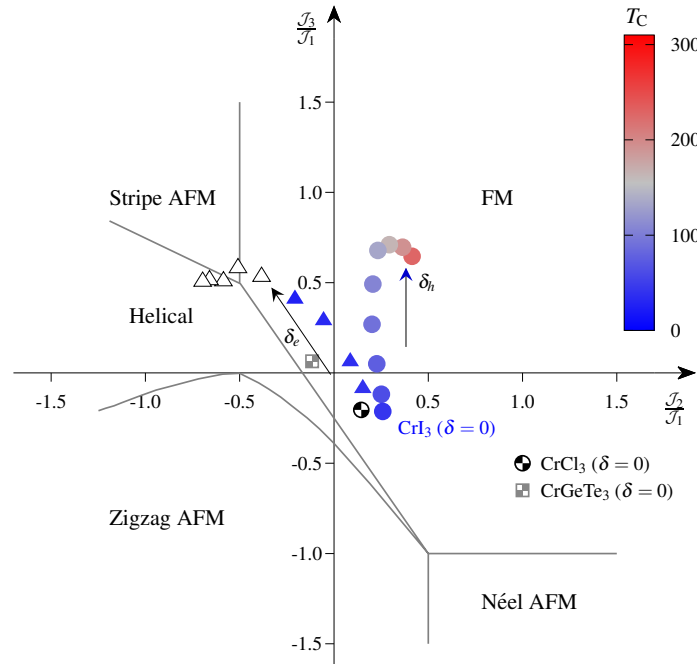


Figure 6.11: The phase diagram of the monolayer CrI₃ is qualitatively similar as shown in Figure 6.10 for CrBr₃, and we followed the same convention. Figure reprinted from (365) by permission of American Physical Society.

layer CrI₃ in Figure 6.11 is qualitatively similar to that of the CrBr₃ (Figure 6.10). However, the $\mathcal{J}_3/\mathcal{J}_1$ ratio is much smaller in CrI₃, limiting the achievable ordering temperature at the highest doping level. We have also shown the neutral ground state for the monolayers of CrCl₃ and CrGeTe₃ on the phase diagram. We note that the FM ground state resides much closer to the FM-helical phase boundary, and a helical magnetic phase may emerge under perturbation. Indeed, a magnetic skyrmionic phase has been detected in CrGeTe₃ flakes. (379) Therefore, the ultra-thin magnetic 2D materials may become the ubiquitous testbed for various spin models.

Present results may be exploited in devices where magnetism is electrically controlled to revolutionize energy-efficient spin-based technologies. For example, a spin field-effect transistor (FET) can be realized, (380–382) where gate voltage controls the direction of magnetic easy-axis and a longitudinal in-plane source-drain voltage produces spin current. Since the spins in FM CrBr₃ monolayer switch from out-of-plane to the in-plane direction upon electron doping, the spin reorientation at the undoped/doped interface will significantly modulate the device resistance. While the spin-FET is naturally designed in the on-state with low resistance, the gate-controlled electron doping beyond critical doping creates a magnetic ($\uparrow\uparrow \mid \Rightarrow \mid \uparrow\uparrow$) interface, resulting in a high-resistance state due to strong scattering. Besides, the 2D CrBr₃ can also be employed in all-vdW magnetic tunnel junction (MTJ), where graphene or h-BN may be used as the barrier. (308; 383) The critical advantage will be that CrBr₃-MTJ may be voltage-controlled and operate at a high temperature.

6.4 Conclusions

We demonstrate that charge doping in Mott insulating CrBr₃ renders nontrivial evolution in magnetism and a rich phase diagram emerges. The microscopic origin of the phase diagram is explained in terms of carrier dependent long-range exchange and anisotropic parameters obtained from the relativistic first-principles calculations. While the undoped CrBr₃ monolayer orders around 30 K, the Curie temperature is dramatically modulated due to carrier doping, which monotonically increases with hole doping and is surprisingly elevated above room-temperature for an experimentally achievable density. Voltage-controlled room-temperature ferromagnetism addressed here in atomically thin material provides unprecedented opportunities in two-dimensional spintronics, magnetoelectrics, as well as in the context of emergent quantum states.

Chapter 7

Superconductor/ferromagnet van der Waals heterostructure: Appearance of Majorana zero mode

Emerging quantum states may appear when two materials with different quantum states are brought in close proximity. One promising system for exploring these states is the superconductor/ferromagnetic van der Waals (vdW) heterostructure, which is believed to be a cleaner system for investigating Majorana zero-energy modes. In this context, we investigate a two-dimensional (2D) superconductor NbSe₂, ferromagnetic insulator CrI₃, and their vdW heterostructure using first-principles density functional theory calculations and Hamiltonian modelling. Our calculations accurately reproduce the electronic and magnetic structures of individual NbSe₂ and CrI₃ monolayers. In the vdW heterostructure, the proximity effect induces a finite magnetic moment, and the magnetic layer influences the spin-splitting of NbSe₂ at the valley points. We modelled this heterostructure using a low-energy tight-binding Hamiltonian of NbSe₂ supplemented with an external magnetic field term using the Bogoliubov-de Gennes Hamiltonian. In the superconducting state, we observed the emergence of six pairs of nodal points within the hexagonal Brillouin zone under an applied in-plane magnetic field. Furthermore, a Majorana flat band appears on the armchair edge of the NbSe₂ nano-ribbon, while

it disappears on the zigzag edge. Our findings suggest that the vdW SC/FM heterostructures hold great promise for exploring emerging quantum states, specifically Majorana zero-energy modes. A manuscript is under preparation based on the results.

7.1 Introduction

Topological superconductors are the essential ingredients to implement topologically protected quantum computing. These quantum simulation information processes realize through induction and manipulation of Majorana zero modes (102–105). Recently, the realization of Majorana zero modes has been reported in several systems such as ferromagnetic atomic chains on superconductor (384), nanowires (105), planner Josephson junction (385; 386) and the interface between magnetic iron clusters and the superconducting helical edge of bismuth (111) thin film (387). The identification of Majorana states in these systems is the appearance of subgap conductance peaks near the system boundaries (98; 388–391). The emergence of topological superconductivity requires the coexistence of superconductivity, magnetism and spin-orbit interactions (392; 393). A few materials or very rare to found one in which all these physical phenomena mutually exist (394; 395). Therefore, it is very hard to observe topological superconductivity in one material or system, except recently discovered in 4Hb-TaS₂ (109). Recently discovered two-dimensional magnetism in the Cr-based trihalides (61; 62) monolayers provide the opportunity to study different emerging phenomena like spin-valley interaction (396; 397), Majorana zero modes (98) and superconducting spin-valve in the van der Waals heterostructure (vdW) (398–400) where magnetic monolayers act as a substrate. The vdW heterostructure of the ferromagnetic insulator/superconductor is the ideal platform to design and tune the topological superconductivity as it hosts superconductivity adjacent to the magnetic layer with strong spin-orbit interactions.

Monolayer NbSe₂ belongs to a large group of two-dimensional materials called transition metal dichalcogenides (TMD). It possesses a hexagonal crystal structure in which the Nb layer is sandwiched between two Sb layers and forms a trig-

onal prismatic structure (401; 402). This particular crystal symmetry manifests as out-of-plane mirror symmetry but lacks in-plane inversion symmetry. Therefore, in-plane moving electrons feel an effective magnetic field due to asymmetric spin-orbit interactions (403). This magnetic field orient electron spins out-of-plane direction and provides spin-split bands at the valley points (K and K'). This type of spin-orbit interaction is known as Ising spin-orbit coupling (404–406). Similar to several other TMD monolayers such as NbS_2 and TaS_2 , the NbSe_2 monolayer is shown superconducting transition below 3 K (404; 406–408). It also shows the charge-density-wave (CDW) at the T_c of 5 K (407; 408). Recently, theoretical work shows that the CDW phase and superconducting phase are driven by electron-phonon interactions (409). Due to strong Ising soc, it possesses very high in-plane upper critical field H_{c2} , approximately six times greater than the Pauli limit field H_p (404; 406; 410; 411). In a recent report, the external in-plane magnetic field provides the topological superconducting nodal phase in it (115). When the NbSe_2 layer is placed over the magnetic substrate, CrBr_3 emerges a two-dimensional topological superconducting phase by observing the signatures of one-dimensional Majorana edge modes (98). In another work, a topological superconducting state is realized in a natural material 4Hb-TaS_2 which is formed by superconducting 1H-TaS_2 layers and strongly correlated 1T-TaS_2 layers (109).

In the 2D materials, the long-range ferromagnetic order can not sustain at the finite temperature as the thermal fluctuations may easily destroy this long-range ordering as stated by the Mermin-Wagner theorem (63; 64). To realize low-dimensional magnetism spin-wave spectrum should be gapped, which is a direct manifestation of magnetic anisotropy. Recently, ferromagnetism has been observed in atomically thin CrGeTe_3 (61) and also in bilayer and monolayer of CrI_3 (62) by performing magneto-optical Kerr experiments. After these discoveries, several other 2D crystals like CrBr_3 , VI_3 , CrCl_3 VSe_2 and Fe_3GeTe_2 have shown long range ferromag-

netism (69–76). The monolayer CrI_3 is a 2D Ising ferromagnet with out-of-plane spin orientation. Due to very weak interlayer coupling in bulk, the Curie temperature is reduced only slightly to 45 K in the monolayer compared to 61 K in bulk (412; 413). The magnetic ordering temperature in the monolayers of CrI_3 and CrBr_3 is electrically tuneable, and room temperature ferromagnetism is possible in CrBr_3 (325; 365). These ferromagnetic monolayers are used as the magnetic substrate over which several different class of materials is placed to observe diverse emergent phenomena.

