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Studying and manipulating magnetism in spin glass Fe intercalated ZrSe_2

by

Zhizhi Kong

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor D. Kwabena Bediako, Chair

Professor Jonathan Rittle

Professor Junqiao Wu

Spring 2024

Studying and manipulating magnetism in spin glass Fe intercalated ZrSe_2

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Zhizhi Kong

Abstract

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Doctor of Philosophy in

Chemistry University of

California, Berkeley Professor

D. Kwabena Bediako, Chair

Transition metal dichalcogenides (TMDs) constitute a class of materials wherein transition metals coordinated by bridging chalcogenides form two-dimensional layers that stack via van der Waals (vdW) interactions along the crystallographic c axis. This lamellar structure enables a diverse range of species, including transition metals, to be intercalated into these vdW interfaces. With open-shell intercalants, local magnetic moments can be introduced into the lattice, thereby inducing long-range magnetic order. The versatility of potential intercalants and host lattices has long made this class of materials an appealing choice as tunable platforms for investigating the interplay among composition, structure, and magnetism. More recently, there has been a growing appreciation for the influence of defects and domain structures in these intercalated compounds on exchange interactions and magnetic correlations. This recognition has led to the acknowledgment of complex magnetic phase spaces, highlighting the intricate interplay between structural features and magnetic properties.

We design a spin glass with strong spin frustration induced by magnetic disorder by exploiting the distinctive structure of Fe intercalated ZrSe_2 , where Fe(II) centers are shown to occupy both octahedral and tetrahedral interstitial sites and to distribute between ZrSe_2 layers without long-range structural order. Notably, we observe behavior consistent with a magnetically frustrated and multidegenerate ground state in these Fe_xZrSe_2 single crystals, which persists above room temperature. Moreover, this magnetic frustration leads to a robust and tunable exchange bias up to 250 K. These results not only offer important insights into the effects of magnetic disorder and frustration in magnetic materials generally, but also highlight as design strategy the idea that a large exchange bias can arise from an inhomogeneous microscopic environment without discernible long-range magnetic order. In addition, these results show that intercalated TMDs like Fe_xZrSe_2 hold potential for spintronic technologies that can achieve room temperature applications.

Since Fe intercalated ZrSe_2 is semiconducting which provides us a knob to tune its

physical and chemical properties electrochemically inserting a foreign species (Li^+ ions) into their interlayer spacing. We discover substantial enhancement of light transmission and electrical conductivity in thin (~ 30 nm) Fe intercalated ZrSe_2 nanosheets after Li intercalation due to changes in band structure and the injection of large amounts of free carriers. We also capture the first in situ optical observations of Li intercalation Fe_xZrSe_2 , shedding light on the dynamics of the intercalation process. The high reversibility of the intercalation process might be attributed to the enhanced stability of the structure induced by the intercalated Fe ion between the host lattice layers. The enhancement of electron transport upon the Li intercalation in the materials lays down a robust groundwork for electrostatic control over spin polarization. We also briefly explore the effect of semiconducting spin glass Fe_xZrSe_2 on generating and manipulating spin current in heavy metal, which highlights the potential application of the materials in spintronic technology.

Together, we study the interplay among composition, structure, and magnetism of Fe intercalated ZrSe_2 , explore the impact of electrostatic and electrochemical strategies to manipulate the properties of Fe_xZrSe_2 , lay down the robust cornerstone for the application of Fe_xZrSe_2 in spintronic technology, and inspire the research interest in expanding the knowledge of the magnetic ion intercalated TMDs to diverse 2D heterostructures and twist moiré patterns.

To those whom I love and those who love me.
To this incredible journey.

“What's past is prologue.”
- William Shakespeare

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Chapter 1

Introduction

1.1 Magnetic ion intercalated transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) are a class of materials composed of transition metals TM bonded with chalcogen elements Ch (Ch = S, Se, or Te). They have a unique layered structure where the transition metal atoms are sandwiched between layers of chalcogen atoms, forming extended crystalline planar structures held together by strong in-plane covalent bonds and weak out-of-plane van der Waals forces.¹ According to the coordination environment of the TM, TMDs usually adopt two types of polymorphs: octahedral 1T, prismatic 2H (**Figure 1.1**). TMDs have various fascinating physical, chemical, mechanical, electrical properties resulting from their rich electron–electron and electron–phonon interactions, layer-dependent band structure.^{1,3,4} Furthermore, they are also a great host for unique phenomena, such as superconductivity (SC)⁵ and charge density waves (CDW)^{1,6}. The recent rise of van der Waals material systems presents a promising avenue for the emergence of novel quantum materials. This involves stacking two or more atomic layers of different 2D TMDs⁹ or controlling the twist angle between bilayers,^{10,11}. Such manipulations alter the structural symmetry and band structure, giving rise to fascinating phenomena in spin, valley, and excitonic physics.

Numerous strategies have been employed to tailor the properties of transition metal dichalcogenides (TMDs),¹² including doping,¹³ strain engineering,¹⁴ intercalation,^{15,16} constructing heterostructures,⁹ external electric/optical tuning,¹⁷ size/dimensional tuning,¹⁸ and defect engineering.¹⁹ Among these approaches, intercalation stands out as a potent method for modifying TMD properties through diverse mechanisms, encompassing charge doping,^{20–22} layer expansion,^{23–26} orbital hybridization,^{27–29} and phonon scattering.^{23,30,31} The innate capacity of TMDs to act as intercalation hosts stems from their van der Waals (vdW) gap, where the interlayer distance, represented by the chalcogen (X)-to-chalcogen (X) distance, typically ranges between 3 to 3.5 Å in TMD structures.³²

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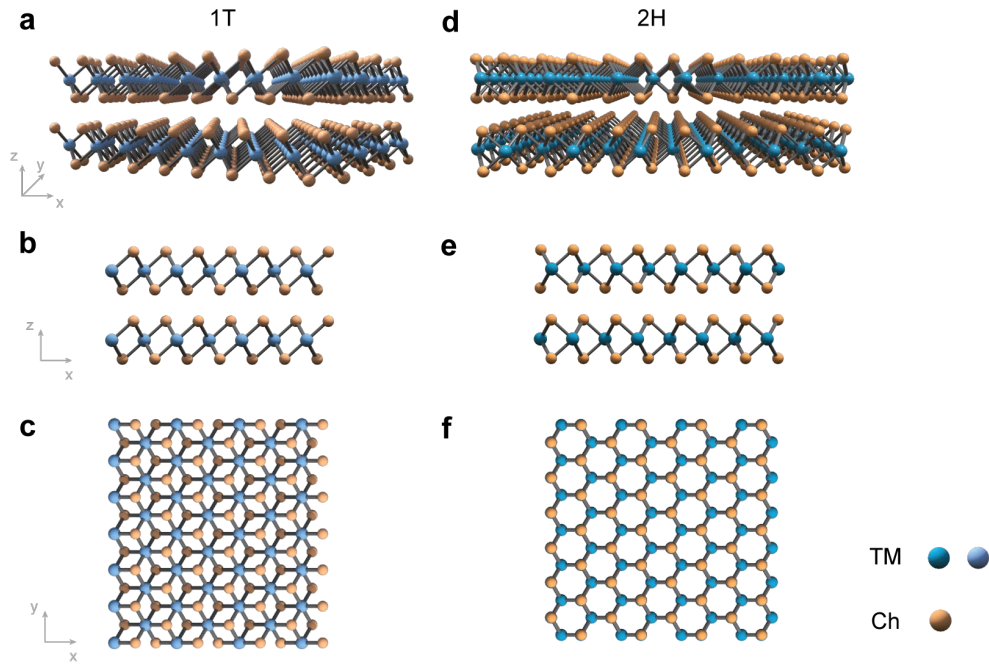


Figure 1.1. The crystal structures of (a) 1T phase and (b) 2H phase.

Structure of magnetic ion intercalated TMDs

In the vdW interface, 1T and 2H polytypes contain both octahedral and tetrahedral interstitial sites (**Figure 1.2**). For most magnetic ion intercalated TMDs, the magnetic ions have been reported to go into octahedral site exclusively.⁸ However, for Fe^{2+} , Co^{2+} , and Ni^{2+} intercalated ZrS_2 ,³³⁻³⁶ and Fe intercalated ZrSe_2 ,³⁷ magnetic ions are able to occupy the both octahedral and tetrahedral sites.

Crystallographic superlattices manifest at specific compositions of intercalated transition metal dichalcogenides (TMDs) with the formula TM_xMCh_2 , where intercalants orderly occupy

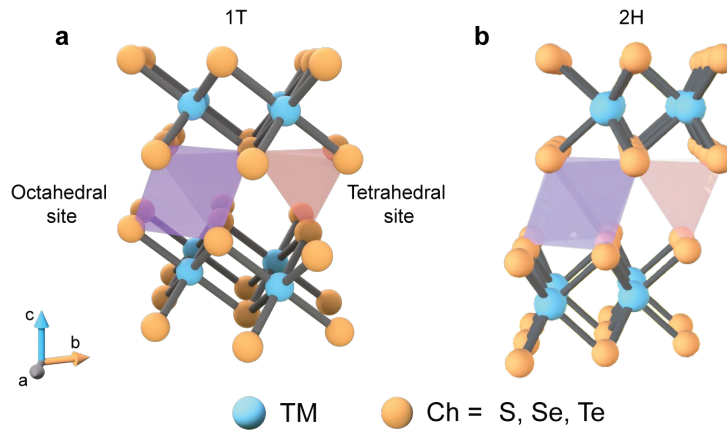


Figure 1.2. The crystal structures of (a) 1T phase and (b) 2H phase with octahedral and tetrahedral sites in vdWs gap.

CHAPTER 1. INTRODUCTION

octahedral interstitial sites. Here, we discuss the most common superlattice for TM_xMCh_2 , which emerges when with $x = 1/4$ and $x = 1/3$. Considering a 2H-MCh₂ TMD with lattice constant a_0 (**Figure 1.3a**), a supercell with $a' = 2a_0$ (denoted $2a_0 \times 2a_0$ and 2×2 for short) results at $x = 1/4$ (**Figure 1.3b**). In this case, the a and b axes of the superlattice coincide with those of the original lattice, and thus the space group of the parent TMDs can stay as $P6_3/mmc$. However, $x = 1/3$, a supercell with $a' = \sqrt{3}a_0$ (denoted $\sqrt{3}a_0 \times \sqrt{3}a_0$ and $\sqrt{3} \times \sqrt{3}$ for short) emerges (**Figure 1.3c**), rotating the a and b axes by 30° . Unlike the parent TMD and the 2×2 superlattice, the $\sqrt{3} \times \sqrt{3}$ superlattice lacks centrosymmetry, having space group $P6_322$. It can be observed that intercalants align in adjacent layers in the 2×2 superlattice, unlike the $\sqrt{3} \times \sqrt{3}$ superlattice along the c crystallographic axis. Along the a crystallographic axis, intercalants in the 2×2 superlattice align in adjacent slabs, while they do not in the $\sqrt{3} \times \sqrt{3}$ superlattice (**Figure 1.4d and e**). Additionally, besides their differing electron filling levels due to distinct compositions, the centrosymmetric nature of the 2×2 superlattice and noncentrosymmetric nature of the $\sqrt{3} \times \sqrt{3}$ superlattice represent significant structural disparities. The absence of inversion symmetry profoundly influences the magnetic characteristics of materials TM_xMCh_2 with $x \approx 1/3$. Specifically, the Dzyaloshinskii–Moriya (DM) interaction emerges due to the noncentrosymmetric nature of the $\sqrt{3} \times \sqrt{3}$ superlattice, inducing spin canting and chiral magnetic ground states.

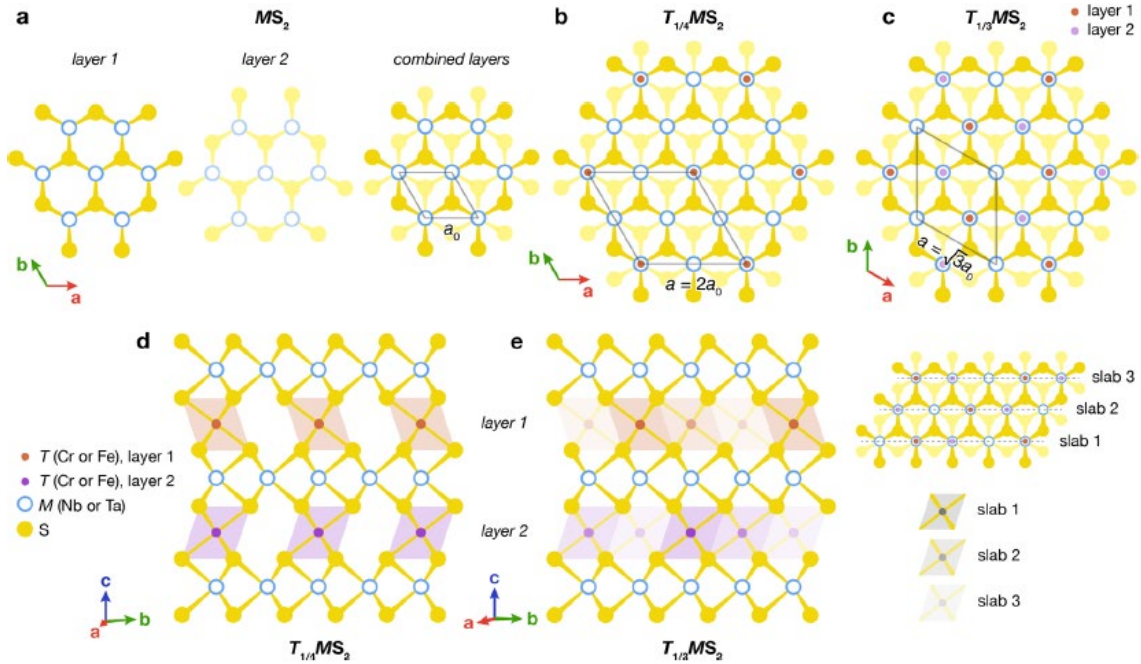


Figure 1.3. The superlattice of intercalated magnetic ions in TMDs. (a–c) Illustrations of the structures of two layers of an unintercalated 2H-MCh₂ parent TMD with lattice constant a_0 ; $\text{TM}_{1/4}\text{MCh}_2$ with an $a' = 2a_0$ supercell; and $\text{TM}_{1/3}\text{MCh}_2$ with an $a' = \sqrt{3}a_0$ supercell, all viewed along the c crystallographic axis. (d–e) Illustrations of the structures of $\text{TM}_{1/4}\text{MCh}_2$ and $\text{TM}_{1/3}\text{MCh}_2$ viewed parallel to the c crystallographic axis along $[2\bar{1}10]$ and $[10\bar{1}0]$, respectively. The slabs in (e) are defined as cuts of the $(2\bar{1}10)$ plane in the $[10\bar{1}0]$ direction, indicated on the right. Adapted from ref. 8

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Notably, the previous discussion only considers the perfect superlattices at precise stoichiometries of $x = 1/4$ and $x = 1/3$ in the intercalated TMDs. Nevertheless, experimental observations of superlattice structures have been documented in various TM_xMCh_2 compounds at x values that deviate from $1/4$ or $1/3$. In those samples, defective superlattices are expected, featuring either absent intercalants or additional interstitial defects depending on whether x falls below or exceeds the "precise" values of $1/4$ or $1/3$. Locally ordered/disordered domains may coexist within these off-stoichiometry compounds, with interactions between these domains influencing bulk magnetic behavior distinct from that of perfect superlattices. For example, giant magnetoresistance was observed in $\text{Fe}_{0.28}\text{TaS}_2$ ³⁸ and the coexistence of antiferromagnetic (AFM) and spin glass order leading to exchange bias in Fe_xNbS_2 for stoichiometries both above and below $x = 1/3$ ³⁹ illustrate the complexity of magnetic phenomena in these systems.

Magnetic properties of magnetic ion intercalated TMDs

Transition metal dichalcogenides (TMDs) intercalated with open-shell first-row transition metals offer versatile platforms for designing magnetic materials with diverse properties: ferromagnetism observed in $\text{Fe}_{1/4}\text{TaS}_2$ ^{2,40-42}, antiferromagnetism in $\text{Fe}_{1/3}\text{NbS}_2$ ⁴³⁻⁴⁵, spin glass behavior in Fe_xNbS_2 ($x = 0.30$ and 0.35)³⁹ and $\text{Fe}_{0.17}\text{ZrSe}_2$ ³⁷, chiral magnetic textures in $\text{Cr}_{1/3}\text{TaS}_2$ and $\text{Cr}_{1/3}\text{NbS}_2$ ⁴⁶⁻⁴⁸. The varied magnetic behaviors of T_xMCh_2 compounds can be precisely tailored by controlling the choice of host lattice, intercalant identity, and stoichiometry of the resulting T_xMCh_2 compound⁸.

Since there are a lot of transition metal intercalated TMDs, here we just discuss intercalated MCh_2 ($\text{M} = \text{IVB group metal, Ti, Zr, Hf}$). Different from group 5 metal TMDs, such as TaS_2 or NbS_2 , being conductive TMDs hosts, previous studies on the electronic character of group 4 TMDs reveal that the predominantly layered materials are semiconductors,⁴⁹⁻⁵¹ making them promising candidates for semiconducting magnetic materials. Furthermore, semiconducting magnets allow the modification of magnetic properties via manipulation of carrier densities.

The magnetic behavior of 3d ions in M_xTiCh_2 compounds is proposed to be itinerant, and the effective moment μ_{eff} of M_xTiCh_2 compounds were reported to be much lower than the anticipated value for free M ions, which might be attributed to the hybridization of Ti 3d–M 3d orbitals.⁵²⁻⁵⁴ This hybridization is supported by band structure calculations conducted on select ordered M_xTiCh_2 ($\text{Ch} = \text{S, Se}$) compounds as well as by photoelectron spectroscopy experiments.^{55,56} Magnetic order depends upon both the stoichiometry of M and Ch, and the intercalant level x of M. Extensive study of the magnetic properties has been reported on the M_xTiS_2 family: at lower x values, the intercalation of 3d metal elements (Cr, Mn, Fe, Co, Ni) into paramagnetic host lattice TiS_2 may lead to spin-glass-like behavior. However, at higher intercalant concentrations $x > 0.4$: Fe_xTiS_2 demonstrates ferromagnetism (FM) over an exceptionally broad range of Fe concentrations, with x ranging from 0.2 to 1.⁵⁷⁻⁶² Additionally, the FM state of Fe_xTiS_2 exhibits robust perpendicular magnetic anisotropy (PMA), characterized by a substantial coercive field (H_c) exceeding 1T.⁵⁸⁻⁶² However, Fe_xTiSe_2 shows antiferromagnetic order, as evidenced by neutron powder diffraction studies for sample with Fe amount, $x = 0.25$ and 0.48 .^{56,63} Moreover, $\text{Cr}_{0.5}\text{TiSe}_2$ also exhibits antiferromagnetic ordering based on the magnetic susceptibility and magnetization measurements.⁶⁴

In TM_xTiCh_2 systems, the valence electrons introduced from the intercalated metal can either transfer to the Ti atoms in the host lattice or form the hybrid states with the nearest

CHAPTER 1. INTRODUCTION

neighbors. In this case, the Fermi level is located within the hybrid band. Since the TM 3d-states retain their spin splitting,^{65,66} it is possible to obtain materials with spin-polarized states at the Fermi level. For TM_xZrTe_2 , the a_0 lattice parameter of the host lattice ZrCh_2 is significantly higher than that in TiCh_2 , which might affect the Zr 4d/TM3d hybrid states and lead to different magnetic behaviors.⁶⁷

For Fe_xZrS_2 ($x = 0.25, 0.33$), spin-glass properties were observed below 15 K.³⁵ Mössbauer spectroscopy shows that the intercalated Fe ions disorderly occupies both tetrahedral and octahedral sites of the van der Waals gap.³⁶ Owing to the non-metallic properties of these compounds, the iron-vacancies disordered distribution and the frustration of the exchange interactions are probably at the origin of its spin glass behavior.

In Cr_xZrSe_2 , Cr atoms were found to also occupy both tetrahedral and octahedral coordination sites. The transition in electrical properties was observed from semiconducting ($x = 0.1$) to metallic ($x > 0.1$). Cr_xZrSe_2 also exhibits the spin glass behavior, however, its exchange interaction was affected by the intercalant amount and temperature, the spin-glass state with antiferromagnetic interaction exists with $x \leq 0.2$, while at $x \geq 0.3$, ferromagnetic contribution arises as well. One can see the spin-glass magnetic ordering for Cr_xZrTe_2 in the Cr concentration range of $x = 0.05\text{--}0.3$.⁶⁸

Synthesis of magnetic ion intercalated TMDs

Chemical vapor transport (CVT) is a most classic and common method that has been extensively applied for the synthesis of magnetic ion intercalated TMDs bulk crystals. **Figure 1.4a** shows the schematic of CVT, where the precursors and transport agent are loaded at one end of the quartz tube, then the tube is sealed under the vacuum. The condensed source is vaporized by a transport agent and recrystallizes at the deposition end, driven by the shift of chemical equilibrium in an established temperature gradient according to Le Chatelier's principle: in the case of exothermic transport reactions, there will be transport to the zone of higher temperature; in the case of an endothermic reaction, to the cooler zone.⁶⁹ The crystal can be direct reaction of the elements, however, in the reported studies, polycrystalline of the host lattice usually is produced first via one pot synthesis, then the obtained polycrystalline, the intercalant species and transport agent will be loaded for CVT synthesis. Obtaining polycrystalline of host lattice will help get a more precise ratio of elements in the host lattice and reduce the formation of chalcogenide defects.⁴¹ With regard to transport agent, iodine is the most common choice for the CVT synthesis of TM_xMCh_2 . Some representative reactions are summarized in **Table 1.1**.