In the van der Waals (vdW) heterostructures, the stack of atomically thin layers is glued together to form complex quantum materials. These heterostructures are formed by a different class of materials like semiconductors, superconductors, ferromagnets and topological insulators to produce new physical properties (394; 395; 414). Such heterostructures naturally hold very large and high-quality interfaces, and this allows to observe robust emergent properties. After the discovery of 2D magnetism in Cr-based trihalides, many vdW heterostructures like graphene/ CrI_3 to study the quantum anomalous Hall effect at high temperatures (415), CrI_3 /graphene bilayer/ CrI_3 for vdW spin-valve (99), NbSe_2 / CrBr_3 for topological superconductivity (98), WSe_2 / CrI_3 for spin-valley interactions (100), magnetic proximity effect in WSe_2 /bilayer CrI_3 (416), magnon-valley Hall effect in heterostructures of CrI_3 with HfS_2 , MoTe_2 and WSe_2 (101), spin caloritronics in CrI_3 / NiCl_2 (417) and giant tunneling magnetoresistance in graphene/bilayer CrI_3 (418) are investigated. These studies indicate that the CrI_3 or CrBr_3 based vdW heterostructures are ideal platforms to study the diverse range of phenomena. A superconducting spin-valve system is realized when the conventional superconductor is sandwiched between two ferromagnetic insulators (399; 400; 419). But when the Ising superconductors like NbSe_2 is in the proximity of ferromagnetic insulators like CrBr_3 a topological superconducting phase is evolved (98).

Here, we report our first-principles study on the monolayers of NbSe₂ and CrI₃ and CrI₃/NbSe₂ vdW heterostructure. We have studied the electronic band structure and density of states of these monolayers and heterostructure. We have calculated the Fermi surface and momentum-dependent Berry curvature to understand the role of Ising soc in monolayer NbSe₂. In the proximity of the ferromagnetic CrI₃ layer, the local magnetic moment of $0.1 \mu_B$ is induced. The valley polarization is also influenced by the in-plane and out-of-plane Cr spins. During Hamiltonian modelling of vdW heterostructure, we find that the nodal points and the Majorana zero modes are observed in the bulk and armchair edge, respectively. These topological features are subjected to change under the effect of Ising and Rashba spin-orbit coupling.

7.2 Computational Methods

The first principles calculations are performed using the plane-wave pseudo-potential method as implemented in the Vienna *ab initio* Simulation Package (182; 183). The exchange-correlation term is described by the PBE functional under the generalized gradient approximation (GGA) (134; 184) and it is supplemented with the Hubbard-like on-site Coulomb interaction U_{Cr} for the localized Cr-3*d* electrons in CrI₃ layer. Electron-ion interactions are described by the projected-augmented wave (PAW) method. We have assigned U_{Cr} to be 2.8 eV under the rotationally invariant Dudarev's approach (327) in all the *ab initio* calculations which are used in recently reported calculations with bilayer CrI₃ (420). We have used a cutoff energy of 600 eV for a plane-wave basis set. All structures are relaxed by minimizing the forces on each atom till the total force on every atom is below 10^{-2} eV/Å. The Brillouin zones are sampled by a Monkhorst-Pack special *k*-point grid (198) of $21 \times 21 \times 1$ for optimization of NbSe₂ and CrI₃ monolayers and an $11 \times 11 \times$

1 k -grid is used for $\text{CrI}_3/\text{NbSe}_2$ heterostructure. The vdW interaction in the heterostructure is implemented by Grimme's method (421). We have evaluated the tight-binding parameters like on-site energies and hopping integrals from the first principles calculations using the maximally localized Wannier function method as implemented in the Wannier90 code (138). Later, we calculated the Fermi surface and the Berry curvature of NbSe_2 monolayer using WannierTools (422).

7.3 Results and Discussion

First, we examine the electronic band structure and orbital projected bands of monolayer NbSe_2 . Later, we explain the role of spin-orbit interactions in this monolayer. After that, we establish the low-energy tight-binding Hamiltonian for it and compare the DFT band structure with the tight-binding band structure. Next, we discuss the crystal structure and band structure of the CrI_3 monolayer. In the next section, we talk about the $\text{CrI}_3/\text{NbSe}_2$ vdW heterostructure and the effect of the magnetic layer on the NbSe_2 layer. Later, we model this vdW heterostructure by the tight-binding Hamiltonian. We see the effect of the magnetic layer on a superconducting state by studying the bulk and armchair edge BdG Hamiltonian and its spectrum.

7.3.1 Pristine NbSe_2

Monolayer NbSe_2 has the trigonal prismatic structure that is derived from bulk 2H- NbSe_2 with space group $P6_3/mmc$, is formed by three planner triangular lattices, in which one Nb atomic layer is sandwiched between two Se layers [Fig. 7.1(a)]. The calculated lattice constant of 3.47 Å is in agreement with experimental measurements and theoretical results (423–425). While the monolayer NbSe_2 possesses out-of-plane mirror symmetry, the in-plane mirror symmetry is broken due

to two different, Nb and Se, triangular sublattices. According to the trigonal prismatic crystal field, the Nb-4d states split into d_{z^2} and a pair of doubly degenerate $d_{xy}/d_{x^2-y^2}$ and d_{xz}/d_{yz} states. The calculated band structure in Fig.7.1(b) indicates that the metallic bands are composed with partially filled d_{z^2} , and $d_{xy} + d_{x^2-y^2}$, which span between -0.5 to $+0.6$ eV with respect to the Fermi level. These bands form two large hole pockets centred at the Γ and K points. Note that the orbital character of these metallic bands switches from d_{z^2} around Γ to $d_{xy} + d_{x^2-y^2}$ around K [Fig.7.1(b)]. While the Se-4p contribution to the conduction band is very small, the hole-like bands around 0.9 eV below the E_F originate from the Se-4p orbitals. Considering this band structure, a three-band tight-binding model captures the essential low-energy physics. (115; 426; 427) The Nb-4d states at the E_F provides a large spin-orbit coupling (SOC). In the absence of in-plane mirror symmetry, the SOC pins the electron spins to the opposite out-of-plane directions for the electrons with opposite momentum, (428) and become insensitive to the lateral external magnetic field that is responsible for Ising superconductivity.

Accordingly, in our calculation, the d_{xy} and $d_{x^2-y^2}$ spins align perpendicular to the NbSe₂ plane and valley polarized at the K and K' points. Further, in the presence of such Ising SO coupling, inversion symmetry breaking in monolayer NbSe₂ induces an anisotropic spin splitting in the vicinity of E_F and around the K-point [Fig.7.1(b)]. To see the effect of Ising spin-orbit coupling, we have calculated S_z projected spin band structure [Fig.7.1(c)]. In this band structure, the maximum spin-splitting is at the K and K' points (valley points), but bands generate around the Γ point. To explain this asymmetric spin-splitting, we have calculated the z-component of the Berry curvature $\Omega_z(k)$ using Kubo-like formula (429). In Fig.7.1(d), the equal and opposite Berry curvature at K and K' points. The Berry curvature acts as an intrinsic magnetic field and provides spin-splitting at the valley points. The responsible band originates from the in-plane $d_{xy} + d_{x^2-y^2}$ states,

and the calculated splitting at the K-point of 153 meV agrees well with the previous calculation, (115) and the recent angle-resolved photoemission spectroscopy (ARPES). (430) The d_{z^2} state does not show such splitting [Fig.7.1(b)]. The Se-4p states, which appeared 0.9 eV below the E_F also exhibit anisotropic spin splitting of about 100 meV at the saddle point along the ΓK cut of the Brillouin zone, which is not shown in Fig.7.1(b). The normal state Fermi surface [Fig. 7.1(e) and (f)] con-

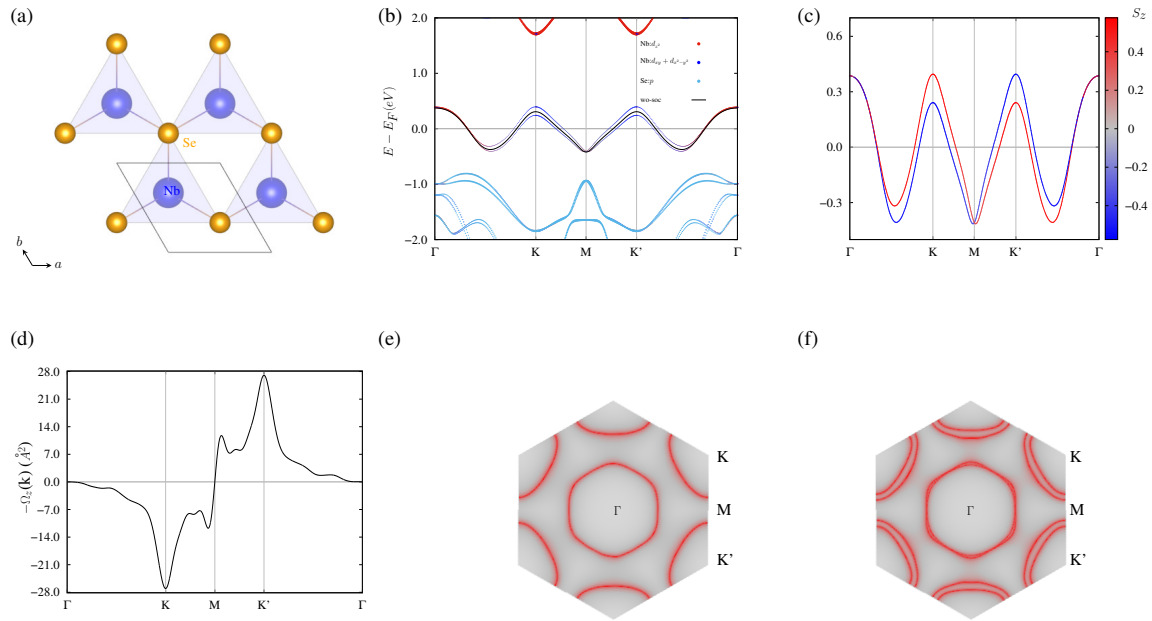


Figure 7.1: (a) The hexagonal crystal structure of NbSe₂ is shown, formed by trigonal prismatic geometry, where an Nb atom is at its centre, packed by six Se atoms at its edges. (b) The orbital projected band structure with spin-orbit coupling reveals that the bands at the Fermi level are mainly composed of three Nb-4d orbitals: dz^2 , $d_{x^2-y^2}$, and d_{xy} . The Se-p orbitals in the valence bands have no effect on the conduction bands. In the presence of spin-orbit coupling, the band structure is asymmetrically split around the Fermi level, with the maximum spin splitting occurring at the valley points (K and K'). (c) The S_z projected spin band structure shows a spin flip at the valley points and a Rashba-type spin crossover at the M point. (d) The momentum-resolved out-of-plane component of the Berry curvature ($\Omega_z(k)$) is shown for the bands that intersect the Fermi level. (e) The 2D Fermi surface without spin-orbit coupling is plotted within the first Brillouin zone. (f) The inclusion of spin-orbit coupling influences the 2D Fermi surface.

sists of large hexagonal and triangular hole pockets centred at the Brillouin zone

centre Γ and at the zone corners K and K', respectively. While the Γ pocket is derived from d_{z^2} state, the pockets at K and K' originate from degenerate $d_{xy}/d_{x^2-y^2}$ states, which further spin splits in the presence of SOC due to the lack of inversion symmetry [Fig. 7.1(g)]. The calculated features of the band structure [Fig. 7.1(d) and (e)] and Fermi surface [Fig. 7.1(e)] agree well with the spin-resolved ARPES measurements (115; 431; 432). In the context of superconductivity, an electron in one of the two spin-split Fermi surfaces around the K valley naturally couples to form singlet Cooper pair with the electron with opposite spin and momentum around K'. This mechanism gives rise to Ising superconductivity that has been observed and argued in NbSe₂ (404–407; 433) and other transition-metal dichalcogenides. (434; 435) The out-of-plane spin texture is responsible for the observed robustness of superconductivity against the in-plane magnetic field. (404) Further, the spin-split Fermi surface is expected to induce the mixing of spin-singlet and triplet order parameters leading to topological superconductivity (115; 393; 436).

7.3.2 CrI₃ monolayer

In monolayer CrI₃, the Cr³⁺ ions are arranged in a honeycomb network of edge-sharing Cr³⁺I₆[−] octahedra [Fig. 7.2(a)]. The calculated lattice parameter of 6.98 Å is consistent with previous reports. (62) The individual CrI₃ layers are van der Waals stacked, and the stacking sequence along with relative displacement of the layers determine the corresponding bulk structures, monoclinic $C2/m$ and rhombohedral $R\bar{3}$. The high-temperature $C2/m$ structure undergoes a phase transition to $R\bar{3}$ at 240 K. (437) The bulk CrI₃ shows layered Ising ferromagnetism below a Curie temperature of 61 K with the out-of-plane easy axis. (412; 413) The half-filled t_{2g}^3 state with spin $S = 3/2$ is consistent with the saturation magnetization. The intralayer ferromagnetism is described by the Anderson-Goodenough-Kanamori Cr- t_{2g} –I–Cr- t_{2g} ferromagnetic superexchange with 90° bond angle since electrons

cannot hop between orthogonal orbitals. The present results for the monolayer

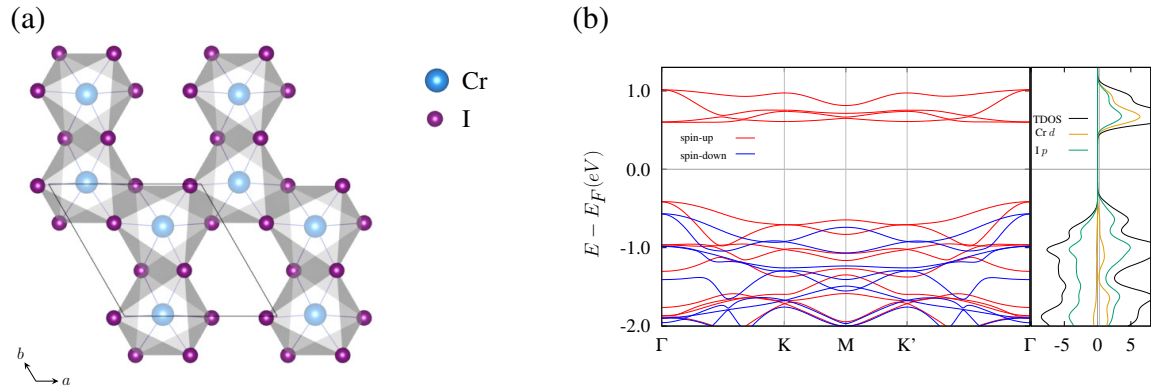


Figure 7.2: (a) Top view of honeycomb lattice structure of CrI₃ monolayer. (b) Spin-resolved GGA + *U* band structure and density of states indicate the monolayer CrI₃ to have insulating electronic structure.

CrI₃ are consistent with these findings. In the monolayer limit, the magnetic easy axis remains perpendicular to the CrI₃ plane with calculated anisotropy of 0.87 meV/Cr, which lifts the Hohenberg-Mermin-Wagner restriction on the magnetic ordering in 2D. Therefore, in the absence of continuous rotational symmetry, a ferromagnetic phase emerges below 45 K in the monolayer. (61) The band struc-

Table 7.1: The structure parameter and average magnetic moment per atom on Cr atoms in the CrI₃ monolayer with different theoretical levels.

CrI ₃	Experiment	PBE	PBE+ <i>U</i>	PBE+ <i>U</i> +SOC
<i>a</i> (Å)	6.86	6.99	7.08	7.08
magnetic moment (μ_B)	3.00	3.10	3.46	—

ture and the corresponding density of states (DOS) in Fig. 7.2(b) indicate that CrI₃ is an insulator, which is consistent with earlier experimental and theoretical results. (62; 77; 415; 438) The GGA + *U* calculation predicts a direct gap of 1.01 eV, which including spin-orbit coupling (SOC), reduces the gap to 0.72 eV since I⁻ ion has very strong SOC. The calculated DOS indicates that the top of the valence band

is constituted by I-*p* orbitals, and the conduction band is predominantly formed by unoccupied Cr-*d* orbitals hybridized with I-*p* states.

7.3.3 Superconductor/FM vdW heterostructure: NbSe₂/CrI₃

Here, we introduce the NbSe₂/CrI₃ heterostructure and discuss its formation, magnetization of NbSe₂ layer and spin-valley interactions. The formation of heterostructure is quite compatible as Cr ions, as well as Nb-Se, form the hexagonal structure. To form the heterostructure, we use a 2×2 supercell of NbSe₂ with a unit cell of CrI₃. The in-plane lattice constant of NbSe₂ and CrI₃ layers are 6.95 Å and 6.99 Å, respectively. In the heterostructure, we see the lattice parameter of NbSe₂ that puts a 0.5 % compressive strain on the CrI₃ layer, which is very minimal with respect to other chromium trihalides-based heterostructures (415; 439).

To study the NbSe₂/CrI₃ interface, we have considered three different stacking, namely hollow-Se [Fig.7.3(a)], hollow-NbSe [Fig.7.3(b)] and hollow-Nb [Fig.7.3(c)]. In hollow-Nb and hollow-Se configurations, the Nb and Se atoms are placed at the hollow site around the edge-shared octahedra CrI₆ respectively, whereas both Nb and Se atoms reside around the hollow site for the hollow-NbSe arrangement. The hollow-Nb and hollow-NbSe configurations are energetically similar configuration with hollow-Nb being more stable by 6 meV. In both these configurations, the average interlayer distance (vdW-gap) is around 3.35 Å. The hollow-Se structure is energetically less stable by 90 meV from the other two structures and also has a larger vdW-gap of around 3.53 Å. Similar observations are shown on NbSe₂/CrI₃ heterostructure with hollow-Nb as ground state configuration. (98) With a relatively more stable and lesser vdW gap, we have used hollow-Nb configuration for further studies. We also estimate the binding energy of the heterostructure, which is defined as $E_b = (E_{NbSe_2} + E_{CrI_3} - E_{CrI_3-NbSe_2})/A$, where E_{NbSe_2} , E_{CrI_3} and $E_{CrI_3-NbSe_2}$ are the total energies for the NbSe₂ and their heterostructure re-

spectively, and A is the surface area of the heterostructure. The binding energy for the $\text{CrI}_3/\text{NbSe}_2$ heterostructure is about $74 \text{ meV}\cdot\text{\AA}^{-2}$, which is comparable to other reported heterostructure based on chromium trihalides and also with lesser vdw-gap, this heterostructure has strong vdW interaction than graphene/ CrI_3 heterostructure (415). To study the magnetic NbSe_2 layer, we analyse the structure,

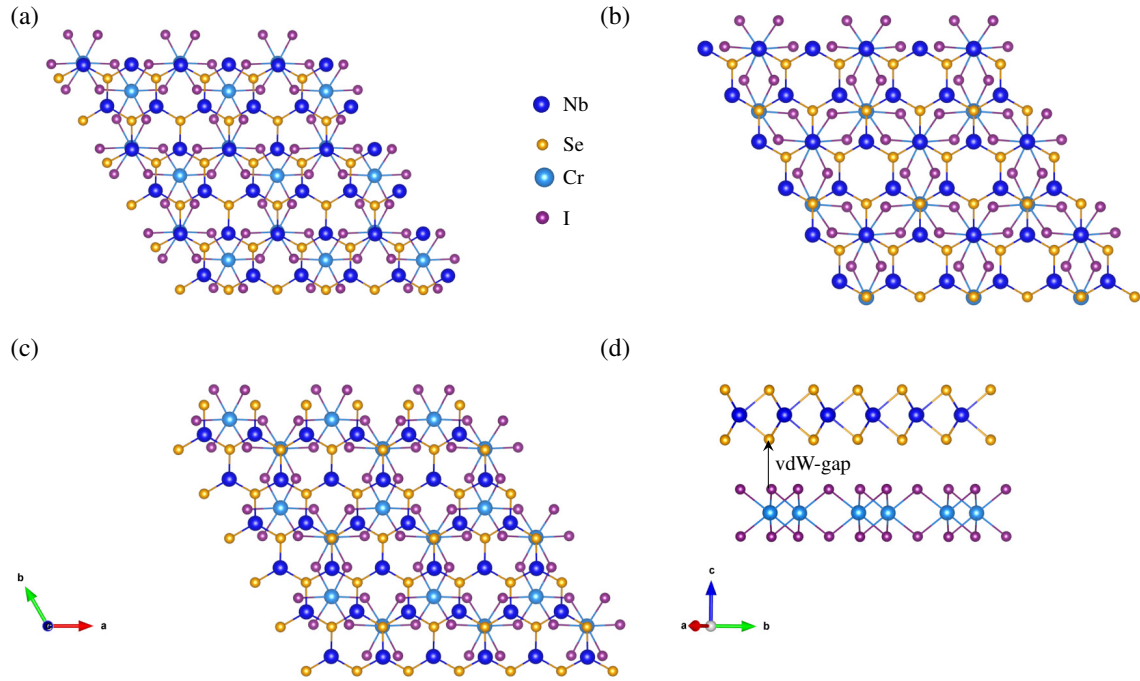


Figure 7.3: The $\text{CrI}_3/\text{NbSe}_2$ heterostructure can form three different configurations based on the relative arrangement of Cr, Nb, and Se atoms, namely, hollow-Se, hollow-NbSe, and hollow-Nb. (a) Top view of the hollow-Se configuration where Se atoms are positioned at the hollow sites of CrI_3 . (b) Top view of the hollow-NbSe configuration in which both Nb and Se atoms surround the hollow site of CrI_3 . (c) Top view of the hollow-Nb configuration where Nb atoms occupy the hollow sites of CrI_3 . (d) A side view shows the interlayer distance marked as the vdW gap, an important parameter for vdW heterostructures.