Chemical vapor deposition (CVD) is a powerful technology for producing high-quality TMDs thin films. The fundamental process consists of the following common elementary steps⁷⁰ (**Figure 1.4b**). First, the carrier gases (and reactant gases) are transported into the reactor. The solid precursor evaporates at elevated temperature, becomes gaseous and mixes with carrier gases. The gases then either react with each other or decompose in the gas phase to form intermediate reactants and gaseous by-products via homogeneous reactions or diffuse directly through the boundary layer to the substrate. In both scenarios, the reactant gases and intermediate reactants adsorb to the heated substrate surface and diffuse across it. Subsequent heterogeneous reactions at the gas-solid interface initiate the process of continuous thin film formation, involving nucleation, growth, and coalescence, alongside the generation of gaseous reaction

CHAPTER 1. INTRODUCTION

Table 1.1. Parameters for CVT synthesis of magnetic ion intercalated TMDs

Product	Source	Transport agent	Temperature (°C)		Time	Ref
Fe_xTaS_2 ($0.15 < x < 0.50$)	Ta, S, Fe	I_2	950	850	10 days	71
Fe_xNbS_2 $x \sim 0.33$	Fe, Nb, S	I_2	950	800	7 days	72
Fe_xTiS_2 ~ 0.5	Fe, Ti, S	I_2	950	850	14 days	57
Fe_xZrS_2 $0 \sim 0.5$	Fe, Zr, S	I_2	900	800	100 hours	33
Ni_xZrS_2 $0 \sim 0.5$	Ni, Zr, S	I_2	900	800	100 hours	33
Co_xZrS_2 $0 \sim 0.5$	Co, Zr, S	I_2	900	800	100 hours	33
Fe_xHfS_2 $0 < x < 0.22$	Hf, Zr, S	I_2	900	800	100 hours	73
Fe_xZrSe_2 $x = 0.17$	Fe, Zr, Se	I_2	1050	900	14 days	37

byproducts. Ultimately, gaseous products and unreacted species detach from the surface and get carried away from the reaction furnace with the carrier gas.

Considering the complication of TM_xMCh_2 ternary system, CVD has not been widely applied for the synthesis of this materials. **Figure 1.4b** shows the schematic for the low-pressure CVD (LPCVD) synthesis of Fe_xZrSe_2 under dynamic vacuum (10^{-1} Torr). The precursor is single source $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$, which contains Fe, Zr, and Se with ratio of Zr:Se to be 1:2. After the experiment carried out at 1000 °C for 1 hour, the polycrystalline Fe_xZrSe_2 thin film was obtained.⁷⁴ Same method was also applied for the synthesis of Fe_xTiSe_2 thin films via LPCVD from the single-source precursor $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]_2$.⁷⁵

Molecular beam epitaxy (MBE) traditionally excels in epitaxial growth of ultra-thin films due to its precise control over source flux and the employment of in situ characterization techniques like reflection high energy electron diffraction (RHEED). There are a lot of advantages of MBE for the growth of high quality TMDs thin films: the employment of high-purity source materials (typically 99.9999%) and an ultra-high vacuum growth environment (typically lower than 10^{-9} Torr) serves to minimize impurity concentration in the material. Moreover, the lower growth temperature typically employed in MBE facilitates the growth of vertical heterostructures with minimal material degradation or intermixing/interaction among different materials. Additionally, the slow growth rate characteristic of MBE (typically on the order of $1 \text{ \AA min}^{-1}$) ensures precise thickness control, which is crucial for the thickness-dependent band structure in TMDs.

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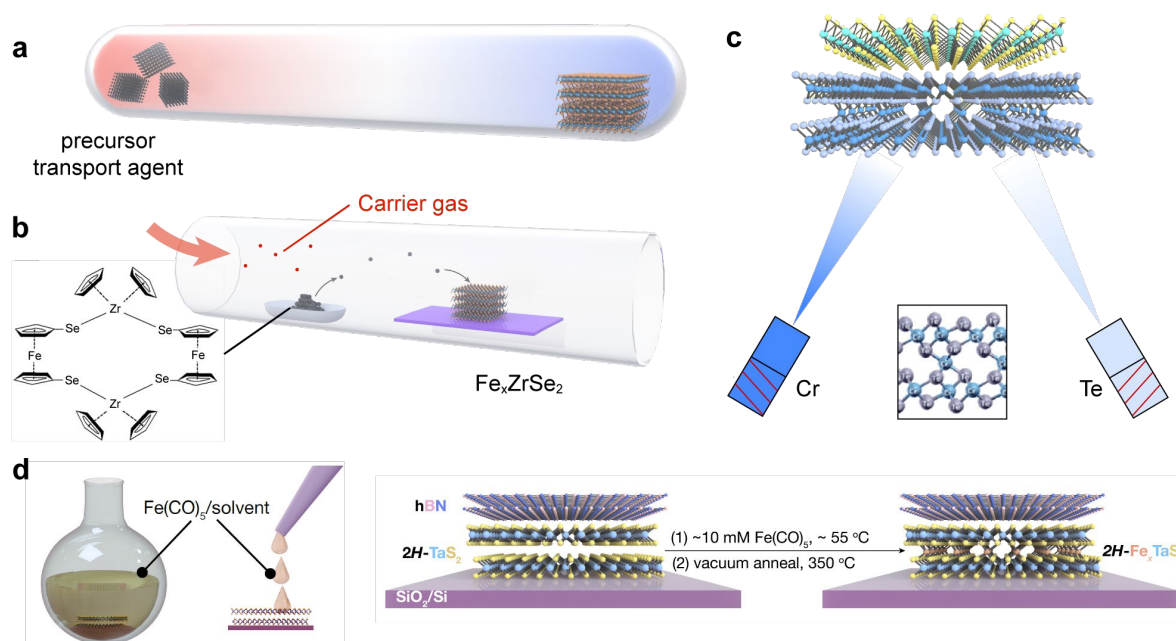


Figure 1.4. Synthesis strategies for magnetic ion intercalated TMDs. (a) Chemical vapor transport: precursors and transport agents are sealed in an ampoule and placed in a furnace with a temperature gradient. (b) Chemical vapor deposition: schematic of synthesizing Fe intercalated ZrSe_2 using precursor $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$. (c) Molecular-beam epitaxy: schematic showing the growth self-intercalated transition metal (Ti-, V-, and Cr-) tellurides compounds. (d) Liquid phase intercalation: schematic of synthesizing Fe_xTaS_2 by depositing Fe precursor $\text{Fe}(\text{CO})_5/\text{solvent}$ onto 2H-TaS_2 crystals on SiO_2/Si substrate. Adapted from ref. 2

Figure 1.4c shows that MBE is applied for the synthesis of self-intercalated transition metal (Ti-, V-, and Cr-) tellurides compounds via codeposition of transition metal and tellurium in an ultrahigh vacuum MBE chamber on van der Waals substrates (HOPG or MoS_2). These substrates were freshly cleaved in air and subsequently outgassed in vacuum at 300°C for a minimum of 2 hours prior to growth. V, Ti, and Cr were evaporated from a mini e-beam evaporator, while Te was codeposited from a K-cell. The quality and stoichiometry of the thin film can be tuned by the flux of Te and the transition metal. Moreover, the growth temperature also affects stoichiometry, for instance, intercalated compounds such as Cr_3Te_4 , V_3Te_4 , and Ti_3Te_4 were grown at substrate temperatures ranging from 300 to 350°C . ML CrTe_2 was stabilized at substrate temperatures around 200°C . The growth rate of all the studied TMDs was adjusted to approximately 1 monolayer per 15 minutes.

Solution-based intercalation is a powerful method to synthesize transition metal intercalated TMDs thin film down to 2 layers via the intercalation of zero-valent intercalant.^{2,76-79} Conventionally, the insertion of charged species into these materials has been practiced, constraining the intercalant concentration due to the necessity of altering the oxidation state in host materials. However, zero-valent intercalation method is able to preserve the morphology and structure of the host material, resulting in high intercalant concentration that had never been previously achieved. Furthermore, this strategy was shown to be general in Bi_2Se_3 nanoribbons,

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which allows the various zero-valent guest species Cu, Ag, Au, Co, Fe, In, Ni, and Sn.^{77,79} Later on, the zero-valent intercalation method is extended to different 2D host materials, such as TaS₂.²

In a typical procedure, 2H-TaS₂ flakes were mechanically exfoliated onto SiO₂/Si substrates and encapsulated with hexagonal boron nitride (hBN) to protect the TaS₂ basal plane from degradation, while exposing edges of the TMD flake. Under an inert atmosphere, the 2H-TaS₂ flakes/SiO₂/Si substrates were immersed in a 10 mM solution of Fe(CO)₅ in toluene, acetone, or acetonitrile at 50–55°C for approximately 24 hours (**Figure 1.4d**), following washing with fresh solvent, samples underwent annealing under high vacuum conditions (10⁻⁷ torr) at 350°C for 30 minutes to facilitate the ordering of intercalants.

1.2 Spin glass

Spin glass definition

A spin glass comprises interacting magnetic moments, originating from spins, wherein the magnetic interactions are randomly distributed in sign. In contrast to ferromagnets (**Figure 1.5a**), where interactions are positive, aligning moments along the same direction and resulting in a net macroscopic magnetization, or antiferromagnets (**Figure 1.5b**), where interactions are negative, driving moments to antialignment and establishing two interpenetrating ferromagnetic sublattices oriented in opposite directions, spin glasses represent a mixture of both scenarios.

The introduction of a random distribution of atomic magnetic elements in alloys and compounds results in significant disorder and deviations from a regular interaction pattern (**Figure 1.5d**). The interaction between magnetic constituents becomes randomized in both size and, in certain cases, sign. This leads to the emergence of new magnetic phases and phenomena. An interacting magnetic Ising system can be described by its spin Hamiltonian^{80,81}

$$H = - \sum_{i,j} J_{i,j} S_i S_j \quad \text{Equation 1}$$

where $J_{i,j}$ represents the exchange interaction strength between spin S_i and spin S_j , with spins in an Ising system oriented either up or down.

The magnetic moments (or spins) engage in random sign interactions, wherein each

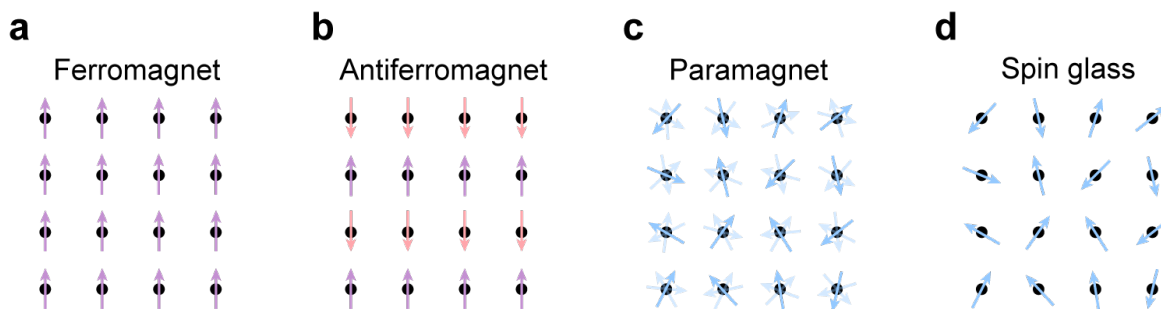


Figure 1.5. Schematic for magnetic phases. (a) Ferromagnet. (b) Antiferromagnet. (c) Paramagnet. (d) Spin glass.

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moment experiences conflicting influences from its neighbors. This situation, termed frustration, precludes the existence of a simple symmetric configuration of the spin set in an equilibrium state. Instead, a plethora of spin configurations with similar energy values arises, leading to a vast number of metastable states (**Figure 1.6**). These states are separated by free-energy barriers of varying heights, resulting in a wide spectrum of response times ranging from paramagnetic timescales to astronomical scales. Consequently, determining the absolute minimum energy state proves exceedingly challenging, rendering a spin glass virtually always out of equilibrium from a practical standpoint. At low temperatures, the spin glass enters a (partially) frozen phase, yet this state undergoes slow evolution without an apparent time limit.

Spin glasses offer a valuable entry point into understanding the physics of strongly disordered magnetic systems and are therefore discussed in some detail below. The spin glass problem can be defined using *Equation 1*, wherein the spatial dimension of the system and the distribution and range of interaction $J_{i,j}$ are set. In the **Sherrington–Kirkpatrick (SK) model**,⁸² the sum is taken over all pairs (i, j) of N spins, with a Gaussian distribution of $J_{i,j}$ having a zero mean. The renowned Parisi solution of this problem, employing replica symmetry breaking (RSB), constitutes one approach to modeling spin glasses, known as the RSB or mean-field picture.

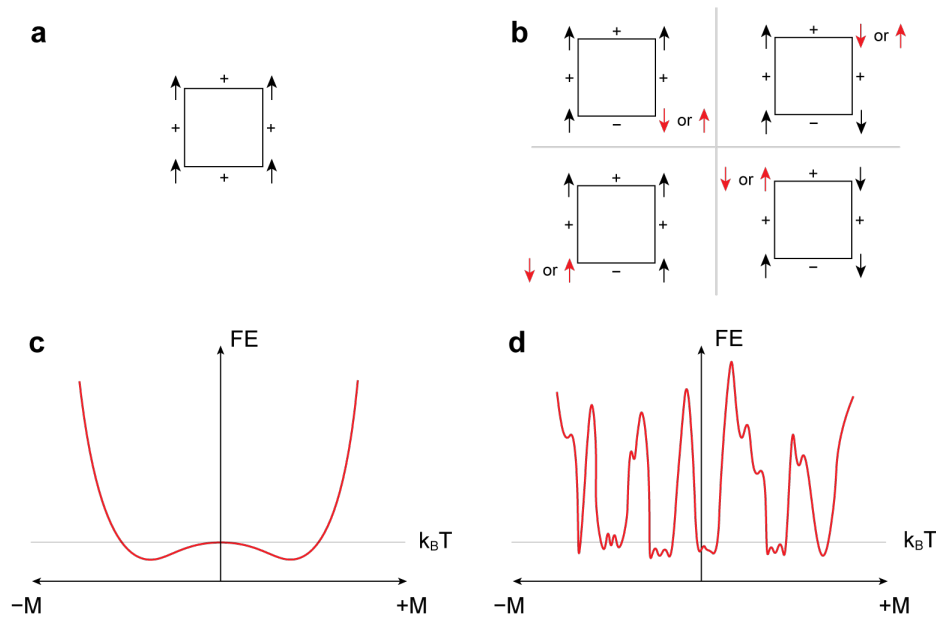


Figure 1.6. Spin configuration and energy landscape of ferromagnet and spin glass. Spin configuration of ferromagnet (a) and spin glass (b). Energy landscape of ferromagnet (c) and spin glass (d). In a ferromagnet, the exchange interaction results in the alignment of spins along the direction of the applied field, leading to only one most stable energy state in each direction of the applied field. Conversely, in a spin glass, an oversimplified model may consist of one antiferromagnetic exchange interaction while all other exchange interactions are ferromagnetic. This configuration yields eight degenerate energy states. Consequently, in real spin glasses with a multitude of competing exchange interactions, a vast number of metastable states emerge.

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An alternative model to describe finite-dimensional systems is the **droplet model**,⁸³ which relies on the scaling hypothesis and produces a spin glass with properties remarkably different in some aspects from mean-field predictions. One key disparity concerns the behavior of the spin glass in a magnetic field: while the droplet picture suggests the absence of an equilibrium spin glass phase, the RSB model predicts the existence of a phase line, known as the Almeida–Thouless line, in the field-temperature (H - T) plane, separating the paramagnetic phase from the spin glass phase. However, in zero magnetic fields, both models anticipate a low-temperature phase characterized by relaxation processes lasting over exceedingly wide timescales and a nonstationary nature of a system quenched to a temperature below its spin glass temperature (T_{irr}).⁸¹

Spin disorder and geometry frustration in spin glass

In the previous section, we discussed spin disorder induced by competing ferromagnet and antiferromagnet exchange interactions (**Figure 1.7a**). Materials with competing exchange interactions face challenges in forming magnetic long-range order due to the presence of numerous nearly degenerate electronic configurations. However, there is another type of spin frustration, named geometric frustration, which arises solely from the arrangement of spins in space. **Figure 1.7b** depicts a fundamental unit of geometric frustration: the equilateral plaquette with one-dimensional, or Ising, spins. Equal and competing nearest-neighbor interactions lead to a paradox. In this scenario, two of the three spins on the triangle can couple antiferromagnetically, whereas the third cannot be due to geometric spin frustration.^{81,84}

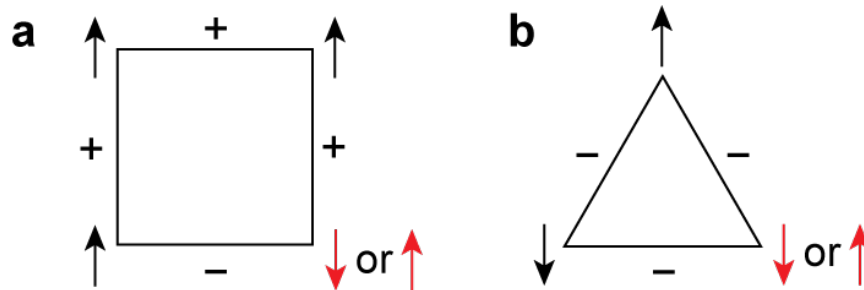


Figure 1.7. Exchange interaction disorder (a) and geometric frustration (b).

Spin glass characteristics

A frozen state For spin glass, a bifurcation can usually be observed between field-cooled (FC) and zero-field cooled (ZFC) curves. Below the bifurcation temperature (T_{irr}), the magnetic behavior becomes history-dependent, with spins entering a frozen phase (**Figure 1.8a**). During cooling from the paramagnetic phase, the magnetization increases until reaching T_{irr} , below which the FC curve remains essentially flat. This observed "solidification" of the spin system at T_{irr} , with no further significant evolution of magnetization, suggests a collective behavior of spins, culminating in a sudden freezing into a long-range correlated state. Theoretical models for spin-glass systems predict that in the limit of weak magnetic fields, the spin freezing temperature with strong irreversibility follows the $T_{\text{irr}} \propto H^n$. $n = 2$ for systems with weak irreversibility characteristics (Gabay–Toulouse (GT) line), while $n = 2/3$ for systems with strong one. (de

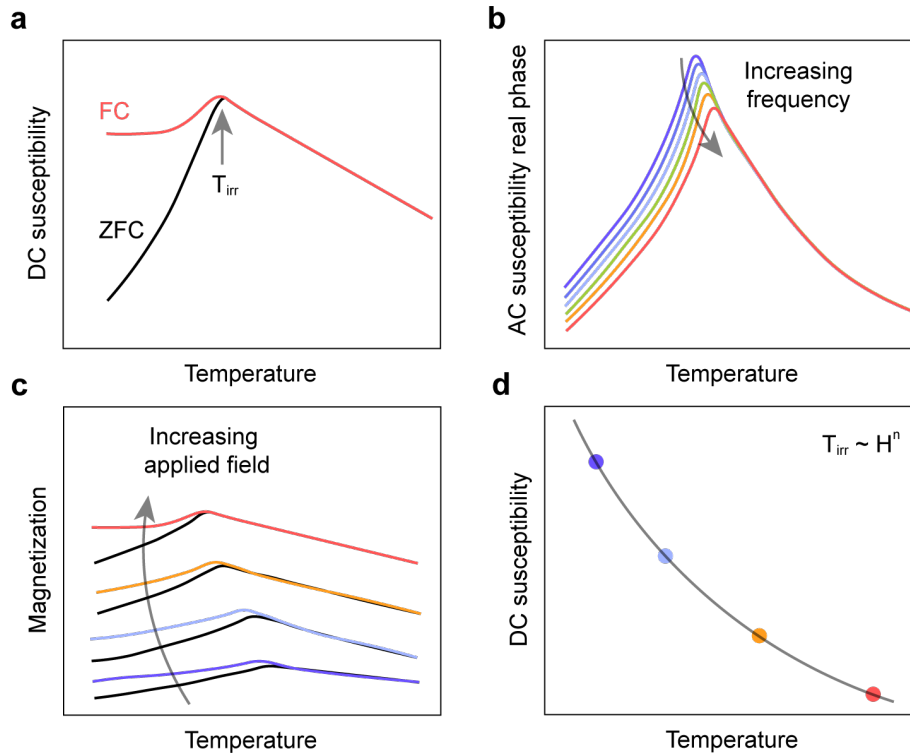


Figure 1.8. Temperature dependence of dc susceptibility and ac susceptibility (a) dc Magnetic susceptibility for spin glass. ZFC and FC curves are represented by black and red lines. (b) The ac susceptibility real phase measured for Ising spin glass under the weak ac field. (c) The DC magnetic susceptibility for spin glass under a series of applied magnetic fields. The ZFC and FC data at a given field are represented by black and color lines, respectively. (d) The temperature of bifurcation, T_{irr} , of ZFC and FC traces for different applied fields (solid dots), fit to the equation $T_{irr}(H) = T_{irr}(0)(1 - AH^n)$.