band structure, magnetic exchange splitting and SOC splitting of bands in the heterostructure under different theoretical levels. The magnetic moment of the Nb layer has around $0.1 \mu_B/\text{Nb}$ atom in the heterostructure. To enhance its magnetic moment, we add the Hubbard U parameter to Cr d orbitals. The Cr d orbitals in

the valence band get more localised and increase the Cr magnetic moment by 11 %. But, the enhancement of the Cr magnetic moment does not alter the magnetic moment of the Nb layer. As the heavy atoms are present in the heterostructure,

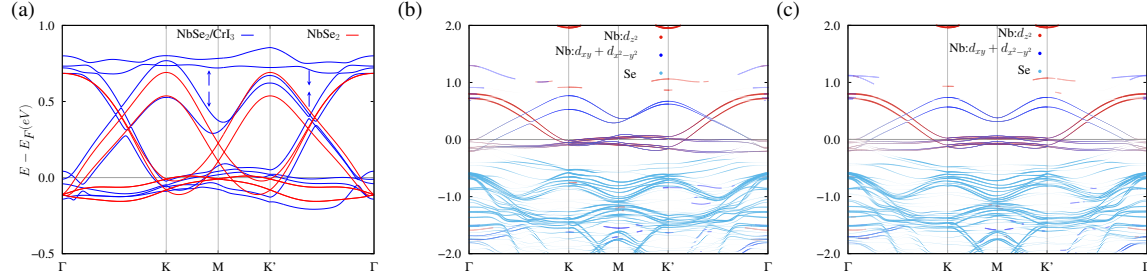


Figure 7.4: We investigate the impact of magnetic layers on the electronic band structure of NbSe₂/CrI₃ heterostructure to understand the orbital characteristics and spin splitting near the Fermi level. (a) The blue-coloured heterostructure bands, compared to the red-coloured pristine NbSe₂ bands, show enhanced spin splitting at K and quenched at K' point. (b) For out-of-plane Cr spin configuration, bands around the Fermi level reveal in-plane orbitals such as $d_{x^2-y^2}$ and d_{xy} near the valley points (K and K'), whereas the Γ point is dominated by out-of-plane orbital d_{z^2} . (c) For Cr spin along the in-plane direction, similar orbital nature of heterostructure bands near the Fermi level with slightly enhanced spin splitting at valley points.

Table 7.2: The average magnetic moment per atom on the Cr and the Nb atoms in the NbSe₂/CrI₃ heterostructure .

magnetic moment (μ_B)	PBE	PBE+U	PBE+U+SOC
Cr	3.12	3.36	3.36
Nb	0.09	0.09	0.09

we incorporate the spin-orbit interaction into our calculations to see its effect on the Nb magnetic moment. We find that the Nb magnetic moment, as well as Cr magnetic moment, remain unchanged. The Nb moment remains constant to 0.1 μ_B /Nb atom under all three theoretical levels [Table 7.2]. The possible reason for the origin of the Nb moment may be the distortion of the NbSe₂ trigonal prismatic

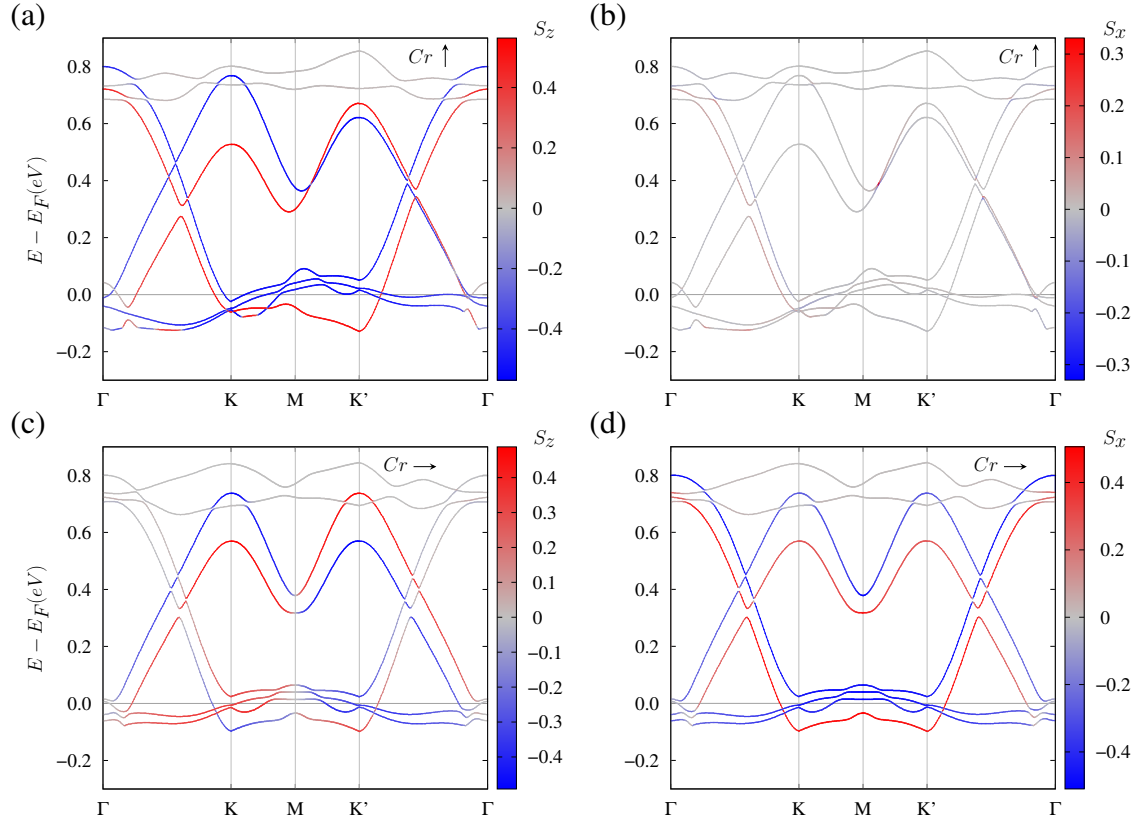


Figure 7.5: Spin-projected bands near the Fermi level in a hollow-Nb arrangement of the heterostructure, under different Cr spin configurations. (a) When the Cr spin is oriented out of the plane (upward arrow), the S_z -projected spin band exhibits opposite spin-splitting behaviour at the valley points. (b) The out-of-plane Cr spin configuration results in the absence of in-plane S_x -projected spin bands. On the other hand, when the Cr spin is in-plane (rightward arrow), both (c) S_z -projected spin and (d) S_x -projected spin bands are observed.

structure or due to magnetic exchange splitting for the collinear case. As we do not get any large change in the Nb-Se bond that rules out the distortion of the trigonal prismatic structure. We observe that the large magnetic exchange splits around 72 meV, and it remains unchanged with and without U calculations. The Nb d band splits into a spin-up and a spin-down band around the Fermi energy with non-symmetric magnetic exchange splitting. The only $I p$ states can influence the Nb d band near the Fermi energy. For the non-collinear case, the Nb layer gets magnetised due to SOC splitting. The band around the K point splits by 247 meV,

which is 94 meV more than the pristine band splitting. The bands near the Fermi level mix with Nb d orbitals [Figure 7.4(a)-(b)]. The presence of I p orbitals can provide extra SOC splitting around the K point. To examine the metallic nature of

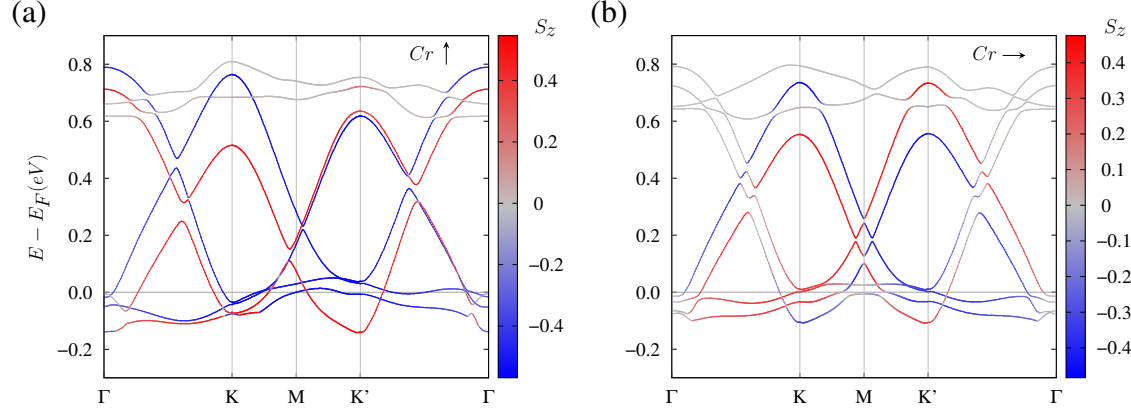


Figure 7.6: In the hollow-NbSe configuration, both out-of-plane and in-plane orientations of the Cr spin (indicated by upward and rightward arrows, respectively) influence the S_z -projected Nb bands, similar to the hollow-Nb. (a) When the Cr spin is oriented along the z -direction, the magnitude of spin splitting enhancement or diminution differs from other heterostructure configurations. (b) With in-plane Cr spin, the out-of-plane spin projection exhibits more splitting at the valley points.

the NbSe₂ layer, we look into the partial density of states (pDOS) of Nb d orbitals at the Fermi level. We get pdos 1.3 states/eV-u.c. at the Fermi level. The Nb states do not change either by adding the U parameter or the U parameter with SOC due to the minimum presence of Cr d and I p states near the Fermi level. Its pdos at the Fermi level in the heterostructure reduce by 9 % in comparison to pristine.