Almeida-Thouless (AT) line) (Figure 1.8c,d).^{85,86}

Spin-glass phase through ac field measurements,⁸¹ which complement the dc procedures outlined earlier. When a weak ac magnetic field is applied, the observed ac susceptibility χ is typically decomposed into two components: χ' (real component) and χ'' (imaginary component). Figure 1.8b illustrates the ac susceptibility of a spin glass at a frequency $\omega/2\pi$, plotted as a function of temperature. χ' exhibits the same shape as the ZFC (dc) magnetization curve in Figure 1.8a, which can be regarded as an ac measurement at a frequency equivalent to the inverse of the time spent at each heating temperature step in the ZFC curve.

Slow dynamics⁸¹ After cooling from above to below T_{irr} in a field, spin glass reaches a state where the magnetization stabilizes, however, this frozen state is not in equilibrium. When the magnetic field is then set to zero, the magnetization does not drop to zero, which, due to symmetry, should be the equilibrium value. This non-zero remanent magnetization obtained in this process is termed thermo-remanent magnetization (TRM) and gradually relaxes over time. The protocol for TRM is depicted in Figure 1.9a and the remanence after removing the applied magnetic field is plotted on a logarithmic time scale in Figure 1.9b, illustrating this relaxation

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phenomenon. These experiments involve a second time parameter known as the waiting time t_W . The sample undergoes rapid cooling in a weak field ($H = 0.1$ Oe) from above T_{irr} to below (quench) and is maintained at temperature T for a specified t_W . Following the waiting period t_W , the field is removed, and relaxation is measured as a function of the observation time t since the field cutoff. The inflection points of the curves (maximum of the relaxation rate) shifts towards longer times as t_W increases, consistently occurring around $t \approx t_W$. When presented as a function of the ratio t/t_W , the curves closely overlap. Thus, with a longer waiting time t_W , the response to the field change slows down, with characteristic times of the order of t_W itself.^{81,87} While the FC magnetization remains relatively constant, the spin-glass phase evolves during the time spent below T_{irr} , becoming more frozen, a phenomenon referred to as aging, which is inspired by similar effects observed in polymer mechanics.⁸⁸

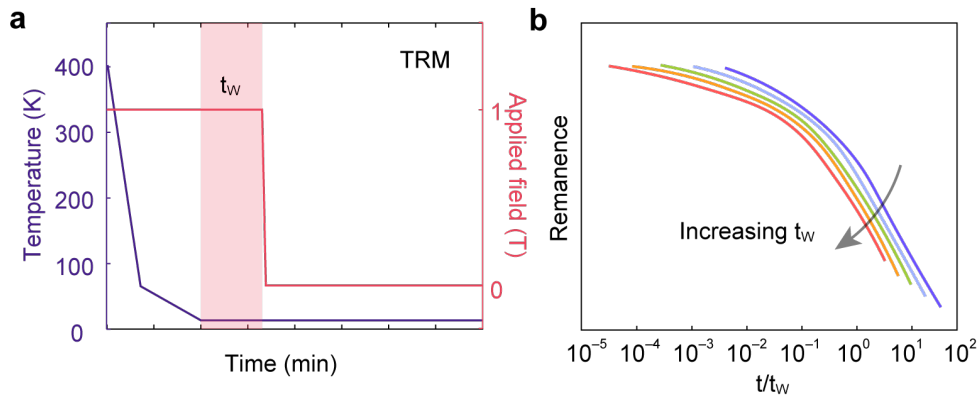


Figure 1.9. Slow dynamics of spin glass. (a) Illustration of thermoremanent magnetization (TRM) measurements. The material is first fast cooled from above T_{irr} to below. After reaching the target temperature, hold spin glass in applied field for a designated wait time, t_W , the field is then removed and the TRM data is collected. (b) Relaxation of TRM of the spin glass. The magnetization decay curves obtained for a range of t_W are presented on a logarithmic scale, as a function of t/t_W to emphasize their t_W -dependence (called aging).

Memory effects The memory effect remains one of the most enigmatic dynamical processes in spin glasses. It emerges from a scenario where the system is held at a temperature $T_1 < T_g$ for a duration t_W , where T_g signifies the spin glass transition temperature, and then further lowering the temperature to T_2 . Surprisingly, during this temperature drop, the spin glass magnetization behaves as if no waiting had occurred at T_1 , a phenomenon known as rejuvenation or temperature chaos. However, upon warming the spin glass back to T_1 , the previous waiting time effect is reinstated, a phenomenon termed memory.⁸¹ The memory effect can be observed in both dc⁷ and ac measurements.⁸⁹

Figure 1.10a,b depicts memory effect dc and ac magnetization using various measurement modes. The measurement proceeded as follows:⁷

Step 1: The sample was cooled in $H = 100$ Oe from above to below T_g then to 2 K, with intermediate stops of duration $t_W = 1$ h each at $T_{\text{stop}} = T_1, T_2$, and T_3 (and T_4, T_5, T_6 in **Figure 1.10b**). During each stop, T was maintained constant while H was reduced to zero. After each

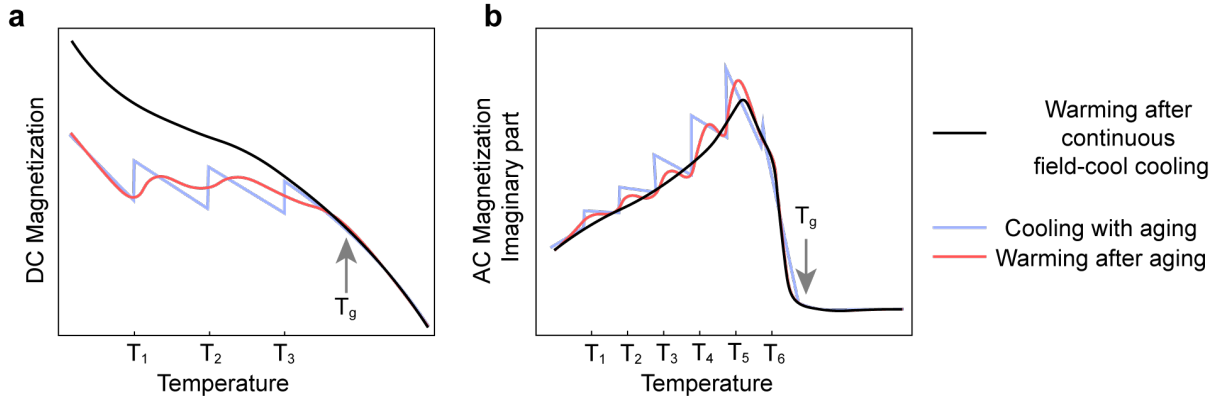


Figure 1.10. Memory effect of spin glass. (a) FC memory effect in the temperature variation of dc magnetization of spin glass. (b) ac magnetization imaginary part memory effect in the temperature variation of ac magnetization of spin glass. The curves are obtained on spin glass sample by cooling with aging (blue line), warming after aging (red line), and reference curve, warming after continuous field-cool cooling (black line). dc and ac curve are adapted from ref. 7 and 12, respectively.

stop, H was reapplied, and cooling resumed, resulting in a step-like M - T curve (**Figure 1.10a**, cooling with aging, blue line).

Step 2: After reaching 2 K, the sample was heated back in $H = 100$ Oe, producing the so-called memory curves (**Figure 1.10a,b**, warming after aging, red line).

Step 3: A reference curve was also recorded by allowing the sample to heat in $H = 100$ Oe after being field-cooled in the same field without any stop (**Figure 1.10a,b**, warming after continuous field-cool cooling). The temperature ramp rate in all measurements (including during field cooling) was maintained at a fixed 1 K/min.

For dc measurement, during heating, a significant memory effect was observed, indicating non-ergodic behavior of the low- T phase. At each T_{stop} , the sample exhibited a clear upturn, revealing the previous history of stops in zero field at that T . This manifestation of memory in the low- T phase was evident. Whereas for ac measurement, beginning from temperatures above T_g where the imaginary susceptibility χ'' equals 0 for paramagnetic phase. χ'' increases upon crossing T_g . When the cooling process halts at T_{stop} , the relaxation of χ'' owing to aging is observed over a duration of t_W . Upon warming, the memory of each aging stage conducted during cooling manifests as "memory dips" in χ'' , retracing the lower value of χ'' achieved at each aging temperature. Hence, the spin glass retains simultaneous memory of 5 or 6 consecutive aging stops, conducted at progressively lower temperatures. The curve obtained during subsequent temperature increase unveils these memories while simultaneously erasing them.

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1.3 Overview of remaining chapters

In Chapter 2, we design a spin glass with strong spin frustration induced by magnetic disorder by exploiting the distinctive structure of Fe intercalated ZrSe_2 , where Fe(II) centers are shown to occupy both octahedral and tetrahedral interstitial sites and to distribute between ZrSe_2 layers without long-range structural order. Notably, we observe behavior consistent with a magnetically frustrated and multidegenerate ground state in these $\text{Fe}_{0.17}\text{ZrSe}_2$ single crystals, which persists above room temperature. Moreover, this magnetic frustration leads to a robust and tunable exchange bias up to 250 K. These results not only offer important insights into the effects of magnetic disorder and frustration in magnetic materials generally, but also highlight as design strategy the idea that a large exchange bias can arise from an inhomogeneous microscopic environment without discernible long-range magnetic order. In addition, these results show that intercalated TMDs like $\text{Fe}_{0.17}\text{ZrSe}_2$ hold potential for spintronic technologies that can achieve room temperature applications.

Chapter 3 explores the effect of intercalant concentration on the magnetic phases and the exchange bias behaviors of Fe intercalated ZrSe_2 . For Fe_xZrSe_2 , localized moments interact indirectly by polarizing the itinerant holes, establishing short-range magnetic interactions. Adjusting the amount of intercalated Fe in Fe_xZrSe_2 can impact its magnetic behavior in its exchange interaction as well as the formation of magnetic domains. We synthesized Fe_xZrSe_2 ($x = 0.25, 0.33$) and magnetic characterization reveals spin frustration and exchange bias behavior in both crystals, underscoring the tight bond between the spin glass phase and the exchange bias phenomenon and suggest a powerful strategy for designing highly tunable exchange bias systems with near-room temperature transition temperatures, which could have potential applications in future spintronics devices.

Chapter 4 describes the observation of the dynamics of Li ions intercalation into semiconducting $\text{Fe}_{0.17}\text{ZrSe}_2$ electrochemically. The intercalation process shows high reversibility and stability, characterized through in situ structural, optical, and electrical property analysis. The unique structure of $\text{Fe}_{0.17}\text{ZrSe}_2$, with Fe ions situated between the layers of the host lattice ZrSe_2 , likely contributes to the robustness of the flakes during the intercalation process. This Li intercalation resulted in a significant 27-fold increase in electrical conductivity of $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes, establishing a solid foundation for electrostatic control over spin polarization. The capability to reversibly engineer the physical properties of $\text{Fe}_{0.17}\text{ZrSe}_2$ opens exciting opportunities in optoelectronics and rapid data storage and retrieval with minimal power consumption.

Chapter 5 studies the effect of semiconductor spin glass Fe_xZrSe_2 on the generation and manipulation of spin-polarized current for spintronic devices. Spin fluctuations have been discovered to play an important role for the effective enhancement of the spin current. Spin-glass systems present a promising candidate. Spin glasses exhibit significant short-range order that enables the induction of large fluctuations, making them valuable for exploring spin-current enhancements. Spin glass Fe_xZrSe_2 on the top of Pt thin film induced anomalous Hall effect and spin hall effect in the Pt at room temperature due to the magnetic proximity effect, which indicates the potential application of spin glass Fe_xZrSe_2 in the spintronic technology.

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Chapter 2

Near room-temperature intrinsic exchange bias in an Fe intercalated ZrSe₂ spin glass

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2.1 Introduction

In a system that displays magnetic hysteresis, the magnetization depends on the history (sweep direction) of the external magnetic field, produces a remanent magnetization at zero-field, and a non-zero coercive field is needed to reestablish a zero-magnetization state following polarization.³ Magnetic hysteresis loops are usually centered on zero-field. However, some systems display a shift in the center of the hysteresis loop away from zero field—usually when cooled under an external magnetic field—an effect that is termed “exchange bias”.⁴⁻⁵ Magnetic materials that exhibit this exchange bias effect play a crucial role in spin-based memory and electronic devices (including spin valves,⁸⁻⁹ magnetic read heads,¹⁰ and magnetic random access memory¹¹), since the shifted hysteresis loop prevents random noise from inadvertently reversing the magnetization of a component. Traditionally, magnetic heterostructures and thin-films have been the primary platforms for engineering and studying exchange bias—including ferromagnetic (FM)/antiferromagnetic (AFM) bilayers¹²⁻¹⁶ (e.g. NiFe/FeMn), FM/ferrimagnetic (FiM) architectures¹⁷⁻¹⁸ (e.g. NiFe/TbCo), and FiM/AFM heterostructures¹⁹ (e.g. Fe₃O₄/CoO). Yet, despite the extensive study of exchange bias within a variety of such systems over seven decades, a comprehensive mechanism behind exchange bias remains lacking. One key unresolved issue is an understanding of the critical role of disorder and/or spin frustration at the interfaces of the constituent layers.

In canonical exchange bias constructs comprised of layers of a FM on an AFM, the traditional explanation of exchange bias involves interfacial pinning of the FM layer to the adjacent AFM layer, resulting in a hysteresis loop that is polarized with the orientation of the

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AFM moment at the interface.²⁰ This simplistic picture has since been replaced by a model in which exchange bias is driven by a disordered magnetic state—a spin glass (SG)—that is incidentally formed at the interface of the FM and AFM layers. This SG, which is characterized by random and frustrated exchange interactions, is believed to stem from the interplay of structural disorder,^{16,21–22} interface roughness,^{13,23–24} chemical intermixing²⁵ and/or opposing, yet energetically similar, exchange interactions.²⁶ Several studies have suggested that the spin glass itself is indeed closely tied to the exchange bias phenomenon, since this effect has been observed not only in prototypical magnetic heterostructures including FM/SG bilayers,²² but also in apparently intrinsic single phase spin glass materials, including magnetically glassy dilute metal alloys,²⁷ single crystals of compounds with inherently coexisting magnetic phases of AFM and SG,²⁸ and geometrically frustrated lattices.²⁹ Still, the role of magnetic disorder and frustration on the emergence of exchange bias remains unclear, though evidently critical for optimizing material and device performance.³⁰

Layered transition metal dichalcogenides (TMDs) are a class of materials in which two-dimensional layers of MCh_2 (M = transition metal; Ch = S, Se, Te) are stacked via van der Waals (vdW) interactions along the crystallographic c -axis. The vdW interfaces allow for the intercalation of a range of chemical species, such as atoms,³¹ molecules,³² and ions.^{33–35} TMDs intercalated with open-shell first-row transition metals, T , are versatile platforms for designing magnetic materials, where the spin density and magnetic ordering can be precisely controlled through the choice of host lattice, intercalant, and stoichiometry of the resulting T_xMCh_2 compound. When $x = 1/4$ or $x = 1/3$, it is possible for intercalants to fully order with commensurate superlattices (of size $2a \times 2a$ or $\sqrt{3}a \times \sqrt{3}a$, respectively, where a is the lattice constant of the primitive MCh_2 lattice) and to exhibit long-range magnetic order.^{36–38} However, when the extent of intercalation deviates from these stoichiometric compositions, some T_xMCh_2 materials have been found to exhibit spin-glass phases.^{28,39–40} Analytis and colleagues recently synthesized slightly off-stoichiometric $Fe_{0.33\pm\delta}NbS_2$ ($\delta \leq 0.03$), which displayed a predominant AFM order coexisting with a minor spin-glass phase, exhibiting a large exchange bias below 40 K.²⁸ Interestingly, the spin glass in this material, though a very minor component, may also enable ultralow current-induced switching of the AFM order, a technology that holds promise for low power spintronics.^{31,32} Intercalant site disorder coupled with the oscillatory nature of the purported Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction (*i.e.*, exchange mediated by conduction electrons) was proposed as the origin of the crucial spin glass phase. In turn, the coupling between an uncompensated spin glass and a highly anisotropic AFM within a single crystal was suggested as the source of the highly enhanced exchange bias effect.

To directly interrogate the role of intercalant disorder on spin-glass behavior in intercalated TMDs, we sought to explore a system possessing the spin glass itself as the predominant magnetic component. To accomplish this, we chose Fe_xZrSe_2 for three reasons. First, structurally, $ZrSe_2$ is a promising intercalation host lattice for constructing a predominant spin glass phase that may enable the study of an intrinsic spin glass-derived exchange bias effect. While the $2H$ and $1T$ polytypes of TMDs contain both octahedral and tetrahedral vacancy sites in the interlayer vdW sites, the experimentally determined crystal structures of most Fe-intercalated TMDs compounds show that intercalants occupy the octahedral sites exclusively.⁶ However, Fe-intercalated Zr-based TMDs (Fe_xZrCh_2 ; Ch = S, Se) are unique in that intercalants can occupy

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both tetrahedral and octahedral sites (**Figure 2.1**), with Fe atoms distributed between both sites.⁴¹⁻⁴² The difference in coordination environment of intercalated Fe at different sites, combined with the variation in the distance between magnetic sites and the oscillatory nature of potential exchange interactions (including p - d hybridization for semiconductors,⁴³⁻⁴⁴ RKKY for metals⁴⁵⁻⁴⁷), should lead to variations in sign and magnitude of the coupling between adjacent magnetic centers, potentially resulting in spin frustration that might be expected to manifest as a spin-glass phase. Second, the development of systems with high transition temperatures closer to room temperature is crucial for any potential technological application. In this regard, selenide analogues of intercalated TMDs are promising, as these compounds generally exhibit higher magnetic ordering temperatures compared to their related sulfides (likely due to the stronger spin-orbit coupling in heavier selenide compounds and/or greater orbital overlap).^{41-42,48-50} Finally, Fe_xZrSe₂ has been reported to be semiconducting.⁴² The interaction of any localized moments with conduction band electrons has a profound effect on exchange interactions. To a greater extent than metals, semiconducting materials permit the strong modulation of their charge carrier densities electrostatically⁵¹⁻⁵³ or electrochemically,⁵⁴ offering the possibility of achieving electrically controlled magnetism.

As a consequence of inherent intercalant disorder, we expect Fe_xZrSe₂ to exhibit spin glass properties. While there have been suggestions that the material displays glassy magnetic behavior,⁴² the unambiguous experimental verification of this spin glass state has not yet been reported, and the resultant manifestation of exchange bias has not been demonstrated. Here, we show that Fe_xZrSe₂ ($x \sim 0.17$) consists of high-spin Fe²⁺ ions located without long-range order in both octahedral and tetrahedral sites between the layers of 1T-ZrSe₂. This material displays semiconducting behavior with a bandgap of about 0.4 eV, and magnetic characterization reveals a high degree of spin frustration above room temperature, much higher than the glassy transition temperatures (< 40 K) reported for other Fe_xMCh₂ materials. Consequently, upon magnetic field cooling, Fe_xZrSe₂ displays a measurable, apparently intrinsic, exchange bias for temperatures ≤ 250 K. These results indicate that the spin glass phase is closely linked to the exchange bias phenomenon and suggest a powerful strategy for designing novel exchange bias systems with near-room temperature transition temperatures, which could have potential applications in future spintronics devices.