7.3.4 Hamiltonian modelling of vdW heterostructure

To understand the topological superconducting phase under the influence of a magnetic field, we model the vdW heterostructure with a low-energy TB Hamiltonian. In the energy bands of the heterostructure, the conducting NbSe₂ bands appear between the valence bands and conduction bands of CrI₃. There is minimal overlap between the NbSe₂ bands and CrI₃ bands near the Fermi level. Thus,

we can model the low-energy physics of their heterostructure with TB Hamiltonian based on Nb d orbitals hopping provided with external magnetic field term. The NbSe₂ bands near the Fermi level is dominated by the three Nb-4 d orbitals namely, d_{z^2} , d_{xy} and $d_{x^2-y^2}$ [Fig.7.1(b)].

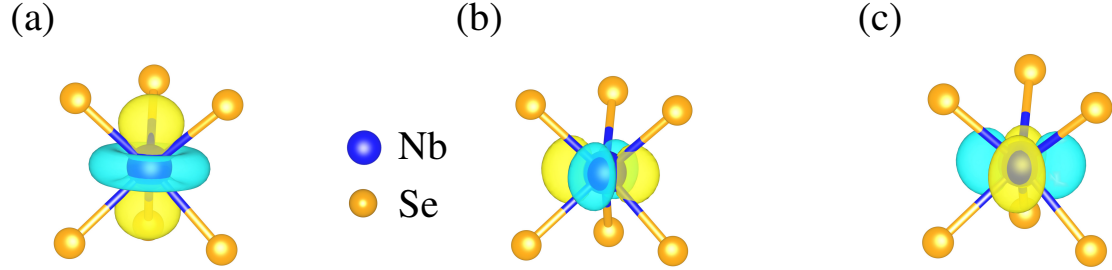


Figure 7.7: Three Wannier functions were used to evaluate tight-binding parameters: (a) a d_{z^2} -orbital-like Wannier function and two planar Wannier functions, (b) a $d_{x^2-y^2}$ -shaped Wannier function, and (c) a d_{xy} -shaped Wannier function.

As discussed earlier, the conducting bands in [Fig.7.1(b)] have an asymmetric Ising spin-orbit splitting around the valley points and show a Rashba spin-orbit splitting near the M point. With these observations, we construct TB Hamiltonian with the Ising spin-orbit interaction H_I , Rashba spin-orbit term H_R and external magnetic field term B (B_x , B_y , B_z) in the basis of [$c_{\mathbf{k},d_{xy},\uparrow}$, $c_{\mathbf{k},d_{x^2-y^2},\uparrow}$, $c_{\mathbf{k},d_{z^2},\uparrow}$, $c_{\mathbf{k},d_{xy},\downarrow}$, $c_{\mathbf{k},d_{x^2-y^2},\downarrow}$, $c_{\mathbf{k},d_{z^2},\downarrow}$]. The standard tight-binding Hamiltonian, which includes hopping terms up to third-nearest neighbours, is expressed as (115; 426),

$$H_N(\mathbf{k}) = I_2 \otimes H_{TNN}(\mathbf{k}) + \sigma_z \otimes H_I + \frac{1}{2} \mu_B g (B_x \sigma_x + B_y \sigma_y + B_z \sigma_z) \otimes I_3 \quad (7.1)$$

Here, σ_x , σ_y and σ_z are the Pauli matrices, μ_B is the Bohr magneton, g is the gyromagnetic ratio of electron and I_2 , I_3 are identity matrix of 2×2 and 3×3 dimen-

sion respectively. The third-nearest neighbors term $H_{TNN}(\mathbf{k})$ is written as (426):

$$H_{TNN}(\mathbf{k}) = \begin{pmatrix} V_0 & V_1 & V_2 \\ V_1^* & V_{11} & V_{12} \\ V_2^* & V_{12}^* & V_{22} \end{pmatrix} \quad (7.2)$$

The detailed expression for the above matrix elements is explained in this work (426).

Table 7.3: Hopping integrals and on-site energies for the three orbitals TB Hamiltonian of monolayer NbSe₂, calculated for third nearest hopping. These parameters are in the units of eV.

	t_0	t_1	t_2	t_{11}	t_{12}	t_{22}	u_0
u_1	u_2	u_{11}	u_{12}	u_{22}	r_0	r_1	r_2
r_{11}	r_{12}	λ	E_1	E_2			
	-0.231	0.312	0.346	0.2795	0.279	-0.054	0.068
-0.038	0.054	0.06	-0.018	-0.043	0.004	-0.0997	0.039
0.032	0.099	0.0784	1.447	1.85			

To evaluate the 3×3 Hamiltonian matrix in the Eq.(7.2) requires hopping integrals and on-site energies for these orbitals d_{z^2} , d_{xy} and $d_{x^2-y^2}$. We have constructed the three Wannier functions [Fig. 7.7] based on these orbitals to calculate the tight-binding parameters from the first-principles calculations (138). These parameters are provided in Table 7.3. To explain the spin-splitting at the valley points, the Ising soc term is added as:

$$H_I = \frac{1}{2}\lambda L_z \quad (7.3)$$

Where λ is the spin-orbit splitting term at the valley points (K and K'). The out-of-

plane projection of the orbital angular momentum L_z is given by (426):

$$L_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -2i \\ 0 & 2i & 0 \end{pmatrix} \quad (7.4)$$

We have calculated the TB band structure by diagonalizing the 6×6 Hamiltonian matrices (with magnetic field term $B = 0$) in the Eq.(7.1) for the line k points of hexagonal BZ. It reproduces the *ab initio* band structure near the Fermi level [Fig. 7.8(a)]. The Rashba Hamiltonian, denoted by H_R , can be expressed in terms of the Pauli matrices σ_x and σ_y as follows (115; 440):

$$H_R(\mathbf{k}) = V_r \left[(\sqrt{3} \sin \beta \cos \alpha) \sigma_x - (\sin 2\alpha + \sin \alpha \cos \beta) \sigma_y \right] \quad (7.5)$$

Here, α and β are defined as $\alpha = \frac{1}{2}k_x a$ and $\beta = \frac{\sqrt{3}}{2}k_y a$, respectively. The parameter V_r is a constant representing the strength of the Rashba spin-orbit coupling, and $\mathbf{k}$ is a vector containing the wave vector components k_x and k_y . By incorporating the Rashba term into the Eq.(7.1), we have computed the band structure in the vicinity of the M point, in the absence of any magnetic field. We have then compared this computed band structure with the band structure obtained from DFT calculation [Fig. 7.8(b)]. To simulate the vdW heterostructure, we have numerically solved the Eq.(7.1) separately for the cases where the external magnetic field is oriented along the out-of-plane and in-plane directions. Our calculations show that when the magnetic field is oriented out-of-plane, there is an enhancement of the spin-splitting at the K point, while it is reduced at the K' point [Fig. 7.9(a)]. This trend is similar to the DFT band structure of NbSe₂/CrI₃ in [Fig. 7.4(a)]. On the other hand, when the external magnetic field is oriented along the x-direction, we observe a slight improvement in spin-splitting at the valley points and lifting

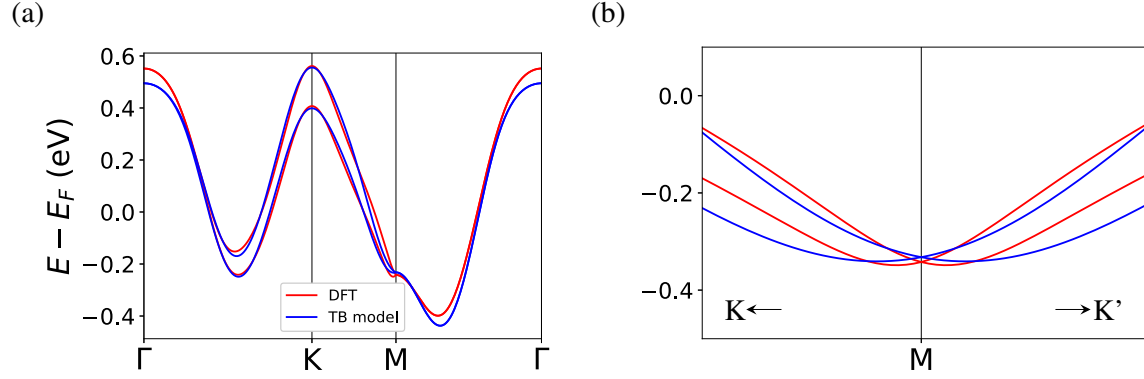


Figure 7.8: The third nearest neighbour tight-binding (TB) band structures of NbSe₂ are compared with DFT bands, represented in blue and red colours, respectively, with the inclusion of (a) Ising spin-orbit coupling and (b) Rashba spin-orbit interaction in the TB Hamiltonian.

of band degeneracy at the Γ point [Fig. 7.9(b)]. A similar observation is found in heterostructure bands in the [Fig. 7.4(c)]. Therefore, our calculations employing Eq.(7.1) establish the qualitative trend of the band structure of NbSe₂/CrI₃. To study the superconducting phase, we employ the TB Hamiltonian $H_N(\mathbf{k})$ in the Bogliubov-de-Gennes (BdG) formalism with the Nambu spinor basis. The 12×12 BdG Hamiltonian matrix for the bulk monolayer NbSe₂ is written as (115):

$$H_{BdG}(\mathbf{k}) = \begin{pmatrix} H_N(\mathbf{k}) - \mu I_{6N} & -i\sigma_y \Delta \otimes I_{3N} \\ i\sigma_y \Delta \otimes I_{3N} & -H_N^*(-\mathbf{k}) + \mu I_{6N} \end{pmatrix} \quad (7.6)$$

Here, Δ is the superconducting gap, μ is chemical potential and I_6 is 6×6 identity matrix. The local density of states (LDOS) in the superconducting state is numerically evaluated using retarded Green's function method. The expression for LDOS is given by (115):

$$\rho(E) = -\frac{1}{\pi} \text{Tr} \left[\text{Im} G^R(E) \right] \quad (7.7)$$

Here, the retarded Green's function is defined as $G^R(E) = [E + i\eta - H_{BdG}(\mathbf{k})]^{-1}$. We have numerically solved the Eq.(7.6) with magnetic field along x-direction (B_x

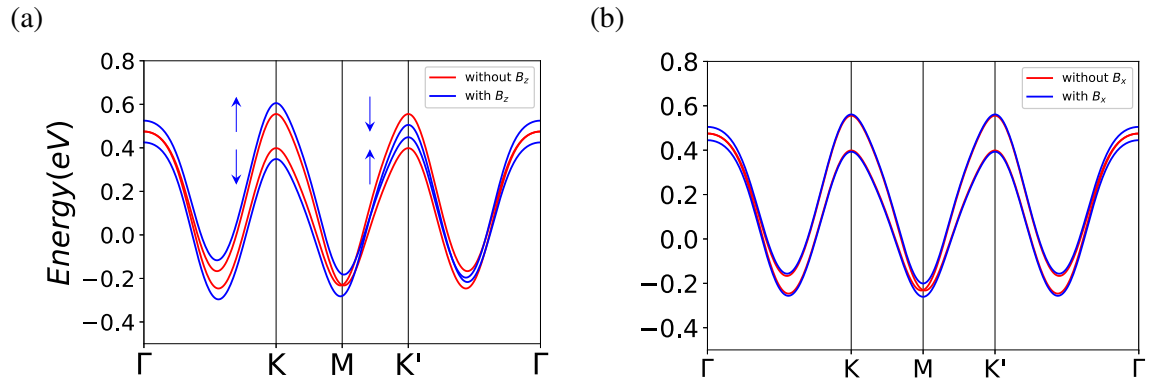


Figure 7.9: The low-energy bands of the tight-binding Hamiltonian are compared with and without an external magnetic field term (B). The inclusion of the external magnetic field reproduces the qualitative trend of heterostructure bands near the Fermi level. (a) The tight-binding band structure with (blue line) and without (red line) an out-of-plane magnetic field (B_z) is shown. The blue arrows indicate the direction of spin splitting, which is similar to the heterostructure bands at valley points. (b) The tight-binding band structure with and without an in-plane magnetic field (B_x) is shown, revealing a small improvement in spin splitting at the valley points.

$> H_p$, where H_p is the Pauli limit field, $\Delta = 0.02$ eV) for the line kpoints along M1- Γ -M1, M2- Γ -M2 and M3- Γ -M3 within the hexagonal BZ [Fig. 7.10(d)]. The applied in-plane magnetic field closes the superconducting gap in the bulk BdG spectrum and provides two pairs of point nodes along each line kpoints [Fig. 7.10(a)-(c)]. These feature match with previous study (115). We have also evaluated the local density of states for the bulk BdG Hamiltonian under the in-plane magnetic field using Eq.(7.7). It provides the V-shaped LDOS near the zero energy, which confirms the appearance of point nodes within the BZ [Fig. 7.10(e)]. To understand the topology within the superconducting phase, we model the zigzag and armchair edges of NbSe₂ nano-ribbon. In the nano-ribbon, armchair edge along y-direction [Fig. 7.11(a)] and zigzag edge along x-direction [Fig. 7.11(b)] where varying N indicates the width of the edges. The model Hamiltonian for zigzag edge is written in terms of 3rd NN hoppings and on-site energies of three Nb 4- d orbitals. The 3N

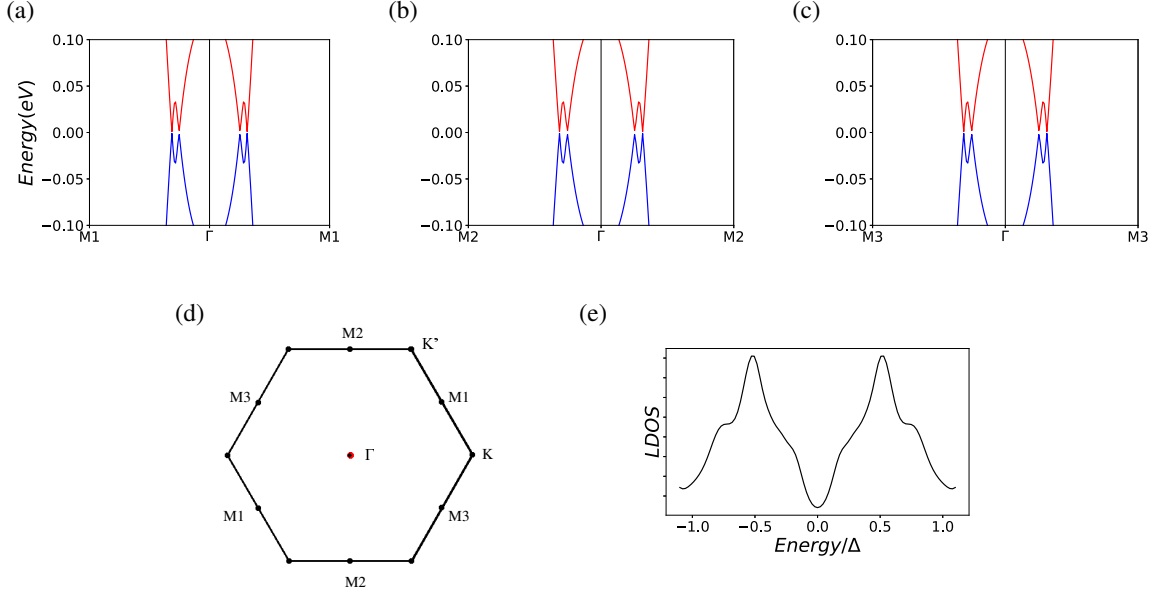


Figure 7.10: The bulk BdG spectrum exhibits the appearance of point nodes under the application of an in-plane magnetic field and their corresponding local density of states (LDOS). Along the (a) M1- Γ -M1, (b) M2- Γ -M2, and (c) M3- Γ -M3 lines, two pairs of point nodes emerge, which combine to form six pairs of nodal points within (d) the hexagonal Brillouin zone. (e) The LDOS is evaluated for the bulk BdG Hamiltonian with an in-plane magnetic field.

× 3N Hamiltonian matrix for the zigzag edge is described as follows (426):

$$H_{\text{zigzag}}^0(k_x) = \begin{bmatrix} h'_1 & h'_2{}^\dagger & & & \\ h'_2 & h'_1 & h'_2{}^\dagger & & \\ & h'_2 & h'_1 & \ddots & \\ & & \ddots & \ddots & h'_2{}^\dagger \\ & & & h'_2 & h'_1 \end{bmatrix} \quad (7.8)$$

where the matrix elements are defined as $h'_1 = H_{\text{zigzag}}^{n,n}$ and $h'_2 = H_{\text{zigzag}}^{n,n-1}$. These matrix elements depend upon hopping parameters and on-site energies. The detailed expressions for these matrix elements are provided in this work (426). Next, we have added the Ising spin-orbit term and external magnetic field term to the

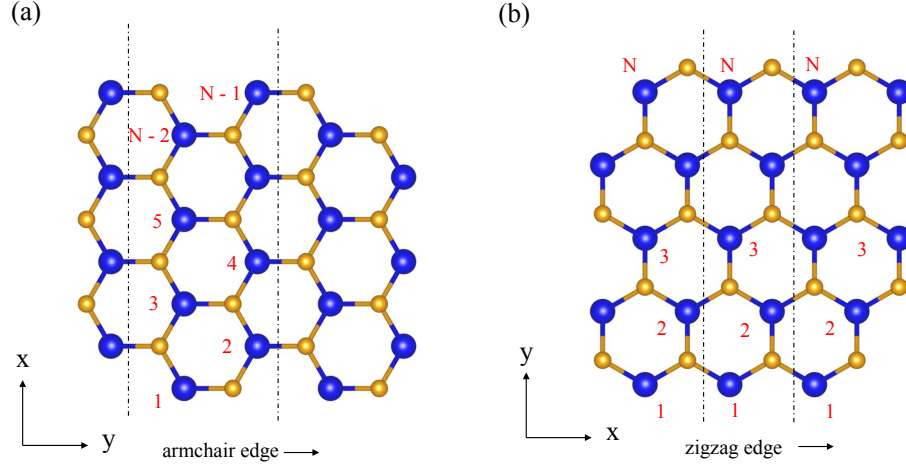


Figure 7.11: The unit cell of a NbSe₂ nanoribbon with (a) an armchair edge along the y-direction and (b) a zigzag edge along the x-direction.

zigzag Hamiltonian. The $6N \times 6N$ Hamiltonian matrix $H_{\text{zigzag}}(k_x)$ is defined as:

$$H_{\text{zigzag}}(k_x) = I_2 \otimes H_{\text{zigzag}}^0(k_x) + \sigma_z \otimes I_N \otimes \frac{1}{2}\lambda L_z + \frac{1}{2}\mu_B g(B_x \sigma_x + B_z \sigma_z) \otimes I_{3N} \quad (7.9)$$

Here, I_2 , I_N and I_{3N} are the identity matrices of dimension 2×2 , $N \times N$ and $3N \times N$ respectively. The superconducting Hamiltonian for zigzag edge is described as:

$$H_{\text{zigzag}}^{\text{BdG}}(k_x) = \begin{pmatrix} H_{\text{zigzag}}(k_x) - \mu I_{6N} & -i\sigma_y \Delta \otimes I_{3N} \\ i\sigma_y \Delta \otimes I_{3N} & -H_{\text{zigzag}}^*(-k_x) + \mu I_{6N} \end{pmatrix} \quad (7.10)$$