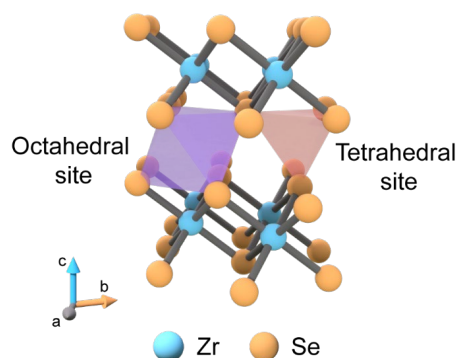


Figure 2.1. Intercalants can occupy octahedral and tetrahedral interstitial sites in 1T-ZrSe₂

2.2 Results

Synthesis, Composition, and Structure of Fe-intercalated ZrSe₂

Single crystals of Fe_xZrSe₂ were synthesized using chemical vapor transport (CVT). A

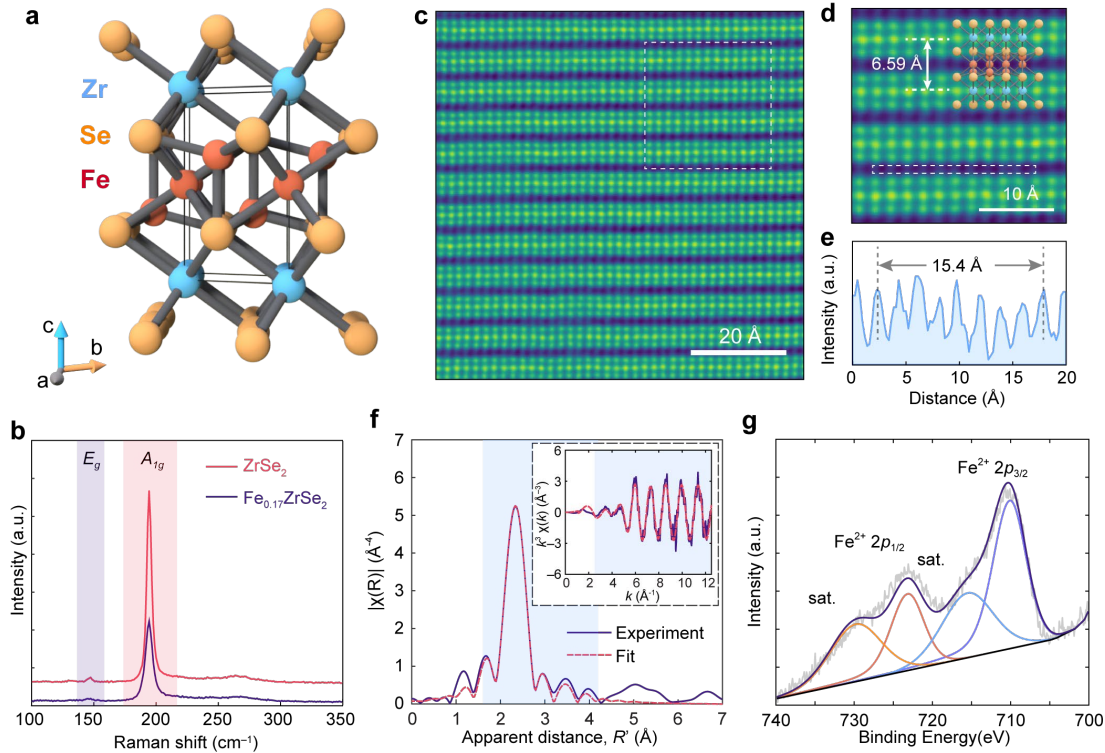


Figure 2.2. Compositional and structural characterization of Fe_{0.17}ZrSe₂. (a) The crystal structure of Fe_{0.17}ZrSe₂ is that of 1T-ZrSe₂ with iron atoms intercalated in both octahedral and tetrahedral vacancy sites in the vdW interface. The occupancies of octahedral and tetrahedral sites are 0.1 and 0.07, respectively. The unit cell is framed in solid lines. (b) Raman spectra of 1T-ZrSe₂ (purple line) and Fe_{0.17}ZrSe₂ (red line) flakes with 532 nm excitation. (c) Cross-sectional HAADF-STEM image of an Fe_{0.17}ZrSe₂ sample along the [10 $\bar{1}$ 0] zone axis. (d) Zoomed-in image of white dashed line area in (c) overlaid with the Fe_{0.17}ZrSe₂ structure. (e) Line profile integrating intensity along the white dashed box in (d) revealing presence of intercalant ions between layers 1T-ZrSe₂. (f) Fe K-edge EXAFS spectra obtained at room temperature in a He atmosphere. Experiments are fitted by means of ARTEMIS program. The figures show Fourier transforms $|\chi(R)|$ of the k^3 -weighted EXAFS spectrum (not corrected for phase shift). The inset shows k^3 -weighted background-subtracted EXAFS spectrum. Experimental data is plotted as a solid purple trace and fits are shown as dashed red lines. The regions highlighted in blue are the fitting regions. (g) Fe 2p XPS spectra in Fe_{0.17}ZrSe₂. The Fe 2p_{3/2} and Fe 2p_{1/2} features located at 710.09 eV (purple) and 723.15 eV (red), respectively, are attributed to Fe²⁺ centers. The peaks located at 715.5 eV (blue) and 729.8 eV (orange) are attributed to the Fe satellite peaks.

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mixture of source materials Fe, Zr, Se in a ratio of 0.5:1:2 with transport agent I₂ (1 mg/cm³) was loaded into an evacuated quartz ampoule and placed in a two-zone furnace with temperature set points of 900 °C and 1050 °C (see Section 2.5.1 for additional experimental details and **Figure 2.7** for set-up). After 15 days, hexagonal plate-shaped silver-black crystals with lateral dimensions of several millimeters were obtained (**Figure 2.7c**). The crystals were thoroughly rinsed with toluene to remove the excess I₂ and stored in an argon-filled glove box.

To determine the composition of Fe_xZrSe₂ crystals, scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) was performed (see Section 2.5.2 for experimental details). Prior to SEM-EDS measurements, the as-grown crystals were cleaved with adhesive tape to expose a fresh surface. The SEM image of the as-grown crystal and the corresponding EDS spectrum and elemental mapping are shown in **Figure 2.8**. The elemental maps are consistent with a uniform spatial distribution of Fe, Zr, and Se over a large area of approximately 90,000 μm² with the Fe, Zr, Se in the ratio 0.17:1:2.02. This composition is consistent with the empirical formula Fe_{0.17}ZrSe₂ determined through single-crystal X-ray diffraction (SCXRD) refinement (Table 2.2). The main X-ray diffraction peaks can be well integrated using the trigonal space group ($P\bar{3}m1$). The lattice parameters ($a = b = 3.7662(2)$ Å, $c = 6.1236(4)$ Å) at room temperature were found to be close to those of reported structures for ZrSe₂,⁵⁵⁻⁵⁸ indicating that the intercalated Fe atoms did not significantly affect the interlayer distance. **Figure 2.2a** depicts the unit cell of the single-crystal structure solution, where the ZrSe₂ host lattice is preserved in the CdI₂ (1T) structure, with Fe atoms partially occupying both tetrahedral and octahedral sites coordinated by Se atoms within the interlayer region.

Figure 2.2b presents Raman spectra of ZrSe₂ and Fe_{0.17}ZrSe₂ crystals obtained using 532 nm excitation. ZrSe₂ exhibits the characteristic phonon modes, out-of-plane A_{1g} (194 cm⁻¹) and in-plane E_g (147 cm⁻¹) vibrations, consistent with previously reported values.⁵⁹ The spectral features observed in Fe_{0.17}ZrSe₂ were found at the same Raman shifts as those of ZrSe₂, providing additional evidence that the intercalation of Fe atoms did not break the crystal symmetry of host lattice 1T-ZrSe₂.⁶⁰ No Raman peaks corresponding to a superlattice were detected in Fe_{0.17}ZrSe₂, suggesting that Fe centers are disordered between the layers and no long-range superstructure is formed.⁶⁰ The absence of superlattice formation is also supported by selected area electron diffraction (SAED), as only diffraction spots corresponding to the host lattice were observed (**Figure 2.9**). Furthermore, the decrease in peak intensities and the broadening of peak widths observed in the Raman spectrum of Fe_{0.17}ZrSe₂ are attributed to the site disorder induced by the disordered distribution of Fe centers in the lattice⁶⁰⁻⁶¹.

To more directly establish the presence of Fe between ZrSe₂ layers, we performed high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of cross-sectional samples. **Figures 2.2c,d** show HAADF-STEM cross-sectional images taken along the [10 $\bar{1}$ 0] direction, revealing high crystallinity of the ZrSe₂ lattice. Inspection of these HAADF-STEM images shows significant intensity between ZrSe₂ layers, and **Figure 2.2e** displays a line intensity profile along the dashed rectangle in **Figure 2.2d**, confirming that substantial atomic contrast is present between the layers of ZrSe₂, consistent with intercalated Fe centers.

The local electronic and geometric features of Fe centers in Fe_{0.17}ZrSe₂, were revealed with X-ray absorption spectroscopy, XAS (including X-ray near-edge spectroscopy, XANES,

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and extended X-ray absorption fine structure, EXAFS) and X-ray photoelectron spectroscopy (XPS) on Fe_{0.17}ZrSe₂ crystals. Fitting to the EXAFS of the Fe_{0.17}ZrSe₂ crystals (**Figure 2.2f**) revealed that the majority of Fe atoms occupy octahedral positions, with a minority occupying tetrahedral sites. Paths were generated from the crystal structure of Fe_xZrSe₂ (**Figure 2.2a**) where Fe atoms were placed in either tetrahedral or octahedral positions. For each fit, paths corresponding to Fe–Se and Fe–Fe single-scattering for both tetrahedral and octahedral sites were included. There is minimal signal beyond $R = 2.8$ Å, shorter than all Fe–Fe and Fe–Zr paths, suggesting no clustering of Fe atoms near each other. No viable fits were obtained when any Fe–Zr scattering was included. To evaluate the ratio of octahedral to tetrahedral sites, the amplitude factor in the fits for the octahedral and tetrahedral paths were weighted by a factor x or $1-x$, respectively, where $x = 1$ corresponds to 100% of Fe atoms in octahedral sites and $x = 0$ corresponds to 100% in tetrahedral sites. In a given fit, x was constant and a series of fits with the same parameters were performed where x was varied in steps of 0.05 or 0.1 from 0 to 1. The best fit corresponds to 90% of the Fe atoms modeled in octahedral sites (see Section 2.5.7 **Figure 2.11** for details).

XPS spectra of Fe_{0.17}ZrSe₂ single crystals (**Figure 2.2g**) are also consistent with Fe in the +2 oxidation state, displaying peaks at 710.09 eV ($2p_{3/2}$) and 723.15 eV ($2p_{1/2}$), which are consistent with what have been reported for Fe²⁺ in Se-based coordination environments.⁶²⁻⁶³ The comparison of Fe K -edge XANES spectra for Fe_{0.17}ZrSe₂ and the standard Fe-based compounds in **Figure 2.10b** also confirms the oxidation state of intercalated Fe atoms to be +2.

Bandgap and Electronic Properties

The electronic properties of the bulk Fe_{0.17}ZrSe₂ crystal were characterized using scanning tunnelling spectroscopy (STS) and diffuse reflectance spectroscopy (DFS) at room temperature (**Figure 2.3**). STS measurements were performed on a freshly cleaved bulk sample in ambient conditions. The sample was mounted into the STS sample holder using carbon tape to attach the top of the sample to an STS probe (see Section 2.5.9 **Figure 2.12a** for details). At a fixed tip–sample separation, the tunneling current between the tip and the Fe_{0.17}ZrSe₂ crystal was monitored while the bias voltage (V) was swept over a given range. In this measurement, V modulates the position of the fermi level within the electronic bands, which is manifest as a variation in the tunneling current, I , and therefore also a modulation in differential conductance, dI/dV (the instantaneous slope of the I – V trace). When the Fermi level lies within the bandgap, I and dI/dV approach zero, and non-zero I and dI/dV values are expected when the Fermi level lies within the valance or conduction band. **Figure 2.3a** shows dI/dV tunneling spectra of ZrSe₂ and Fe_{0.17}ZrSe₂ determined from this STS measurement (**Figure 2.12b-e**). The flat region of $dI/dV \cong 0$ near the origin corresponds to the band gap,⁶⁴ revealing a band gap of approximately 0.43 eV. The comparison between STS for ZrSe₂ and Fe_{0.17}ZrSe₂ shows that the intercalation of Fe into ZrSe₂ substantially decreases the size of the band gap. Likewise, analysis of the DFS Tauc plot of Fe_{0.17}ZrSe₂ yields a band gap of ~ 0.44 eV (**Figure 2.3b**) (see Section 2.5.10 for details), which is consistent with the results of STS. Furthermore, the photoluminescence spectrum (PL) for Fe_{0.17}ZrSe₂, as shown in **Figure 2.13**, exhibits the absence of peaks in the photon energy range of 0.41 – 0.60 eV from 77 to 300 K, consistent with an indirect band-gap semiconductor (see Section 2.5.10 for details).

Variable Temperature Magnetic Measurements

Figure 2.4a shows temperature-dependent magnetic susceptibility data for Fe_{0.17}ZrSe₂ acquired with a magnetic field of 2000 Oe applied along (purple) or perpendicular (red) to the *c*-axis of the crystal. These data show that the in-plane magnetic susceptibility for Fe_{0.17}ZrSe₂ is substantially weaker than the out-of-plane magnetic susceptibility, revealing strong magnetocrystalline anisotropy (MCA), consistent with the previous reports.⁴² This MCA may arise from the trigonally distorted pseudo-octahedra of the majority of Fe²⁺ centers. We observe a $\sim 3.4\%$ trigonal compression from the size of Fe octahedral site extracted from SCXRD, which results in the qualitative *d*-orbital splitting depicted in **Figure 2.14**. The unevenly occupied *e_g* (*d_{xy}*, *d_{x²-y²}*) set of octahedral high-spin Fe²⁺ would result in unquenched orbital angular momentum and thus to MCA.

As a function of temperature, the magnetization of Fe_{0.17}ZrSe₂ between 350 and 400 K follows the Curie–Weiss law with $\chi = C/(T - \theta_{\text{CW}})$ (**Figure 2.15**), where *C* and θ_{CW} are the Curie

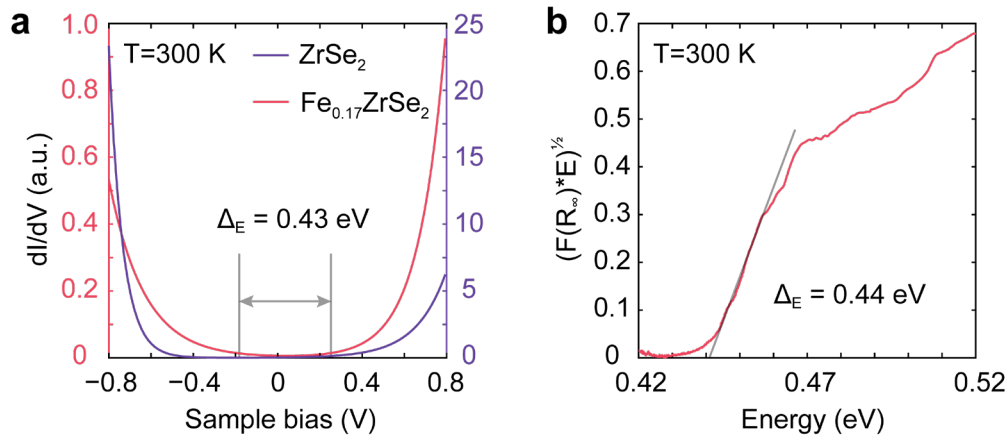


Figure 2.3. Bandgap characterization of Fe_{0.17}ZrSe₂. (a) Scanning tunneling spectra of ZrSe₂ crystal (purple line) and a Fe_{0.17}ZrSe₂ crystal (red line) at room temperature. (b) The Tauc plot of the Fe_{0.17}ZrSe₂ crystal. The linear part of the plot is extrapolated to the x-axis. The value of the absorption spectra $F(R_\infty)$ was transformed from the raw diffuse reflectance spectra by applying the Kubelka–Munk function.

constant and Curie–Weiss temperature, respectively. We find $\theta_{\text{CW}} = -223$ K, consistent with the predominance of antiferromagnetic exchange interactions in the high temperature regime. *C* is determined to be 3.20 emu K/mol_{Fe}·Oe and the calculated effective magnetic moment μ_{eff} of 5.06 μ_B is close to the theoretical value of 4.90 μ_B for high spin Fe²⁺ ions, assuming $g = 2$ and $S = 2$ (see Supplemental Information for details). **Figure 2.4b** depicts the zero-field cooled (ZFC) and field cooled (FC) dc magnetization under various applied fields ranging from 200 to 2000 Oe. These ZFC and FC curves bifurcate around 300 K, arising from irreversibility induced under different cooling protocols. Such bifurcation has been reported in spin-glass and superparamagnetic systems.^{42,65–68} To investigate the nature of this state, we determined the irreversible temperatures T_{irr} at each applied field by identifying the bifurcation point of the ZFC

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and FC curves. In the low-field region, the T_{irr} can be described as a function of the applied magnetic field, H , by the following expression:

$$T_{\text{irr}}(H) = T_{\text{irr}}(0)(1 - AH^n),$$

where A is a constant and $T_{\text{irr}}(0)$ is the limit of the irreversible temperature in the absence of a magnetic field. Theoretical models for spin-glass systems predict that in the limit of weak magnetic fields, the spin freezing temperature with weak irreversibility follows the Gabay–Toulouse (GT) line ($T_{\text{irr}} \propto H^2$), while the de Almeida-Thouless (AT) line ($T_{\text{irr}} \propto H^{2/3}$) is followed by systems with strong irreversibility characteristics.⁶⁹⁻⁷⁰ The experimentally observed field dependence of T_{irr} along with the fit to the above equation are shown in the **inset of Figure 2.4b**. The value of n obtained from the fit is 0.63, which reveals that T_{irr} follows an approximately $H^{2/3}$ behavior that is consistent with the strong irreversibility of the glassy system.

In **Figure 2.4b**, we observe that with decreasing temperature below T_{irr} , the ZFC curves display a plateau in the measured moment followed by a downturn, whereas the FC curves show continuously increasing moments. ZFC curves in applied fields of 200 and 500 Oe reveal a broad peak near 110 K, and the ZFC trace measured in a field of 500 Oe also shows a transition near 40 K. The upturns observed below 14 K are likely a Curie tail from a paramagnetic impurity. Ac heat capacity measurements of Fe_{0.17}ZrSe₂ in the absence of magnetic field (**Figure 2.17**) show that no distinct thermodynamic phase transitions are present. This absence of a response in heat capacity measurements is consistent with glassy order.⁷¹ The magnetization measurements with

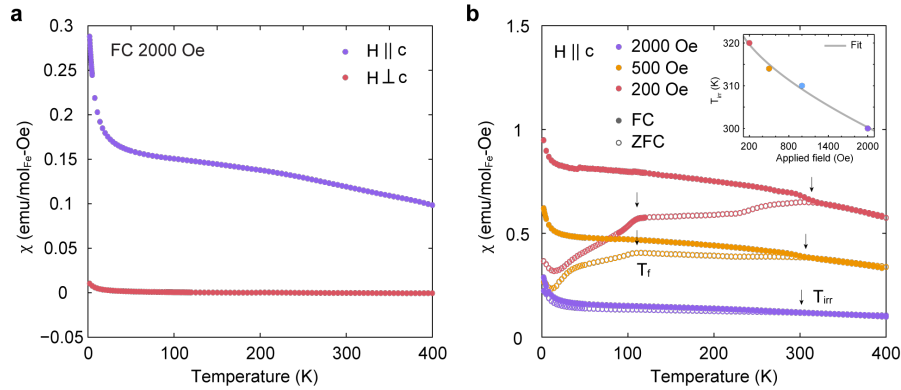


Figure 2.4. Temperature dependence of magnetic susceptibility of Fe_{0.17}ZrSe₂. (a) Temperature dependence of out-of-plane (purple dotted line) and in-plane (red dotted line) DC magnetic susceptibility of Fe_{0.17}ZrSe₂ single crystals measured with field cooling ($\mu_0 H_{\text{FC}} = 2000$ Oe). (b) Temperature dependence out-of-plane zero-field-cooled (ZFC) and field-cooled (FC) DC magnetic susceptibility for an Fe_{0.17}ZrSe₂ single crystal under applied magnetic fields ranging from 200 to 2000 Oe. The ZFC and FC data at a given field are represented by open and closed symbols, respectively. Inset shows the temperature of bifurcation, T_{irr} , of ZFC and FC traces for different applied fields (solid dots), fit to the equation $T_{\text{irr}}(H) = T_{\text{irr}}(0)(1 - AH^n)$.

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applied field perpendicular to the c -axis of the crystal also show a bifurcation between the ZFC and FC traces (**Figure 2.18**), revealing that the spin glass behavior is also anisotropic.