In order to establish the normal state Hamiltonian for the zigzag edge, we numerically solved the Hamiltonian in Eq.(7.8) for a MoS₂ nanoribbon with edge width $N=8$. The resulting energy bands for the zigzag edge, as shown in Fig. 7.12(a), are consistent with the reported zigzag band structure (426). Next, we calculated the zigzag band structure with Ising spin-orbit coupling for a NbSe₂ nanoribbon, as shown in Fig. 7.12(b). In this case, most of the edge bands are located near the Fermi level. For the superconducting state, we diagonalized the Hamiltonian matrix in Eq.(7.10) under an applied in-plane magnetic field ($B_x > H_P$ with $\Delta = 0.02$

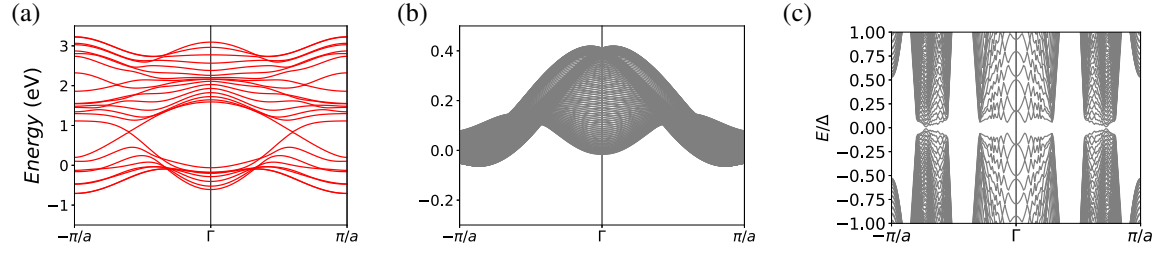


Figure 7.12: The calculated energy spectrum for zigzag nanoribbons in the normal and superconducting state. (a) Edge band structure (in red) of MoS₂ zigzag edge with width (N = 8). (b) Edge band structure of NbSe₂ zigzag edge with width (N = 101). (c) Superconducting BdG spectrum of NbSe₂ zigzag edge with similar edge width.

eV). The applied magnetic field closes the gap near $\pm \frac{\pi}{a}$, but does not result in a Majorana flat band. Therefore, the zigzag edge spectrum does not show a Majorana flat band at zero energy, as shown in Fig. 7.12(c). After the zigzag edge, we study the armchair edge of the nano-ribbon. The normal state $3N \times 3N$ Hamiltonian matrix is written as (115):

$$H_0 = \begin{pmatrix} h_1 & h_2 & h_3 & h_4 & h_5 & 0 & \dots & 0 \\ h_2^\dagger & h_1 & h_2 & h_3 & h_4 & h_5 & & \vdots \\ h_3^\dagger & h_2^\dagger & h_1 & h_2 & \ddots & \ddots & \ddots & 0 \\ h_4^\dagger & h_3^\dagger & h_2^\dagger & \ddots & \ddots & \ddots & h_4 & h_5 \\ h_5^\dagger & h_4^\dagger & h_3^\dagger & \ddots & \ddots & \ddots & h_3 & h_4 \\ 0 & h_5^\dagger & \ddots & \ddots & \ddots & h_1 & h_2 & h_3 \\ \vdots & & \ddots & h_4^\dagger & h_3^\dagger & h_2^\dagger & h_1 & h_2 \\ 0 & \dots & 0 & h_5^\dagger & h_4^\dagger & h_3^\dagger & h_2^\dagger & h_1 \end{pmatrix}_{N \times N} \quad (7.11)$$

where h_n ($n = 1$ to 5) is the 3×3 hopping matrix between different Nb lattice sites, and its expression is provided in this work (115). The $6N \times 6N$ Hamiltonian matrix

with Ising soc and magnetic field term is described as:

$$H_{\text{arm}}(k_y) = I_2 \otimes H_0(k_y) + \sigma_z \otimes I_N \otimes \frac{1}{2}\lambda L_z + \frac{1}{2}\mu_B g(B_x \sigma_x + B_z \sigma_z) \otimes I_{3N} \quad (7.12)$$

The Rashba term for armchair edge is explained as,

$$\begin{aligned} H_R^{\text{arm}} = & \hat{c}_{n,s}^\dagger \hat{c}_{n+1,s'} \left[-\sigma_x \sqrt{3} \sin \beta - i\sigma_y \cos \beta \right]_{ss'} + \hat{c}_{n+1,s}^\dagger \hat{c}_{n,s'} \left[-\sigma_x \sqrt{3} \sin \beta + i\sigma_y \cos \beta \right]_{ss'} \\ & + \left[i\sigma_y \right]_{ss'} \hat{c}_{n+2,s}^\dagger \hat{c}_{n,s} + \left[-i\sigma_y \right]_{ss'} \hat{c}_{n,s}^\dagger \hat{c}_{n+2,s} \end{aligned} \quad (7.13)$$

where $n, n+1$ and $n+2$ indices for Nb lattice sites and s and s' spin indices.

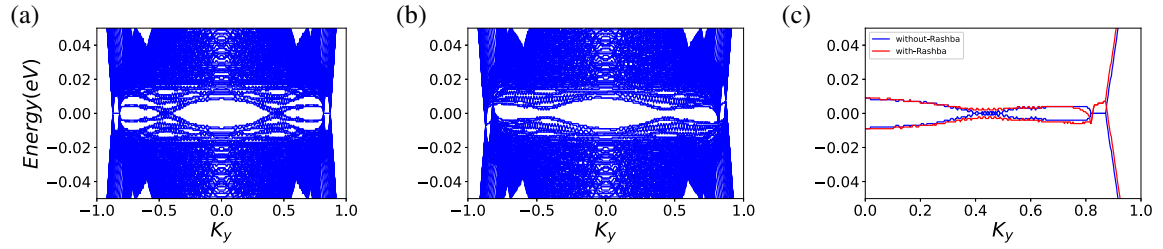


Figure 7.13: The BdG edge spectrum of an armchair NbSe₂ nano-ribbon. (a) A Majorana zero energy mode emerges under an applied in-plane magnetic field. (b) The inclusion of Rashba spin-orbit coupling affects the zero energy mode. (c) A zoomed-in view of the Majorana zero energy mode with and without the Rashba spin-orbit coupling.

For superconducting state, $12N \times 12N$ BdG Hamiltonian is described as:

$$H_{\text{arm}}^{\text{BdG}}(k_y) = \begin{pmatrix} H_{\text{arm}}(k_y) - \mu I_{6N} & -i\sigma_y \Delta \otimes I_{3N} \\ i\sigma_y \Delta \otimes I_{3N} & -H_{\text{zigzag}}^*(-k_y) + \mu I_{6N} \end{pmatrix} \quad (7.14)$$

We have solved the above Hamiltonian for the in-plane magnetic field to get the BdG spectrum. In this spectrum, we observe a Majorana flat band at zero energy [Fig. 7.13(a)], and It matches with recent theoretical calculations on NbSe₂ with external magnetic field(115). Later, we added to the superconducting Hamiltonian

the Rashba spin-orbit coupling using the Rashba expression for the armchair edge. The introduction of Rashba interaction opens the gap and tilts the flat band at the zero energy [Fig. 7.13(b)-(c)]. To better describe the Cr spin in the vdW heterostructure, we are studying the topological superconducting state under the out-of-plane magnetic field.

Finally, we have established that a three $4d$ orbital tight-binding (TB) model, incorporating up to third-nearest neighbour hopping, is suitable for accurately modelling the low-energy bands of a NbSe₂ monolayer. Furthermore, our TB band structure exhibits a strong agreement with the band structure obtained through DFT [see Fig. 7.8]. In order to accurately reproduce the spin splitting of the bands near the valley points, we have included Ising spin-orbit interactions within our TB model Hamiltonian. Our results are consistent with recent studies in this area(115; 426; 441). We have also extended our analysis to model the NbSe₂/CrI₃ heterostructure by adding an external magnetic field to our TB Hamiltonian. We found that, by changing the orientation of the magnetic field, the trend of spin splitting closely matches that observed in NbSe₂/CrI₃ DFT bands at valley points[see Fig. 7.4(a) and Fig. 7.9]. These results of spin-valley interactions follow the trend of recent experimental and theoretical works(442–445). Next, we investigated the superconducting nature of NbSe₂ under the CrI₃ layer using the BdG formalism. To establish its non-trivial topological nature, we explained the bulk as well as two edges of NbSe₂ with finite edge width under the presence of the in-plane magnetic field. The applied in-plane magnetic field closed the gap in the bulk BdG spectrum and formed six pairs of nodal points along the $M-\Gamma-M$ line within the hexagonal Brillouin zone. This observation matches recent theoretical studies(115; 441), and it is distinct from other topological superconductors that have a bulk superconducting gap with topologically protected gapless edges. The Ising spin-orbit interactions protected vortices formation due to the magnetic field, causing this

nodal phase to appear. We further investigated the topological nature by modelling the armchair and zigzag edges. On the zigzag edge, we did not observe a topologically protected flat band at zero energy. This result is consistent with recent studies, where bulk nodal phases are cancelled out while projecting over the zigzag edge(115; 441). On the other hand, we observed the appearance of a Majorana flat band at zero energy on the armchair edge under an applied in-plane magnetic field. The appearance of this flat band is influenced by Ising and Rashba spin-orbit interactions. This realization of a Majorana flat band at zero energy will provide a peak in the zero energy LDOS that can be measured by STM experiments.

7.4 Conclusion

This chapter describes the *ab initio* calculations performed on monolayers of NbSe₂ and CrI₃ and their vdW heterostructure. The electronic band structure of NbSe₂ and its spin-splitting at the valley points and 2D Fermi surface are explained under the Ising spin coupling. In contrast, a ferromagnetic insulating state is observed for monolayer CrI₃. The vdW heterostructure shows a finite magnetic moment of 0.1 μ_B on the Nb atom, which is influenced by the orientation of the Cr spin. The low-energy tight-binding (TB) Hamiltonian is established for NbSe₂ and the vdW heterostructure by comparing its band structure and spin splitting at the valley points with the *ab initio* results. The BdG formalism is applied to study the bulk state, zigzag and armchair edge states of the superconducting phase under an applied magnetic field. In the bulk state, six pairs of nodal points emerge within the hexagonal Brillouin zone. A Majorana flat band appears on the armchair edge but disappears on the zigzag edge under an applied in-plane magnetic field. These findings suggest that the NbSe₂/CrI₃ vdW heterostructure is a promising platform

for investigating Majorana zero-energy modes.