Relaxation of magnetization for the spin-glass phases of Fe_{0.17}ZrSe₂

A multivalley energy landscape arising from spin frustration emerges when cooling a spin glass through its freezing temperature.^{7,65,67} The non-ergodicity of the glass system in turn engenders complex magnetic relaxation processes that are apparent in isothermal remanent magnetization (IRM) and thermoremanent magnetization (TRM) measurements as a slow relaxation of the magnetization over time (**Figure 2.5**). For the investigation of the slow relaxation dynamics of Fe_{0.17}ZrSe₂, IRM and TRM measurements were performed following the protocols outlined in **Figure 2.19a** and **2.19b**, respectively. In short, IRM measurements were carried out by cooling samples down to the target temperature without application of a field, applying a field for a given waiting time (t_w), removing the field, and measuring the magnetization as a function of time. TRM measurements were carried out by cooling down to target temperature in the presence of a field, holding at this applied field for t_w , removing the field, and then monitoring the change in magnetization as a function of time. See Supplemental Information for additional methodological details. **Figures 2.5a,b** show that magnetization relaxes in time upon removal of the applied field, a characteristic of glassy systems. Moreover, the relaxation behavior for both IRM and TRM were best fit using the typical stretched exponential decay function of

$$M_R(t) = M_0 + A \exp[-(t/\tau)^{1-n}]$$

where M_0 is the remanent magnetization at $t = 0$ (that is, the intrinsic component of the moment), A is the peak beyond equilibrium values related to glassy component of the magnetization, τ is the characteristic average relaxation time, and n is the time stretch component. The obtained τ values at 2 K are around 17 and 24 minutes and the n is found to be approximately 0.58 (**Table 2.1**). Both values fall in the typical range of glassy systems.^{7,72} Moreover, the relaxation times and time stretch components of IRM and TRM measurements are comparable, indicating a common relaxation mechanism in both routines.

Table 2.1. Magnetization relaxation parameters from isothermal remanent magnetization (IRM) and thermoremanent magnetization (TRM) measurements at 2 K.

	M_0 (μ_B/Fe)	A (μ_B/Fe)	τ (min)	n
TRM	0.0717	0.0104	23.7	0.590
IRM	0.0295	0.00745	16.6	0.571

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To investigate the temperature-dependent dynamics of the glassy state, TRM measurements were conducted at selected temperatures, as shown in **Figure 2.5c** and **Figure 2.20**. The corresponding fitting parameters are presented in **Figure 2.5d** and **Table 2.5**. These measurements show that the slow relaxation behavior persists well above room temperature. Notably, A and τ appear temperature dependent for temperatures between 2 K and 110 K and both parameters decrease with increasing temperature (**Figure 2.5d**), as expected for a system trapped in metastable states separated by finite energetic barriers. Above 110 K, these parameters appear largely independent of temperature, even as M_0 decreases steadily (yet producing a finite M_0 up to 350 K). The onset of the long, temperature-dependent τ values is consistent with the T_f value of 110 K, while the persistent slow relaxation above 110 K may be indicative of a disparate

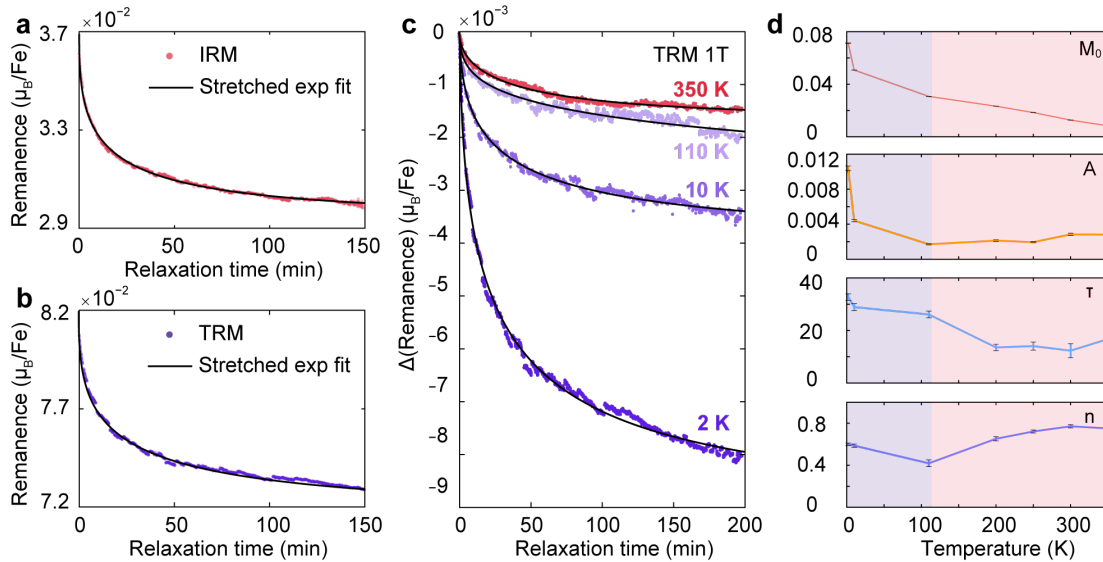


Figure 2.5. Slow magnetic relaxation behavior of Fe_{0.17}ZrSe₂. (a,b) IRM (red dots) and TRM (purple dots) data collected from the protocol described below with 1 hour wait time, respectively, and their corresponding fits (black lines). The material was first fast-cooled from 400 K to 60 K by 10 K/min and then slow-cooled from 60 K to 2 K by 1 K/min under a 1 T under zero field (a) or applied field (b) and held in applied field 1 T for a designated wait time, t_w , at 2 K, the field was then removed and the TRM or IRM data were collected. The appearance of relaxation dynamics is correlated with the glassy state. Both IRM and TRM show similar dynamics, which indicates a common relaxation mechanism in both routines. (c) TRM measurements (dots) performed at various temperatures after the samples were field cooled in a field of 1 T and their corresponding fits (black lines). The remanences at $t = 0$ min for all the TRM curves are normalized to 0 μ_B/Fe . All the fits in the figure were performed using a typical stretched exponential decay function $M_R(t) = M_0 + A \exp[-(t/\tau)^{1-n}]$. (d) The extracted parameters from the fitting were plotted as a function of temperature. The fittings for the temperatures under 110 K were shaded with purple whereas the fitting for the temperatures higher than 110 K were shaded with red.

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glassy state that is characterized by the bifurcation in FC/ZFC traces and T_{irr} value of **Figure 2.4b**. Furthermore, the decay curves in **Figure 2.21** indicate that longer t_w values are associated with higher magnetization values, which is another characteristic feature of a glassy magnetic system.^{7,65}

Magnetic hysteresis and exchange bias

Measurements of magnetization as a function of applied field were performed at 2 K after zero-field cooling the sample. As depicted in **Figures 2.6a,b**, the magnetization of the system exhibits a hysteresis loop with a coercive field, $\mu_0 H_c$, of 866 Oe. At the highest measured applied field of 12 T, the hysteresis loop does not fully saturate, and the moment is measured to be $0.6 \mu_B/\text{Fe}$ (substantially lower than the μ_{eff} of $5.06 \mu_B$ measured from C–W fits (**Figure 2.15**). Variable-field magnetization data were also collected at 2 K after cooling the sample under applied fields of +12 T and –12 T (**Figures 2.6a,b**), revealing hysteresis loops with distinct lateral shifts from near zero to ∓ 166 Oe, respectively, accompanied by a shift along the vertical axis. Upon cooling in a positive (negative) field, the loop exhibited a bias in the negative (positive) direction, which is a signature of exchange bias.^{4,21} The magnitude of the exchange bias field, H_{EB} , was calculated as:

$$\mu_0 H_{\text{EB}} = (\mu_0 H_{\text{int1}} + \mu_0 H_{\text{int2}})/2$$

where $\mu_0 H_{\text{int1}}$ and $\mu_0 H_{\text{int2}}$ are the intercepts on horizontal axes. The magnitude of $\mu_0 H_c$ is defined as the half-width of the hysteresis loop at the average of the vertical intercepts, as depicted in the inset of **Figure 2.6a**.

Plots of $M(H)$ over a range of temperatures are shown in **Figure 2.6c** and the associated temperature-dependent evolution of exchange bias field $\mu_0 H_{\text{EB}}$ and coercive field $\mu_0 H_c$ for $\mu_0 H_{\text{FC}} = 12$ T (compared to the corresponding ZFC case) are presented in **Figures 2.6e,f**. The value of $\mu_0 H_{\text{EB}}$ decreases with increasing temperature, and a finite $\mu_0 H_{\text{EB}}$ persists up to at least 250 K. Likewise, $\mu_0 H_c$ decreases with increasing temperature but the hysteresis loop is not completely closed at 350 K.

The exchange bias behavior at 2 K was also probed at different cooling fields as shown in **Figures 2.6d,g–h**. Substantial increases in $\mu_0 H_{\text{EB}}$ are observed with increasing cooling fields between 0 to 2 T and 8 to 12 T, but $\mu_0 H_{\text{EB}}$ appears unchanged by increasing cooling fields from 2 to 8 T. The value of $\mu_0 H_c$ decreases slightly with increasing cooling field for $\mu_0 H_{\text{FC}} \leq 1$ T, and remains effectively invariant with cooling field beyond 1 T.

2.3 Discussion

Crystal field stabilization energy and steric effects on occupation of intercalated Fe

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The vdW interfaces of 2H and 1T polytype TMDs create both octahedral and tetrahedral sites for intercalated ions (**Figure 2.1**). However, the experimentally determined crystal structures of Fe- intercalated TMDs compounds show that intercalants occupy the octahedral sites exclusively, except for Fe_xZrSe₂.⁶ The preference for octahedral over tetrahedral sites in Fe- intercalated TMD compounds can be related to the increased coordination number of high-spin Fe²⁺ in octahedral complexes, as well as the negative octahedral site preference energy (OSPE) arising from the difference in crystal field stabilization energies (CFSE) between octahedral and tetrahedral complexes.^{6,73-74} The small OSPE in *d*⁶ complexes suggests that geometric effects

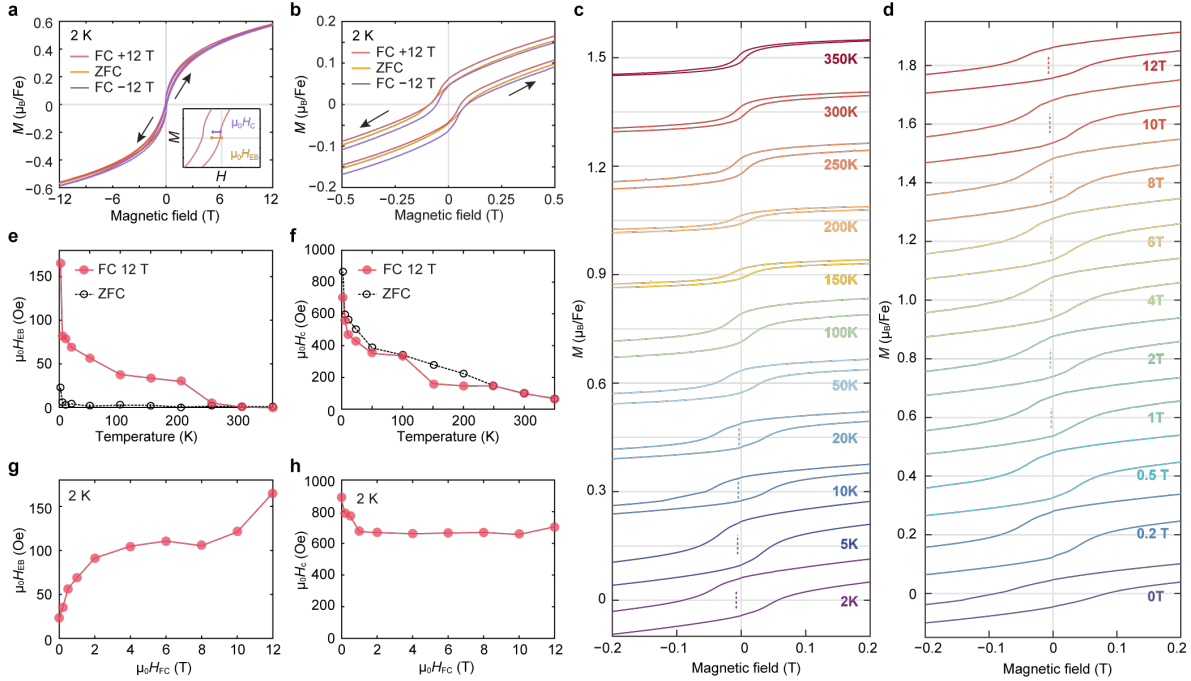


Figure 2.6. Exchange bias. (a) Magnetic hysteresis loops measured after the samples are cooled under 12 T (red curve), -12 T (purple curve), and zero field (orange curve) from 400 K to 2 K. The inset in (a) demonstrates the definition of exchange bias field $\mu_0 H_{EB}$ (purple), and coercive field $\mu_0 H_C$ (orange). $\mu_0 H_{EB}$ was extracted from each loop by taking the average of the x intercepts, $\mu_0 H_{EB} = (\mu_0 H_{int1} + \mu_0 H_{int2})/2$; $\mu_0 H_C$ was calculated from the half-width of the hysteresis loop at the average of the y intercepts. (b) Expanded view of the region between -0.5 and 0.5 T in (a). The shifts of the hysteresis loops collected under applied fields are symmetrical relative to the zero-field loop. (c) Magnetization versus magnetic field measurements performed on Fe_{0.17}ZrSe₂ at various temperatures. Each loop is offset on the y-axis by 0.15 μ_B/Fe . (d) Magnetization versus magnetic field measurements performed on Fe_{0.17}ZrSe₂ under various cooling fields. Each loop is offset on the y-axis by 0.2 μ_B/Fe . (e, f) Temperature dependence of the extracted (e) exchange bias field $\mu_0 H_{EB}$ and (f) coercive fields $\mu_0 H_C$ after cooling in a 12 T (red trace) and 0 T (black dotted trace) from 400 K. (g, h) Cooling field dependence of (g) $\mu_0 H_{EB}$ and (h) $\mu_0 H_C$ after cooling from 400 to 2 K. All the hysteresis loops were collected with the magnetic field applied along the c-axis of the samples.

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could play a role in determining the stability of complexes. An analysis of Se–Se distances in structures of Fe-intercalated TMDs reported so far (**Figure 2.25**) shows how geometric effects may explain the coexistence of Fe²⁺ in tetrahedral and octahedral sites in Fe_xZrSe₂. The Se–Se distances in the Fe octahedron of Fe_xMSe₂ are comparable to analogous Se–Se distance in Fe₇Se₈ (in which Fe is exclusively octahedrally coordinated), and the Fe tetrahedron in Fe_xZrSe₂ is the closest in size to that found in FeSe (in which Fe is exclusively tetrahedrally coordinated) by comparison to other host lattice TMDs. This simple analysis might explain why the tetrahedral intercalant site in 1T–ZrSe₂ may more readily accommodate Fe than the corresponding sites in other TMDs, providing a possible explanation for the distribution of Fe intercalants in both tetrahedral and octahedral sites that are observed by SCXRD, HAADF-STEM, and EXAFS.

Spin glass behavior

Structural and spectroscopic characterization (**Figure 2.2**) demonstrates that Fe_{0.17}ZrSe₂ is a crystallographic single-phase material with Fe²⁺ ions distributed in a disordered fashion between the layers of 1T–ZrSe₂, and the material remains semiconducting (**Figure 2.3**). Multiple measurements of this material display signatures of spin glass behavior up to room temperature. Magnetic susceptibility data (**Figure 2.4**) display a bifurcation in FC and ZFC measurements at a temperature, T_{irr} (around 300 K), that depends on magnetic field—a phenomenon typically attributed to the freezing of moments.^{75–76} This freezing occurs when the crystalline anisotropy of small domains overcomes thermal fluctuations, which leads spins to freeze in random directions. In the low-field region, T_{irr} decreases with increasing applied magnetic field and the dependence of T_{irr} with field (**Figure 2.4b inset**) shows that the system follows the Almeida–Thouless (AT) line with $T_{\text{irr}} \propto H^{2/3}$. This trend is consistent with Fe_{0.17}ZrSe₂ representing a glassy system with strong irreversibility characteristics. A negative Curie–Weiss temperature ($\theta_{\text{CW}} = -223$ K) in the apparently paramagnetic regime (above 350 K), is consistent with the predominance of antiferromagnetic exchange interactions in Fe_{0.17}ZrSe₂ crystals. Indeed, a downturn at in magnetic susceptibility near 110 K in ZFC measurements is observed under both 200 Oe and 500 Oe applied fields (**Figure 2.4b**), which could be suggestive of a weak AFM transition, though no predominant phase transition is observed as evinced by specific heat capacity measurements (**Figure 2.17**). While the ZFC feature at 110 K does indicate a change in magnetic phase, such change in phase could be attributed to an AFM phase coexisting with a spin glass phase either in the high temperature regime or in the low temperature regime. It could also simply correspond to two different spin glass phases, where the secondary low temperature phase is reentrant.⁷⁷

Measurements of magnetization over time (**Figures 2.5** and **2.20**) reveal slow spin relaxation dynamics in Fe_{0.17}ZrSe₂ crystals, another characteristic feature of glassy magnetic materials. Below 110 K, the magnetization relaxation is strongly temperature dependent, with time constants varying from 33 to 26 min between 2 and 110 K. However, from 110 K to 350 K, the time constant of the system is largely invariant with temperature (*ca.* 14 min). These relaxation data suggest two regimes of glassy behavior, with the coexistence of a putative AFM-like phase with phase transition temperature about 110 K (**Figure 2.4b**) serving to further frustrate the spin glass relaxation and significantly increase relaxation times. Such complex magnetic phases, involving the potential coexistence of spin glass and antiferromagnetic phases, might arise from the structural disorder induced by the intercalated Fe atoms occupying both

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tetrahedral and octahedral sites embedded between 1T-ZrSe₂ layers, and the competing exchange interactions between magnetic sites. The coexistence of spin-glass and antiferromagnetic phases has been reported in other Fe intercalated TMDs systems Fe_{0.30}NbS₂ and Fe_{0.14}NbSe₂.^{28,78} However, the behavior of Fe_{0.17}ZrSe₂ contrasts favorably with that of these other compounds, where Fe atoms occupy only the octahedral interstitial sites in the van der Waals gap of the host lattice. Although Fe_{0.30}NbS₂ and Fe_{0.14}NbSe₂ also exhibit a glassy behavior, the associated spin-glass phases are observed at $T < 40$ K and $T < 10$ K, respectively, considerably lower temperatures than the room temperature glassy behavior of Fe_{0.17}ZrSe₂ observed here. This may again be attributed to the occupancy of Fe in both octahedral and tetrahedral sites that introduces a more global intercalant disorder, that may in turn produce an elevated freezing temperature.

Exchange bias effect

Measurements of magnetization as a function of magnetic field (**Figure 2.6**) display magnetic hysteresis with a finite coercivity, $\mu_0 H_c$, a behavior that is commonly associated with ferromagnetic systems. However, it is important to note that the opening of hysteresis loops has also been reported in several spin glass materials.^{27,29,79} Furthermore, the hysteresis loop measured under ZFC at 2 K does not saturate up to 12 T and the small effective moment, which can arise from a frustrated, multi-degenerate ground state of the system,^{7,69} is also consistent with spin glass behavior in Fe_{0.17}ZrSe₂. **Figure 2.6** also shows that when cooled in an applied field, Fe_{0.17}ZrSe₂ exhibits a robust exchange bias. Both $\mu_0 H_c$ and the exchange bias field, $\mu_0 H_{EB}$, decrease upon increasing temperature, but a finite $\mu_0 H_c$ is observed up to 350 K and the onset of exchange bias (between 250 K and 300 K) coincides with T_{irr} around 300 K. Once onset, the magnitude of the exchange bias appears independent with decreasing temperature until around 100 K, below which a large increase in $\mu_0 H_{EB}$ is observed.

Again, these behaviors point to two magnetic regimes of this predominant spin glass, separated by the possible onset of a weak, coexisting antiferromagnetic phase at $T_f = 110$ K. Between 2 K and T_f , increasing temperature results in thermal fluctuations of the magnetization of both antiferromagnetic and spin glass phases, weakening the coupling between the AFM and SG, which leads to a sharp decrease in both $\mu_0 H_{EB}$ and $\mu_0 H_c$.⁸⁰ The coexistence of spin-glass with other magnetic phases has been found in multiple systems besides Fe intercalated TMDs,⁸¹⁻⁸³ and the interaction between spin-glass and antiferromagnetic phases in those systems have been extensively studied using the random-field Ising model.⁸⁴ In artificial bilayer heterostructures of antiferromagnetic and spin glass materials, the interfacial pinning effect of antiferromagnetic domains on spins at the surface of frozen glassy states has been invoked as the origin of an observed exchange bias effect and the interplay between antiferromagnetic order and random fields associated with spin disorder can have a significant impact on the occurrence of spin flips in applied magnetic fields.⁸⁵ Since it is the interplay between two magnetic phases that is generally thought to be the key factor giving rise to exchange bias in metallic multilayers, it is reasonable to expect the coexistence of spin-glass and antiferromagnetic phases in single crystallographic phase materials will also exhibit exchange bias behaviors. Nevertheless, these data show that exchange bias can be observed even when the overwhelmingly dominant component is the spin glass.

The increase in $\mu_0 H_{EB}$ with cooling field, which we observe in the low-temperature,

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putative SG/AFM regime of Fe_{0.17}ZrSe₂ (**Figure 2.6g**), has also been observed in conventional FM/AFM multilayer systems. This effect is explained by considering that the cooling field would act on the AFM component to give rise to an additional induced magnetization. Correspondingly, the magnetic domain size would increase, and both the exchange coupling intensity of the interfacial domains and the unidirectional anisotropy would be strengthened,⁸⁶⁻⁸⁷ resulting in a stronger pinning interaction between AFM and SG phases that enhances $\mu_0 H_{EB}$.⁸⁸⁻⁸⁹ Likewise, the slight decrease in $\mu_0 H_c$ with cooling field that we observe (**Figure 2.6h**) can be explained by considering that larger cooling fields would increase the polarization of the spin glass⁸⁹ weakly ordering this phase and reducing the pinning within the SG domain, leading to the suppression of $\mu_0 H_c$.

To assess the potential applicability of the exchange bias phenomenon in Fe_{0.17}ZrSe₂, we contextualize this system within a framework of representative exchange bias systems, as summarized in **Table 2.8**. The observed exchange bias in Fe_{0.17}ZrSe₂, measuring 166 Oe at 2 K, aligns with values found in various canonical heterostructure systems.⁴ While certain systems can achieve larger exchange bias values, even up to 3 T,²⁸ rendering them suitable for constructing robust biased permanent magnets, a smaller robust bias in the range of hundreds of Oe is more advantageous for spintronics applications, such as creating a platform for magnetic RAM devices or the electrical manipulation of magnetism, due to its enhanced energy efficiency.

2.4 Conclusions

Combined compositional, structural, and spectroscopic characterization reveals that Fe_{0.17}ZrSe₂ crystals exhibit high crystallinity of the 1T-ZrSe₂ host lattice, while Fe atoms occupy both tetrahedral and octahedral sites, distributed in a disordered fashion between TMD layers. Magnetometry measurements of Fe_{0.17}ZrSe₂ demonstrate magnetic irreversibility under zero-field cooling (ZFC), slow relaxation dynamics, the absence of saturation, and a small effective moment under high applied magnetic fields. These findings unveil a frustrated, and multi-degenerate ground state in Fe_{0.17}ZrSe₂ single crystals that persists up to room temperature. Interestingly, a robust exchange bias is observed below 250 K, and the coexistence of spin glass phase and a nominal antiferromagnetic phase at temperatures below 110 K appears to contribute to an even more pronounced exchange bias at low temperatures.

Our results highlight the potential of intercalated TMDs like Fe_{0.17}ZrSe₂ for spintronics technologies that can operate near room temperature. The spin glass-derived exchange bias observed here persists much higher than that found in other intercalated TMDs like Fe_{0.33±δ}NbS₂ and Fe_{0.14}NbSe₂, which only display this behavior below 40 K. Importantly, the semiconducting nature of Fe_{0.17}ZrSe₂ raises the prospect of strongly modulating or switching these magnetic phases with an electrical bias or optical excitation. More generally, exploring exchange bias in systems like Fe_{0.17}ZrSe₂ offers valuable insights into the role of disorder and frustration in magnetic materials more widely, including prototypical metallic magnetic multilayers. This work also opens doors to new design strategies for magnetic film interfaces that leverage materials with inhomogeneous microscopic environments to induce frustration and support exchange bias.

2.5 Experimental

2.5.1 Chemicals

Unless otherwise stated, all materials and reagents were used as received.

The following chemicals were used for the chemical vapor transport (CVT) growth of crystalline iron intercalated zirconium diselenide (Fe_xZrSe_2). Iron powder (spherical, $<10\text{ }\mu\text{m}$, purity $>99.9\%$, metal basis), and selenium powder (200 mesh, purity 99.999% , metals basis) were purchased from Alfa Aesar (Ward Hill, MA, USA). Zirconium pellets (catalog # ZR39X88-10G, purity $>99.9\%$) was purchased from R.D. Mathis Co. (Long Beach, CA, USA). Iodine (catalog # 229695-20G, purity $>99.999\%$, trace metals basis) was purchased from Sigma Aldrich Co., LLC. (St. Louis, MO, USA). $ZrSe_2$ single crystals were purchased from HQ graphene (Groningen, The Netherlands). The as-grown Fe_xZrSe_2 flakes were washed using toluene in an Ar-filled glove box. Glassware was oven-dried at a temperature of $150\text{ }^\circ\text{C}$ for $\geq 4\text{ h}$, and allowed to cool in an evacuated glove box antechamber prior to use. Anhydrous toluene was stored over 3- or 4-Å molecular sieves prior to use.

2.5.2 Chemical vapor transport growth of Fe_xZrSe₂

Fe_xZrSe₂ was synthesized following procedures reported previously.⁹⁰ A mixture of 70.9 mg (0.778 mmol) of zirconium pellet, 123.0 mg (1.557 mmol) selenium powder, 24 mg (0.429 mmol) Fe powder along with transport agent 40.2 mg (0.158 mmol) of I₂ was loaded into 30 cm long quartz ampoule in atmospheric conditions. The ampoule was then evacuated to 1×10^{-2} Torr. The contents of ampoule were then cooled using liquid nitrogen to minimize the vaporization of I₂. When the pressure dropped below 1×10^{-4} Torr, the ampoule was sealed, and placed in a 3-zone furnace. The temperature settings for hot zone and cold zone are shown in **Figure 2.7a**. The heating and cooling rate was around 55 °C/h. **Figure 2.7c** shows that high-quality hexagonal crystals with diameters of several millimeters were obtained. SEM-EDS measurements (**Figure 2.8**) were used to determine elemental composition.

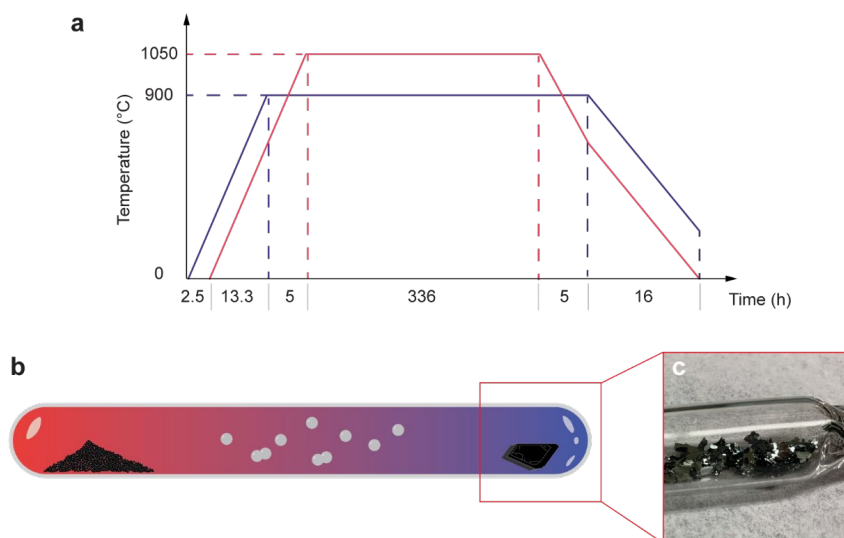


Figure 2.7. CVD growth of Fe_xZrSe₂. (a) Temperature settings of source zone (red line) and growth zone (purple line) for Fe_xZrSe₂ single crystal growth. (b) Schematic of a typical CVT experiment for bulk crystal growth of TMDs. Source materials, Zr pellets, Fe powder, and Se powder as well as transport agent I₂ are placed in one side of ampoule, which is evacuated, sealed, and positioned in a 3-zone furnace with a temperature gradient. (c) The image of as-synthesized iron intercalated ZrSe₂ crystals.

2.5.3. Scanning electron microscopy and energy dispersive x-ray spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS) measurements were performed on the crystal to extract the stoichiometry of iron intercalated between the ZrSe_2 layers. Scanning electron microscopy images were recorded on a Thermo Scientific Scios 2 DualBeam scanning electron microscope (SEM). Energy dispersive x-ray spectroscopy (EDS) of the Fe_xZrSe_2 crystals was performed with an Oxford Symmetry EDX detector using 20 keV accelerating voltage. Elemental compositions were determined by integrating under the characteristic spectrum peaks for each element using the AZtecLive Platform (Oxford Instruments NanoAnalysis).

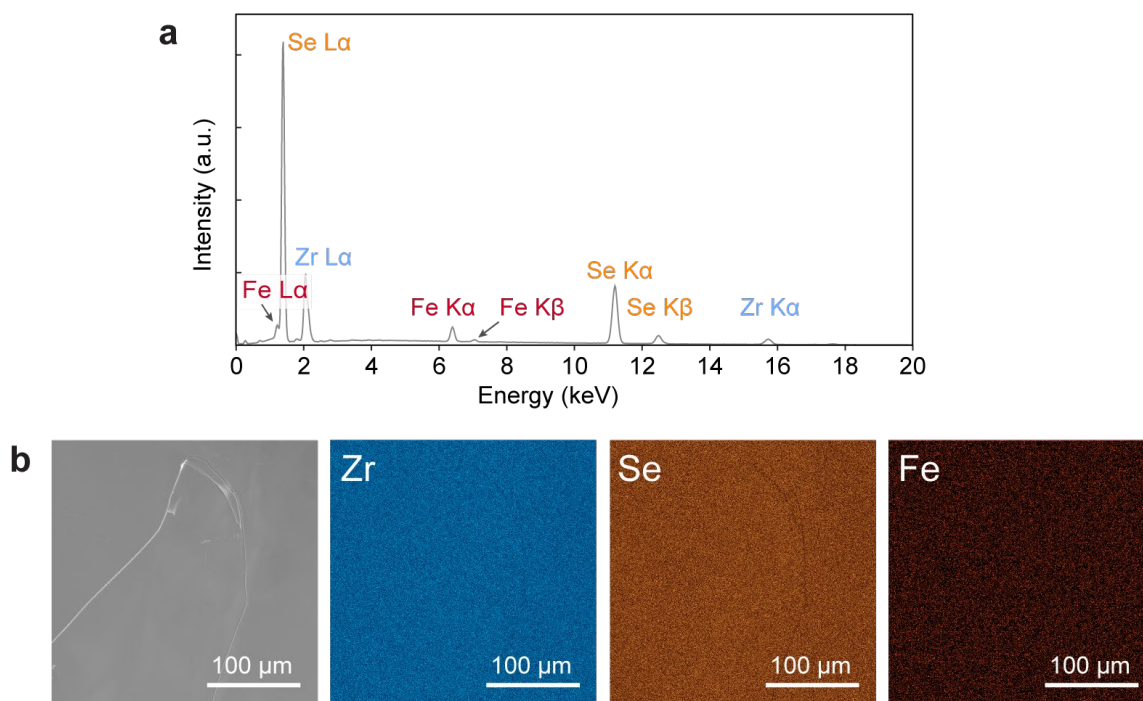


Figure 2.8. EDS measurement of the Fe-intercalated ZrSe_2 is presented. (a) The dispersion spectroscopy give an atomic ratio (Se:Zr:Fe) of 2.02:1:0.17. (b) SEM image and SEM-EDX mapping for elements of Zr, Se, and Fe for an as-grown $\text{Fe}_{0.17}\text{ZrSe}_2$ flake. The elemental maps reveal a uniform spatial distribution of Fe, Zr, and Se over a large area of approximately $90,000 \mu\text{m}^2$.

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2.5.4. Transmission electron microscopy and selected area electron diffraction

TEM samples for imaging along the c-axis:

A single crystal of Fe_{0.17}ZrSe₂ was mechanically exfoliated with Blue Tape (Ultron Systems Inc.) and polydimethylsiloxane (PDMS) films (Gel-Pak) and transferred onto a NORCADA Location Tagged Micro-Porous TEM grid with 0.50 mm × 0.50 mm, 200 nm thick SiN_x membrane with 2-μm holes. Exfoliated flakes with thicknesses < 50 nm were identified using optical microscopy and atomic force microscopy. The TEM grid was cleaned in a vacuum annealer at 2.1×10⁻⁶ torr, 350 °C for 30 min immediately prior to stacking the sample onto the TEM grid.

Selected area electron diffraction (SAED) was performed with FEI TitanX microscope at the National Center for Electron Microscopy (NCEM) at the Molecular Foundry, Lawrence Berkeley National Laboratory. The SAED patterns were obtained at 60 kV applied voltage, collected along the [10 $\bar{1}$ 0] zone axis of the Fe_{0.17}ZrSe₂ flakes. The obtained patterns correspond to a 720 nm sample region, defined using a 40 μm diameter SAED aperture.

Cross-sectional samples for imaging along the *ab*-plane:

The cross-sectional TEM samples were prepared following procedures previously reported.³⁵ In brief, cross-sectional TEM samples were prepared with Thermo Scientific Scios 2 focused ion beam (FIB) scanning electron microscopy (FIB-SEM) systems. Fe_{0.17}ZrSe₂ flakes were exfoliated using Blue Tape and PDMS film onto a SiO₂/Si substrate. A 200 nm coating of Pt or C was deposited over the target Fe_{0.17}ZrSe₂ flake using an electron beam at 5 kV and 1.6 nA. This was followed by a deposition of 2.5 μm Pt or C layer using a gallium-ion beam at 30 kV and 0.1 nA. The initial bulk-out was performed with a 30 kV Ga beam and 3 nA current, while the bulk-out cleaning was performed with a 1 nA current. For the initial thinning, a 30 kV Ga beam was used, while the current was increasingly lowered as the sample became thinner. Initial thinning started with a 1 nA current, while the final current for the rough thinning was typically 0.3 nA. After the sample was approximately 150 nm thick, the FIB beam was switched to the 5 kV and 40 pA settings. The final polishing was performed at 2 kV and 40 pA to reduce the ion beam damage.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of cross-sectional TEM samples was performed on transmission electron aberration-corrected microscope (TEAM0.5) microscope at NCEM. The microscope was operated at 300 kV with a probe convergence angle of 30 mrad.

A single crystal of Fe_{0.17}ZrSe₂ was mechanically exfoliated with blue tape and transferred onto PDMS stamp/glass slide. Exfoliated flakes with thicknesses < 50 nm were identified using optical microscopy. The target flake was dropped onto a TEM grid with 200-nm-thick amorphous SiN_x membrane. Only diffraction peaks corresponding to the host lattice 1T-ZrSe₂ were observed while the diffraction peaks corresponding to ordered superlattices were not.

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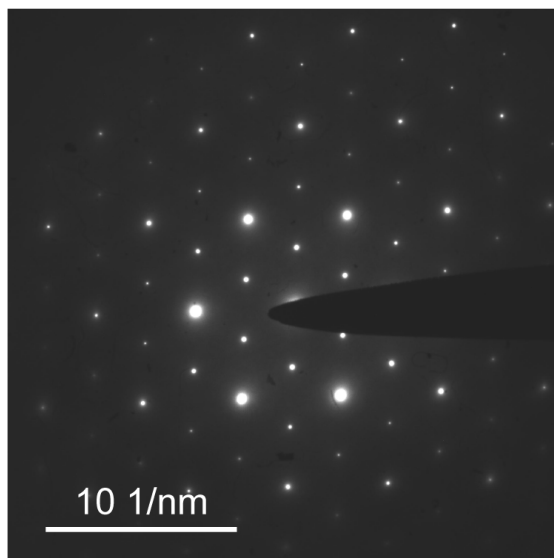


Figure 2.9. SAED pattern of a Fe_{0.17}ZrSe₂ flake.

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2.5.5. Single crystal x-ray diffraction

Single crystal x-ray diffraction (SCXRD) was obtained at UC Berkeley CHEXRAY crystallographic facility. SCXRD analysis was performed on a single crystal coated with Paratone-N oil and mounted on a MiTeGen MicroMount. Data were collected on a Rigaku XtaLab P200 (ChexTWOFACE) equipped with a MicroMax 007HF rotating anode and a Pilatus 200K hybrid pixel array detector using Mo K α radiation ($\lambda = 0.71073$ Å). The temperature of the crystal was maintained at 100(2) K throughout collection. Data collection, refinement, and reduction were performed with CrysAlisPro (version 1.171.41.112a, Rigaku Corporation, Oxford, UK). A multi-scan absorption correction was applied using the SCALE3 ABSPACK scaling algorithm within CrysAlisPro. The structure was solved using direct methods with SHELXS⁹¹⁻⁹² and refined with SHELXL (version 2014/07),⁹³⁻⁹⁴ with refinement of F² on all data by full-matrix least squares, operated in the OLEX2⁹⁵ interface. All atoms were refined anisotropically. The 3D molecular structure figures were visualized with VESTA version 3.5.7 software,⁹⁶ while schematics were drawn in Autodesk 3ds Max and Adobe Illustrator version 27.3.1.

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Table 2.2. Crystal data and structure refinement for Fe_{0.17}ZrSe₂

Empirical formula	Fe _{0.17} Se ₂ Zr
Formula weight (g/mol)	258.63
Temperature (K)	100
Crystal system	Trigonal
Space group	P-3m1
Radiation	Mo K α ($\lambda = 0.71073$)
Unit cell dimensions	$a = b = 3.7564(2) \text{ \AA}$ $\alpha = \beta = 90^\circ$ $c = 6.1078(4) \text{ \AA}$ $\gamma = 120^\circ$
Volume ($\text{\AA}^3$)	74.636(10)
Z	1
Density (calculated) (g/cm^3)	5.754
Absorption coefficient (mm^{-1})	28.516
$F(000)$	112.0
Crystal size (mm^3)	$0.075 \times 0.05 \times 0.003$
θ ($^\circ$)	3.335 to 30.987
Index ranges	$-5 \leq h \leq 5, -5 \leq k \leq 5, -8 \leq l \leq 8$
Reflections collected	3773
Independent reflections	114
Completeness to θ_{full}	1.000
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	114 / 6 / 11
Goodness-of-fit on F^2	0.965
Final R indexes [$I > 2\sigma(I)$]	$R_I = 0.0336, wR_2 = 0.0988$
Final R indexes [all data]	$R_I = 0.0353, wR_2 = 0.1021$
Largest diff. peak / hole ($\text{e \AA}^{-3}$)	1.58 / -1.97

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2.5.6. Raman spectroscopy

Raman spectra were acquired with a HORIBA LabRAM Evo Raman spectrometer using a 532 nm wavelength laser source. A 100× (NA = 0.9) objective (M Plan Achromat lens, Olympus Corporation) was used with a laser spot size of ~1 μm and a laser power of ~ 20 μW. Spectra were acquired with a grating of 600 grooves/mm, 1 s acquisition times, and 20 accumulations in ambient conditions (room temperature, 1 atm pressure). Higher laser powers (> 20 μW) and longer acquisition times (> 5 s) were found to lead to sample degradation.

2.5.7. X-ray absorption spectroscopy

The XAS samples were prepared by sandwiching as-grown Fe_{0.17}ZrSe₂ crystals between two strips of KAPTON tape. XAS data were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline 4-3 at the Fe *K*-edge. Spectra were calibrated against an Fe foil. Samples were placed in a He filled chamber during data collection. No beam damage was observed during data collection.

Data were analyzed in the Demeter 0.9.26 suite of programs using Ifeffit 1.2.12. Spectra were imported to Athena for calibration, merging and spline fitting. The final spectra were imported into Artemis. Input files for path generation in Artemis were created using WebAtoms to convert CIF files into FEFF8 input files. The symmetry of the tetrahedral sites was not perfect, leading to slightly different length Fe–Se scattering paths. No significant difference was found between the choice of these paths. Both R_{eff} values for these paths are reported below with the unused path R_{eff} given in parentheses in the summary. **Table 2.3** is a summary of the paths used in the mode.

Table 2.3. Summary of the paths used in the mode

Type	R effective	Degeneracy
Fe-Se Octahedral	2.623	6
Fe-Fe Octahedral	3.756	6
Fe-Zr Octahedral	3.054	2
Fe-Se Tetrahedral	2.241 (alternative: 2.386)	4
Fe-Fe Tetrahedral	2.831	3
Fe-Zr Tetrahedral	3.050	3

2.5.7.1. X-ray absorption near edge structure

Figure 2.10a shows the Fe K-edge XANES spectrum for Fe_{0.17}ZrSe₂. We attribute the pre-peak A (~7112 eV) to the local Fe tetrahedral ligand field that explicitly allows dipole transitions into 3*d* related states.⁹⁷ The intensity is low due to the low occupation of tetrahedral Fe. The feature B in the rising main absorption edge (the maximum point in the derivative absorption spectrum ~7118 eV) appears due to the 1*s* → 4*p* transition.⁹⁸ We assign the peak-like feature C (~7121 eV) to the 1*s* → 4*p* states admixed with the *d* states of the chalcogen atoms.² The D peak (~7125 eV) of 1*s* → 4*p* main transition is allowed by electric dipole matrix approximation.⁹⁹

Figure 2.10b shows the comparison of Fe K-edge XANES spectra for Fe_{0.17}ZrSe₂ and the standard compound Fe²⁺ (FeO), Fe³⁺ (LaSrFeO₄), and Fe⁴⁺ (SrFeO_{3-x})¹ and for the reported spectrum for FeSe.² The rising main absorption edge for Fe_{0.17}ZrSe₂ spectrum is observed close to the those of Fe²⁺ (FeSe) and Fe²⁺ (FeO), consistent with an oxidation state of +2, consistent with XPS result shown in the main text.