Chapter 8

Summary and Outlook

Exotic quantum states of matter, such as superconductivity and magnetism, and the ability to understand, control, and manipulate them are at the forefront of condensed matter physics with disruptive technological implications. The thesis is devoted to explore superconductivity and magnetism within the first principle approach with a specific goal of tuning it. Further, we explore the possibility of emergent Majorana zero mode at the interface of novel quantum phenomena that emerge at the interface of two-dimensional heterostructures of superconductors and ferromagnets.

The first part of the thesis focuses on the intricate phenomenon of superconductivity by applying the first principles approach. The Migdal-Eliashberg theory has proven to be a highly successful approach in describing conventional superconductivity, where the electron pairing is driven by phonon-induced attraction. The theory has recently achieved notable success in predicting high-temperature superconductivity in hydrogen-rich compounds under high pressure, including rare earth hydrides (446–449) and hydrogen sulfides (450). Subsequently, these predictions have been experimentally confirmed, further validating the theory (451; 452).

In the thesis, we delve into the intricacies of tip-induced superconductivity and endeavour to provide a microscopic comprehension of its presence, emergence, and amplification in various materials such as CuFeSb (181), hcp-Zr (45), and ZrSiS (48). Through our comprehensive analysis, we gain a deeper insight into

the underlying mechanisms that govern the manifestation of superconductivity in these materials. Furthermore, we extend our investigation to explore superconductivity in doped ZrB_2 , which has been observed in recent experiments. While the underlying mechanism for superconductivity in these materials is yet to be addressed, we investigate electronic structure, lattice dynamics, and electron-phonon coupling in V-doped ZrB_2 and consequently examine the origin of the superconductivity. We present a detailed analysis providing a thorough understanding of the factors that might influence superconductivity in doped ZrB_2 . Based on the findings, we concluded that V (or electron) doped ZrB_2 is not a phonon-mediated superconductor (453). In a larger context, these results indicate the applicability of Eliashberg theory of superconductivity in real materials to describe the role of phonons in providing the attractive interaction between two electrons. However, in addition to the electron-phonon coupling, one should notice the importance of Coulomb interaction to gain further predictive power. This requires an additional understanding of Coulomb correlations and their effects on pairing. (141)

The second part of the thesis is devoted to understand magnetism in two-dimensional materials, which was believed to be at odds with the Hohenberg-Mermin-Wagner theorem. However, the continuous rotational symmetry of the spin, which is the fundamental assumption of the Hohenberg-Mermin-Wagner theorem, is broken by the magnetic anisotropy originating from the relativistic spin-orbit coupling in natural materials. Since the landmark discovery of magnetic ordering in two dimensions in 2017, significant efforts have been dedicated to screening and discovering atomically thin magnetic materials. Two-dimensional magnetism presents a unique opportunity to make significant contributions to science and engineering. The field is ripe with potential for exploration, discovery, and innovation, which promises to have a significant impact on various applications such as spintronics, magnonics, and quantum computing.

However, due to the small on-site magnetic anisotropy in reduced dimensions, rapid spin fluctuations occur, resulting in the magnetic ordering at cryogenic temperatures. This limitation hinders their potential technological utilization at present. As a result, the fundamental question of whether magnetism can be externally manipulated arises naturally. In order to predict properties that can guide future experiments, it is necessary to develop a more accurate microscopic model that can both explain and reproduce the wide range of experimental results. In this regard, we aimed to construct a microscopic model Hamiltonian that could effectively explain the experimental data available. In this regard, a long-range anisotropic Heisenberg XXZ model with magnetic interactions beyond the first neighbour is able to explain the experimental observations, particularly in chromium trihalides. (325; 365) The study shows that the magnetic ordering can be dramatically manipulated up to room temperature through external modulation of exchange and anisotropic magnetic interactions by gate-induced charge carrier doping (365). These results are particularly noteworthy as they reveal new possibilities for electrically controlled spintronic and magnetoelectric devices based on atomically thin crystals. We believe that the results presented in this thesis will trigger further experimental attention to test the conclusions.

Further research can explore interesting directions, such as discovering magnetic materials with high transition temperature. This can be achieved by searching for new materials through automated materials screening or by manipulating microscopic magnetic interactions in already known materials through external perturbation. The later one has been the focus of this thesis. While the thesis mainly concentrates on ferromagnetic materials, it is worth noting that another promising research direction is the exploration of 2D antiferromagnetic materials for spintronic applications. These materials exhibit unique characteristics, including ultra-fast dynamics and strong spin-transfer torque, which make them highly

attractive for such applications (454–456). An intriguing research direction is to study the interplay of strong electron correlation, large spin-orbit coupling, and band topology in ultrathin magnetic oxides, including materials that are candidates for Kitaev spin liquids.

Another direction is the utilization of two-dimensional magnets for assembling van der Waals layers into heterostructures holds significant potential for the design and development of novel quantum materials. (307–311) The creation of such heterostructures allows for precise manipulation of the breaking of time-reversal and inversion symmetries, which is crucial for constructing novel topological materials. For example, the coupling between the two-dimensional ferromagnet and superconductor is a promising route for topological superconductivity and observing Majorana zero mode. (98; 109) Another prospect in magnetizing two-dimensional semiconductors by magnetic proximity coupling and new devices are rapidly emerging. (443; 457) Specifically, two-dimensional ferromagnets can be used as exchange-coupled substrates to manipulate valleys in semiconductors and control Kitaev interactions in quantum spin liquids.

As part of this thesis, we explore the possibility of topological superconductivity in a custom-designed heterostructure that comprises a ferromagnetic substrate and a two-dimensional superconductor placed on top of it. Particularly, we investigate the vdW NbSe₂/CrI₃ heterostructure within the first-principles calculations in combination with tight-binding and Bogoliubov-de Gennes Hamiltonians. We find that the Berry curvature present in NbSe₂ acts as an internal magnetic field, leading to spin splitting and spin-flip at the valley points K and K'. After incorporating spin-orbit coupling in our analysis, we observed that the in-plane Cr moment has no impact on the valley splitting, whereas the perpendicular Cr-spin plays a significant role and acts as a magnetic field. In the superconducting state, we noticed the appearance of six pairs of nodal points within the hexagonal Brillouin zone

under an applied in-plane magnetic field. Moreover, a Majorana flat band arises on the armchair edge of the NbSe₂ nano-ribbon but vanishes on the zigzag edge. Based on our findings, we conclude that vdW SC/FM heterostructures hold great promise as a cleaner platform for exploring and realizing Majorana zero modes (MZMs).

Although the detection of MZMs has attracted significant attention owing to their potential use in topological quantum computing, the identification of MZMs remained controversial due to similar experimental signatures arising from other quasiparticles. While several studies have reported the observation of zero-bias peaks, the interpretations of the data remain a subject of debate, and alternative explanations have been proposed. Consequently, various methods have been suggested for distinguishing MZMs from other quasiparticles, such as measuring the spatial distribution of the tunnelling conductance or analyzing the non-Abelian statistics of MZMs. Although researchers have made progress in this regard, the search for robust signatures of MZMs remains a vibrant area of research. ([458](#); [459](#))

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LIST OF PUBLICATIONS

Publications included in this thesis

1. *High spin polarization and the origin of unique ferromagnetic ground state in CuFeSb*
Anshu Sirohi, **Chandan K. Singh**, Gohil S. Thakur, Preetha Saha, Sirshendu Gayen, Abishek Gaurav, Shubhra Jyotsna, L.C. Gupta, Mukul Kabir, Ashok K. Ganguli and Goutam Sheet
Appl. Phys. Lett., 108, 242411 (2016)
2. *Large enhancement of superconductivity in Zr point contacts*
Mohammad Aslam, **Chandan K. Singh**, Shekar Das, Ritesh Kumar, Soumya Datta, Soumyadip Halder, Sirshendu Gayen, Mukul Kabir and Goutam Sheet
J. Phys. Condens. Matter 30, 255002 (2018)
3. *Tip-induced Superconductivity coexisting with preserved topological properties in line-nodal semimetal ZrSiS*
Leena Aggarwal, **Chandan K. Singh**, Mohammad Aslam, Sirshendu Gayen, Prabhat Mandal, Mukul Kabir and Goutam Sheet
J. Phys. Condens. Matter 31, 485707 (2019)
4. *Long-range anisotropic Heisenberg ferromagnets and electrically tunable ordering*
Chandan K. Singh and Mukul Kabir
Phys. Rev. B 103, 214411 (2021)
5. *First-principles study on the superconductivity of doped zirconium diborides*
Sanjay Nayak, **Chandan K. Singh**, Matrin Dahlqvist, Johanna Rosen, Per Eklund, and Jens Birch
Phys. Rev. Materials 6, 044805 (2022)
6. *Electrical tunable room temperature ferromagnetism in CrBr₃*
Chandan K. Singh and Mukul Kabir

Phys. Rev. Materials 6, 044805 (2022)

7. *Superconductor/ferromagnet van der Waals heterostructure: Appearance of Majorana zero mode*

Chandan K. Singh, Surjit Sarkar, G.J. Sreejith and Mukul Kabir

(In manuscript, 2023)

Publications not included in this thesis

8. *Giant Photoresponse Enhancement in Mixed-Dimension Van der Waals Heterostructure through Dielectric Engineering*

P Vindra, M A Gokul, Tamaghna Chowdhury, **Chandan K. Singh**, Shailendra Kumar Chaubey, Takashi Taniguchi, Watanabe Takashi, Mukul Kabir, G.V Pavan Kumar, and Atikur Rahman

Adv. Mater. Interfaces 9, 2102054 (2022)

9. *Flexible Piezoelectric Nanogenerators Based on One-Dimensional Neutral Coordination Network Composites*

Neetu Prajesh, Vijay Bhan Sharma, Shatruhan Singh Rajput, **Chandan Kumar Singh**, Prashant Dixit, Balu Praveenkumar, Jan K. Zareba, Dinesh Kabra, Satishchandra Ogale, Ramamoorthy Boomishankar

ACS Sustainable Chem. Eng. 10, 30, 9911-9920 (2022)