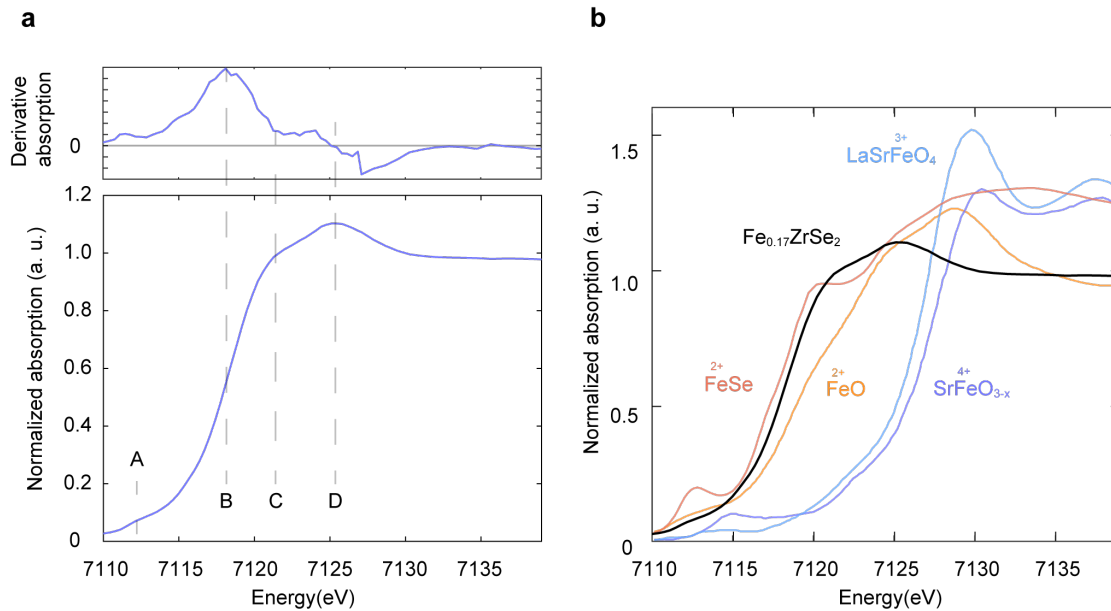


Figure 2.10. Fe K-edge X-ray absorption near edge structure (XANES) for Fe_{0.17}ZrSe₂.

(a) Normalized Fe K-edge XANES spectrum for Fe_{0.17}ZrSe₂ and the corresponding first-order derivative absorption spectrum. (b) Fe K-edge XANES spectra for the standard compound Fe²⁺ (FeO), Fe³⁺ (LaSrFeO₄), and Fe⁴⁺ (SrFeO_{3-x}) and for the reported FeSe, compared to that of Fe_{0.17}ZrSe₂. Fe²⁺ (FeO), Fe³⁺ (LaSrFeO₄), and Fe⁴⁺ (SrFeO_{3-x}) spectra are adapted from ref. ¹FeSe spectrum is adapted from ref. 2

2.5.7.2. Extended x-ray absorption fine structure fitting

EXAFS fits were performed against data in k -space with k , k^2 and k^3 weighted data for k between 3 and 12 Å⁻¹ with a Hanning window and in R -space for R between 1.6-4.2 Å. Each fit had 14.5 independent points with 9 variables. For all fits, the amplitude was set to 0.8, though qualitatively similar results were obtained with amplitude set to 0.7. The amplitude factor in the fits for the octahedral and tetrahedral paths were weighted by a factor x or $1-x$, respectively, where $x = 1$ corresponds to 100% octahedral sites and $x = 0$ corresponds to 100% tetrahedral sites. In a given fit, x was constant and a series of fits with the same parameters were performed where x was varied in steps of 0.05 or 0.1 from 0 to 1. Though the fit at 0.95 has the lowest overall value for the statistical assessments of the fit (i.e., reduced Red. χ^2 and R-factor) (**Figure 2.11**), this fit also contains an unreasonably large value for the change in path length for tetrahedral Fe-Fe scattering path, $\Delta R_{\text{Td, Fe}}$, and a negative value for the Debye-Waller analog for the tetrahedral Fe-Se path, $\sigma^2_{\text{Td, Se}}$. Thus, we identified $x = 0.9$ as the best fit. These fitting results are summarized in **Table 2.4**.

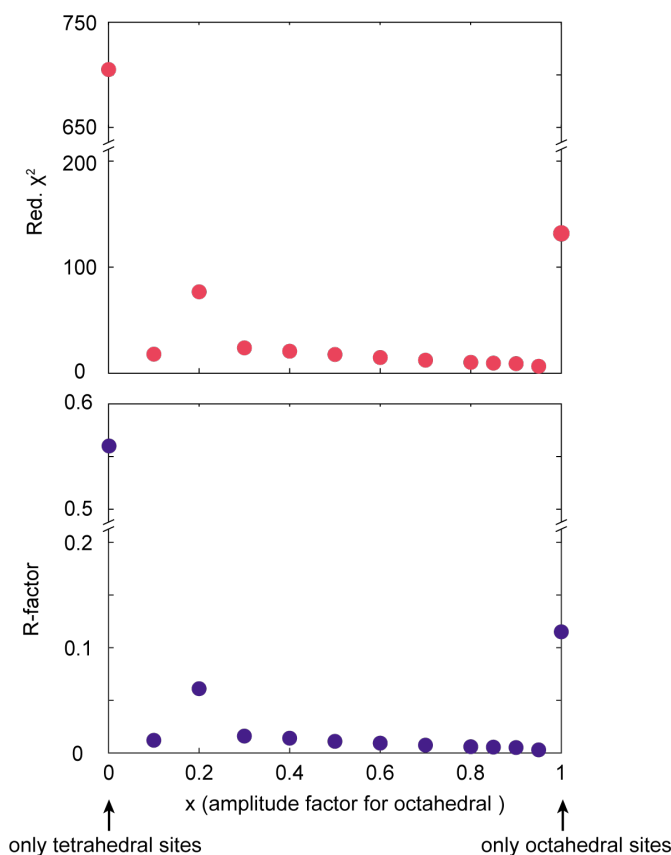


Figure 2.11. EXAFS fits against data in k -space with k , k^2 and k^3 weighted data. The statistical assessments of the fit, i.e., reduced Red. χ^2 and R-factor were plotted against the amplitude factor in the fits for the octahedral and tetrahedral paths. The octahedral or tetrahedral sites were weighted by a factor x or $1-x$.

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Table 2.4. The fitting results of different ratios of octa-Fe to tetra-Fe

x	E^0	$\Delta R_{Oh, Se}$	$\sigma^2_{Oh, Se}$	$\Delta R_{Oh, Fe}$	$\sigma^2_{Oh, Fe}$	$\Delta R_{Td, Se}$	$\sigma^2_{Td, Se}$	$\Delta R_{Td, Fe}$	$\sigma^2_{Td, Fe}$	Red. χ^2	R-factor
1 ^a	6.82	0.027	0.014	0.064	0.0378	0 ^b	0.003 ^b	0 ^b	0.003 ^b	131	0.115
0.95	4.0 ± 0.7	-0.003 ± 0.005	0.0146 ± 0.0003	0.04 ± 0.02	0.033 ± 0.002	0.091 ± 0.004	- 0.0011 ± 0.0004	0.67 ± 0.02	0.001 ± 0.002	4.13	0.0029
0.9	4.8 ± 1.0	-0.007 ± 0.009	0.0120 ± 0.0007	0.04 ± 0.02	0.036 ± 0.004	0.11 ± 0.01	0.0016 ± 0.0007	0.03 ± 0.02	0.001 ± 0.002	6.64	0.0051
0.85	5.0 ± 1.1	-0.01 ± 0.01	0.0105 ± 0.0007	0.04 ± 0.02	0.035 ± 0.004	0.13 ± 0.01	0.0034 ± 0.0008	0.02 ± 0.02	0.002 ± 0.002	7.13	0.0055
0.8	5.5 ± 1.2	- 0.00(7) ± 0.01	0.0093 ± 0.0007	0.04 ± 0.03	0.034 ± 0.004	0.14 ± 0.01	0.0049 ± 0.0009	0.02 ± 0.02	0.002 ± 0.002	7.88	0.0059
0.7	6.5 ± 1.4	- 0.00(3) ± 0.01	0.0077 ± 0.0008	0.06 ± 0.03	0.032 ± 0.005	0.16 ± 0.02	0.007 ± 0.001	0.02 ± 0.02	0.004 ± 0.002	9.96	0.0074
0.6	7.5 ± 1.6	0.0(0) ± 0.01	0.0067 ± 0.0008	0.07 ± 0.04	0.029 ± 0.005	0.18 ± 0.02	0.010 ± 0.002	0.01 ± 0.02	0.005 ± 0.002	12.5	0.0093
0.5	8.5 ± 1.9	0.00(5) ± 0.01	0.0061 ± 0.0009	0.08 ± 0.04	0.027 ± 0.006	0.20 ± 0.03	0.013 ± 0.022	0.01 ± 0.02	0.007 ± 0.002	15.4	0.011
0.4	9.4 ± 2.1	0.01 ± 0.01	0.0055 ± 0.0009	0.10 ± 0.04	0.024 ± 0.006	0.21 ± 0.03	0.017 ± 0.003	0.00 ± 0.02	0.008 ± 0.003	18.5	0.014
0.3	10	0.01 ±	0.0048	0.11 ±	0.019	0.22 ±	0.022	-	0.010	21.7	0.016

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	± 2	0.1	$\pm$ 0.0009	0.05	$\pm$ 0.006	0.04	$\pm$ 0.005	0.00(5) ± 0.03	$\pm$ 0.003		
0.2	4 $\pm$ 3	1.6 $\pm$ 0.1	0.01 $\pm$ 0.02	0.0(3) $\pm$ 0.1	.02 $\pm$ 0.01	0.09 $\pm$ 0.04	0.026 $\pm$ 0.006	-0.13 $\pm$ 0.02	0.0065 $\pm$ 0.0009	75.2	0.061
0.1	10 ± 2	-0.561 $\pm$ 0.009	0.004 $\pm$ 0.001	0.11 $\pm$ 0.04	0.007 $\pm$ 0.004	0.036 $\pm$ 0.008	0.014 $\pm$ 0.001	-0.11 $\pm$ 0.02	0.010 $\pm$ 0.001	15.7	0.012
0 ^a	29	0 ^b	0.003 ^b	0 ^b	0.003 ^b	0.085	0.0192	1.27	0.103	705	0.56

^a Error bars of ± 0.000000 in model output for this row. ^b Initial guess value, parameter not fit under these conditions.

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2.5.8. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-Alpha⁺ (Al K α radiation, $h\nu = 1486.6$ eV) (Thermo Fisher Scientific Inc) equipped with an electron flood gun. XPS data were analyzed using Thermo Scientific Avantage Data System software (version 5.9914), and a Smart background was applied prior to peak deconvolution and integration.

2.5.9. Scanning tunnelling spectroscopy

Scanning tunneling spectroscopy (STS) measurements were performed on freshly cleaved bulk Fe_{0.17}ZrSe₂ crystals using a Park Systems NX10 STM module operated in ambient conditions. Pt–Ir tips were fabricated via electrochemical etching of 0.25 mm Pt–Ir wires in 1.5 M CaCl₂ solutions. The STS I – V curve was acquired by turning off the feedback loop, holding the tip a fixed distance above the surface, and sweeping the voltage from +0.8 to –0.8 V and then back to +0.8 V with duration of 1 s. The dI/dV trace was obtained by taking the derivative of the I – V curve.

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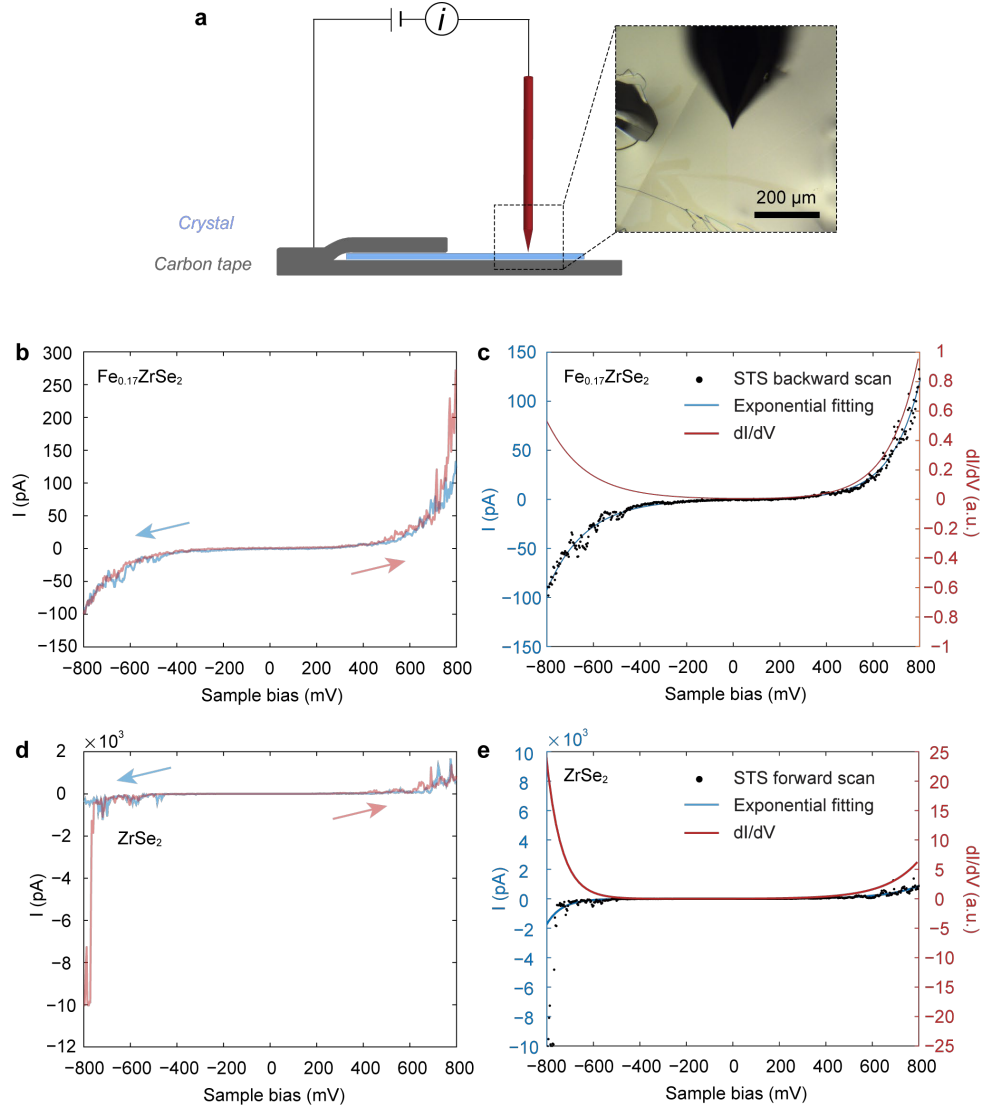


Figure 2.12. Scanning tunnelling spectroscopy. (a) Schematic of STS measurement setup. STS were performed on a freshly cleaved bulk sample in ambient conditions. The sample was mounted into the STS sample holder using carbon tape to attach the top of the sample to an STS probe. At a fixed tip-sample separation, the tunneling current was monitored while the bias voltage was swept from +0.8 V to -0.8 V (backward scan), and from -0.8 V to +0.8 V (forward scan). (b) The raw data of measured current of a $\text{Fe}_{0.17}\text{ZrSe}_2$ crystal with different applied sample bias. The backward scan is marked in a blue line and the forward scan is marked in a red line. (c) To mitigate the impact of raw data noise on the derivative of current versus sample bias, the raw data was fit with a two-term exponential model (blue line). The fitted data was used to obtain the dI/dV curve by taking the derivative of the current with respect to the sample bias (red line). (d) The raw data of measured current of a ZrSe_2 crystal with different applied sample bias and (e) the corresponding fitting and dI/dV curve. Data values at the extremes were excluded for the exponential fitting.

2.5.10. Photoluminescence spectroscopy and UV–vis–NIR diffuse reflectance spectroscopy

Photoluminescence spectra (PL) were acquired with a HORIBA LabRAM Evo Raman spectrometer using a 532 nm wavelength laser source. For the ambient measurement (room temperature, 1 atm pressure), a 100× (NA = 0.9) objective (M Plan Achromat lens, Olympus Corporation) was used with a laser spot size of ~1 μm and a laser power of ~ 20 μW. Spectra were acquired with a grating of 600 grooves/mm, 3 s acquisition times, and 2 accumulations. Higher laser powers (> 20 μW) and longer acquisition times (> 5 s) were found to lead to sample degradation. For low temperature measurement, a 100× objective was used with a laser spot size of ~5 μm and a laser power of ~ 1 Mw. A sample was loaded in a Microscopy Cryostat (Model No.: CFM-1738-102, Cryo Industries of America, Inc. Manchester, NH, USA), which was attached to a Turbo Pumping station with Diaphragm roughing pump (Model: HiCube 80 Eco, DN 63 ISO-K, MVP 015-4, Pfeiffer Vacuum Inc., Nashua, NH, USA) to maintain the pressure of 10⁻² Pa during the measurement. Temperature is adjusted by a Temperature Controller (Model 325, Lake Shore Cryotronics, Inc., Westerville, OH, USA).

Photoluminescence spectra (PL) were collected on pristine ZrSe₂ crystals at room temperature in atmosphere (**Figure 2.13a**) and Fe_{0.17}ZrSe₂ in the temperature range from 77 to 300 K under vacuum (**Figure 2.13b**). No PL peak was observed for ZrSe₂, indicating that ZrSe₂ is an indirect bandgap semiconductor, which is consistent with LAPW band calculations and experimental band structure obtained from APRES.¹⁰⁰ It is important to note that upon intercalation, it is shown that the ZrSe₂ layers themselves do not undergo a phase change from Raman spectrum in **Figure 2.2** in the manuscript. Because of this, it likely undergoes a band filling and Fermi level renormalization instead. Furthermore, no experimental results have shown indirect-to-direct bandgap transitions in a material by inducing disorder or doping so far. Therefore, it is reasonable to expect that Fe intercalated ZrSe₂ remains as an indirect bandgap semiconductor, which is consistent with the PL spectra that no peak was observed for Fe_{0.17}ZrSe₂ in the temperature range from 77 to 300 K. For the future study, ARPES or theoretical calculation might be helpful for further confirming the band structure of Fe_{0.17}ZrSe₂.

Diffuse reflectance spectroscopy measurements were performed on polycrystalline Fe_{0.17}ZrSe₂ samples, which were diluted in BaSO₄ and ground with a mortar and pestle to produce a homogenous powder in Ar-filled glove box. Diffuse reflectance UV-vis-NIR spectra were collected on a CARY 5000 spectrophotometer equipped with a Praying Mantis diffuse reflection accessory (Harrick Scientific Products, Inc.) and interfaced with Varian Win UV software.

The measured diffuse reflectance spectrum of Fe_{0.17}ZrSe₂ was transformed to the corresponding absorption spectrum by applying the Kubelka–Munk function:¹⁰¹

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$

where R_{∞} is the diffuse reflectance, while K and S are the absorption and scattering coefficients, respectively.

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The band-gap energy of semiconductors is usually determined by a Tauc plot,¹⁰² which assumes that the energy-dependent absorption coefficient α could be interpreted by the following equation:

$$(\alpha \cdot h\nu)^{1/\gamma} = A (h\nu - E_g)$$

where h is the Planck constant, ν is the photon's frequency, A is a proportionality constant independent of the photon energy, and E_g is the band gap energy. The value of the γ factor is determined by the nature of the electron transition and is equal to 1/2 or 2 for direct or indirect transition band gaps, respectively.¹⁰³ According to photoluminescence spectrum (PL) for Fe_{0.17}ZrSe₂ in **Figure 2.13b**, no peak was observed in the energy range of 0.41 ~ 0.60 eV, which indicates that Fe_{0.17}ZrSe₂ is an indirect band gap semiconductor. Therefore, the $(F(R_\infty) \cdot E)^{1/2}$ was plotted against photon energy E in the main text. The x -intercept of the linear fit of the Tauc plot gives an estimate of the band gap energy, which is around 0.44 eV.

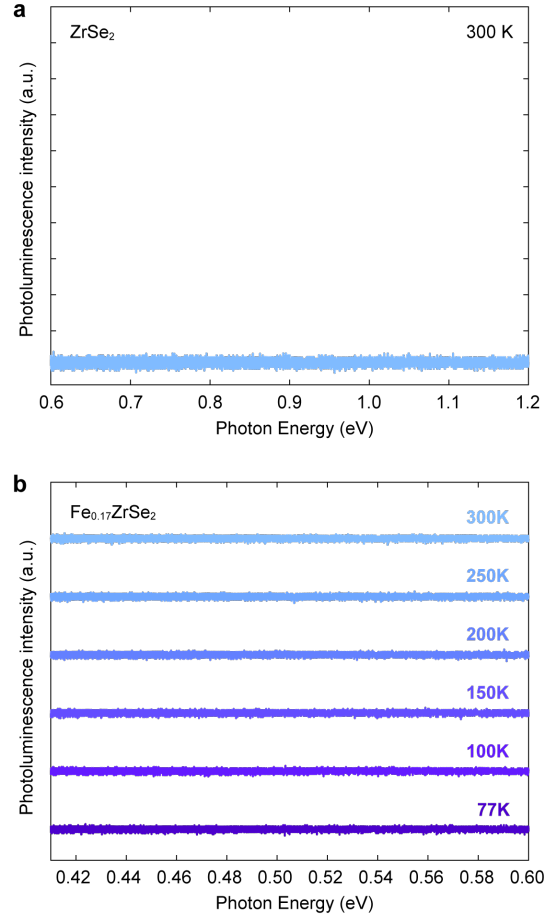


Figure 2.13. PL spectra for 1T-ZrSe₂ and Fe_{0.17}ZrSe₂. PL spectra for (a) pristine ZrSe₂ at room temperature subtracted by SiO₂/Si background. (b) Fe_{0.17}ZrSe₂ at temperature ranging from 77 to 300 K subtracted by SiO₂/Si background.

2.5.11. Magnetometry measurements

DC magnetization measurements as a function of temperature and applied field were carried out in a Quantum Design Physical Property Measurement System (PPMS) Dynacool equipped with a 12 T superconducting magnet using the Vibrating Sample Magnetometer (VSM) option, with a detection limit of 10^{-6} emu. For out-of-plane measurements, 7.89 mg of Fe_{0.17}ZrSe₂ flakes were stacked into polypropylene VSM powder sample holder, which was snapped into the brass half-tube. For in-plane measurements, 2.40 mg of Fe_{0.17}ZrSe₂ flakes were stacked onto MPMS 3 Quartz Paddle Sample Holder (C130A) and secured using Kapton tape.

2.5.12. Magnetocrystalline anisotropy of Fe_{0.17}ZrSe₂

The fractional trigonal distortion is defined as $(a_2 - a_1)/a_1$. For the regular octahedron, the fractional trigonal distortion is zero; for the trigonally elongated/compressed Fe environment, the fractional trigonal distortion is greater/smaller than zero. Values of $a_1 = 3.253$ Å and $a_2 = 3.144$ Å for Fe_{0.17}ZrSe₂ were exacted from the SCXRD solved structure. The fractional trigonal distortion is -3.35% , indicating that oct-Fe atoms in Fe_{0.17}ZrSe₂ locate in trigonally compressed distorted pseudo-octahedral coordination environment. The trigonally distorted pseudo-octahedron coordination environment gives rise to a qualitative d -orbital splitting diagram of e_g (d_{xy} , $d_{x^2-y^2}$), A_{1g} (d_{z^2}), and e_g (d_{xz} , d_{yz}).⁶ XPS showed the oxidization state of Fe is +2. The weak crystal field results in a high-spin d^6 electron configuration for Fe²⁺ ($S = 2$). An unevenly occupied e_g set of Fe²⁺ leads to an unquenched orbital angular momentum and large spin orbit coupling.⁶

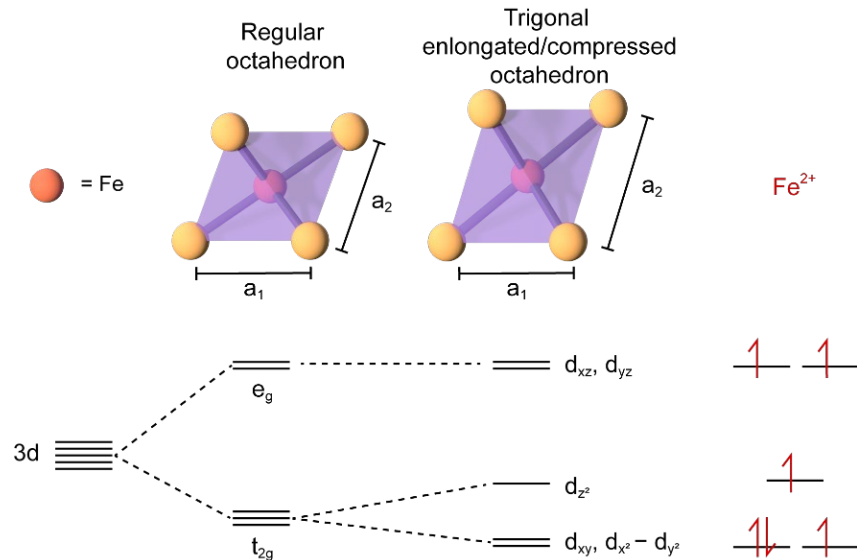


Figure 2.14. Magnetocrystalline anisotropy of Fe_{0.17}ZrSe₂. Schematic of perfect octahedral (left) and trigonally distorted (right) octahedral Fe environments, as seen along the $[2\bar{1}\bar{1}0]$ zone axis of the Fe_{0.17}ZrSe₂ lattice. Qualitative d -orbital splitting diagrams for intercalant high-spin Fe²⁺ in a trigonally distorted pseudo-octahedral coordination environment. Schematic adapted from ref. 6

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2.5.13. Curie–Weiss fit

Curie–Weiss fits were performed on the susceptibility data for Fe_{0.17}ZrSe₂ in the temperature range of 350 – 400 K. (**Figure 2.15**). The following functions were used to calculated effective moment μ_{eff} :

$$\chi = C/(T - \theta_{CW})$$

$$\mu_{eff} = \sqrt{8C}$$

where C is the Curie constant and θ_{CW} is the Curie-Weiss temperature. The extracted C , θ_{CW} , and μ_{eff} are shown below in the **Figure 2.15**.

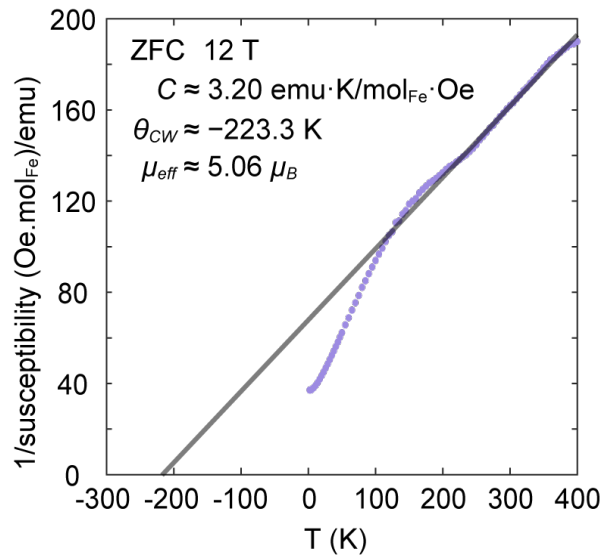


Figure 2.15. Curie–Weiss fit. Inverse susceptibility as a function of temperature for Fe_{0.17}ZrSe₂ (purple dots). The data above 350 K was fitted to the Curie–Weiss model $\chi = C/(T - \theta_{CW})$ (black line).

2.5.14. Out-of-plane magnetization of Fe_{0.17}ZrSe₂

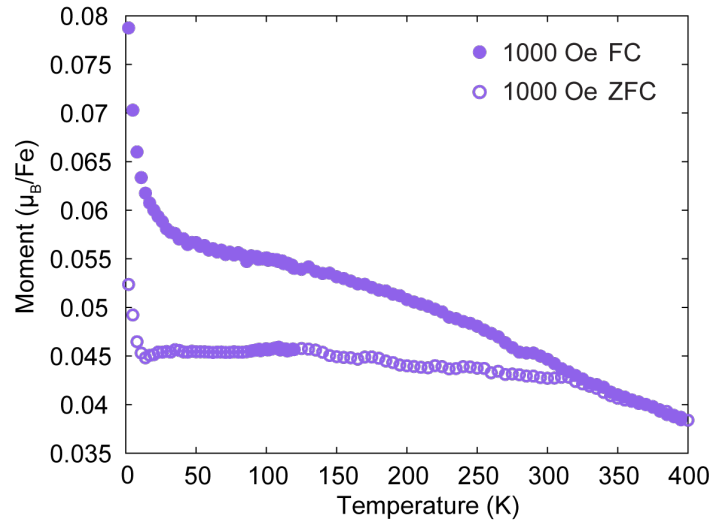


Figure 2.16. Out-of-plane magnetization of Fe_{0.17}ZrSe₂ with applied magnetic field 1000 Oe. Temperature dependence out-of-plane zero-field-cooled (ZFC) (open dots) and field-cooled (FC) (filled dots) DC magnetization for Fe_{0.17}ZrSe₂ under applied magnetic fields 1000 Oe.

2.5.15. Heat capacity

Heat capacity measurements as a function of temperature were carried out in a PPMS Dynacool using the Heat Capacity Option. 3.24 mg of Fe_{0.17}ZrSe₂ crystals were stacked together and compressed into one pellet and mounted onto heat capacity sample puck. The ac heat capacity measurement as a function of temperature was performed on this Fe_{0.17}ZrSe₂ pellet in the absence of an external magnetic field (**Figure 2.17a**). The specific-heat curve of Fe_{0.17}ZrSe₂ displays a broad transition but no sharp features, consistent with glassy order. The freezing of spins in different directions and the presence of frustration result in a distribution of energy levels. As a result, the heat capacity shows a broad maximum rather than a sharp peak.⁷

Further, the absence of sharp transitions in the specific heat capacity vs. temperature trace points to the homogeneity of the samples. The magnetometry data points to the coexistence of AFM and spin glass phases in the Fe_{0.17}ZrSe₂ below 110 K. If the two phases were segregated in discrete volumes throughout the sample, the specific-heat measurement would show a peak associated with the AFM transition overlaid with a broad glassy background. Therefore, the absence of the sharp transition reveals that there is no phase segregation in the sample.

A key characteristic indicating the presence of a spin glass state in the heat capacity measurement is its linear behavior of specific heat at low temperatures. A plot of the specific heat C_p as a function of T and the corresponding linear fitting for Fe_{0.17}ZrSe₂ at low temperature (< 3.5 K) are presented in the **Figure 2.17b**. A positive curvature takes place to force C_p to zero as temperature approaches 0 K as a consequence of the third law of thermodynamics. The linear temperature dependence of the specific heat in low temperature limit can be understood by the two-level tunnelling model, which is the simplified model from the rough *energy* landscape and macroscopic *degeneracy* of *ground states in a spin glass*. A sketch of a two-level energy diagram is shown in **Figure 2.17c**. There are two nearly similar energy minima separated with a tunnelling barrier (adapted from ref. 7). Assuming there is constant density of states for the two-level excitations. The quantum-mechanical tunnelling through the barrier between the two levels can result in a small rearrangement of some spins, which is temperature independent. Therefore, a linear proportionality of specific heat at low T naturally arises for the randomly frozen spin-glass.⁷

Figure 2.17d reveals a plot of the specific heat per unit temperature (C_p/T) as a function of T^2 for Fe_{0.17}ZrSe₂ at low temperature (< 10 K), which can be well expressed by using the following equation:¹⁰⁴⁻¹⁰⁵

$$C_p(T) = \gamma T + \beta T^3 + \delta T^5$$

where γT describes the electronic contribution to the heat capacity and γ is the electron specific heat coefficient (Sommerfeld constant), βT^3 is the phonon contribution and β stands for phonon specific heat coefficient, δT^5 and reflects the deviation term. As a result, the fitted values of parameters γ , β , and δ are 14.7(4) mJ/mol K², 0.55(3) mJ/mol K⁴, and $1.2(3) \times 10^{-3}$ mJ/mol K⁶, respectively.

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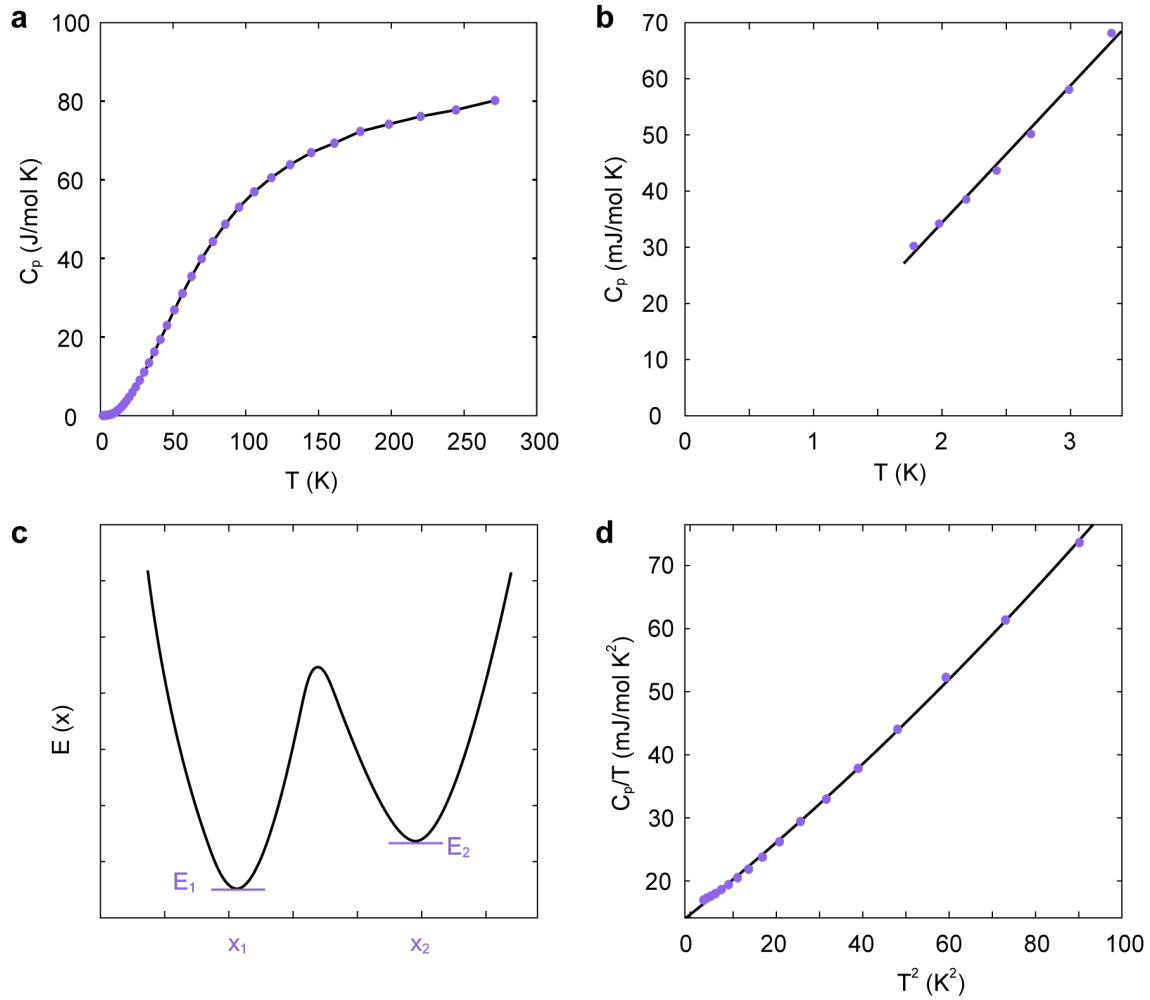


Figure 2.17. Heat capacity of Fe_{0.17}ZrSe₂. (a) Specific heat capacity (C_p) for Fe_{0.17}ZrSe₂ as a function of temperature (purple dots). Smoothed black line is a guide for the eyes. (b) Low temperature region of (a) (purple dots). The black line is the linear fitting curve. (c) A sketch of a two-level energy diagram (adapted from ref. 7). (d) Specific heat capacity divided by temperature (C_p/T) of Fe_{0.17}ZrSe₂ as a function of temperature squared (T^2) (purple dots). The black line is the curve of data fitted to $C_p(T) = \gamma T + \beta T^3 + \delta T^5$.

2.5.16. In-plane magnetization of Fe_{0.17}ZrSe₂

The in-plane magnetization of the Fe_{0.17}ZrSe₂ crystals was measured as a function of temperature with the applied magnetic field parallel to the *c*-axis. The bifurcation between ZFC and FC curves reveals an anisotropic spin glass behavior along *ab*-plane, which has been reported before.⁴² In Section 2.5.8, we discussed the magnetocrystalline anisotropy behavior along the *c*-axis in the Fe_{0.17}ZrSe₂ crystal, which might arise from the unquenched angular momentum of pseudo-octahedral Fe²⁺ coordination environment. However, it is worth noting that the *c*-axis cannot be exclusively considered as the easy axis, as spin glass behavior is also observed for fields perpendicular to the *c*-axis, although to a lesser extent. Therefore, the Fe_xZrSe₂ spin-glass system cannot be described according to a pure Ising model. Generally, the spin-orbit coupling effects in tetrahedral Fe²⁺ complexes are weaker compared to octahedral coordination environments. However, due to the disordered distribution of Fe at the octahedral and tetrahedral sites, a random distribution of spin directions, potentially canted with respect to the *c*-axis, is expected to emerge. Therefore, the Ising character of the octahedral Fe²⁺ spins may be significantly altered, and the anisotropic spin glass behavior may arise.⁴²

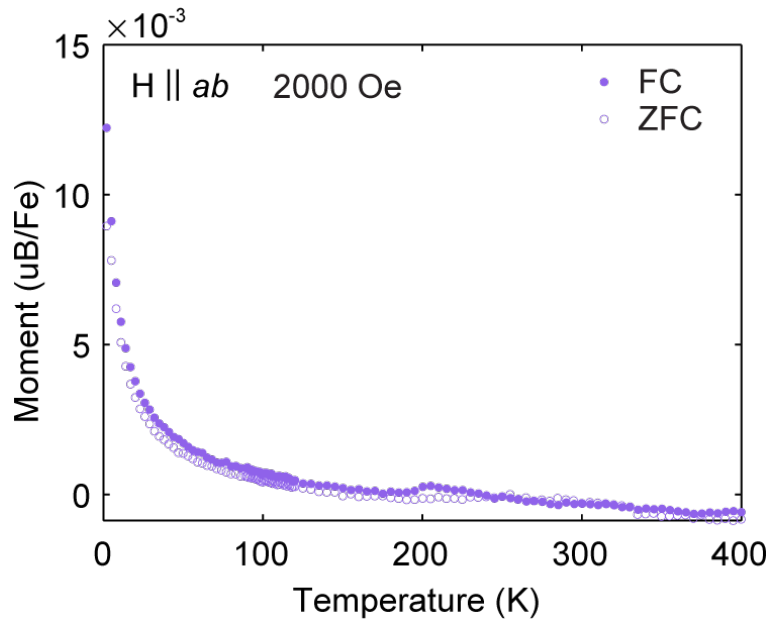


Figure 2.18. In-plane magnetization of Fe_{0.17}ZrSe₂. Temperature dependence in-plane zero-field-cooled (ZFC) and field-cooled (FC) DC magnetization for Fe_{0.17}ZrSe₂ under applied magnetic fields 2000 Oe.

2.5.17. Relaxation analysis

Both isothermal remanent magnetization (IRM) and thermoremanent magnetization (TRM) measurements were performed on Fe_{0.17}ZrSe₂ following the protocols outlined in **Figure 2.19a** and **S13b**, respectively. TRM measurements were conducted in the Quantum Design PPMS with VSM option using the following protocol: (a) warm the sample to 400 K in zero magnetic field, (b) apply the field along crystallographic *c*-axis to 1 T, (c) fast cool the sample to 60 K above the target temperature at 10 K/min, (d) slow cool to the target temperature at 1 K/min, (e) hold the sample in 1 T field for wait time t_w one hour, and (f) set the field to 0 T and measuring the remanent magnetization in the sample over set time.

IRM measurements were conducted with same (a), (c)–(f) steps. For step (b), apply zero field along crystallographic *c*-axis.

The relaxation measurements for both IRM and TRM were best fit using the $M_R(t) = M_0 + A \exp[-(t/\tau)^{1-n}]$, where M_0 is remanence, irreversible part of the change in magnetization, A is peak beyond equilibrium values related to glassy component of the magnetization, τ is the characteristic relaxation time, and n is the time stretch component.

TRM measurements were conducted at different temperatures to study the effect of temperature on slow dynamics of Fe_{0.17}ZrSe₂ crystals. **Figure 2.20a** shows that the remanence decreases with increasing temperature, which was consistent with FC data. **Figure 2.20b** and **Table 2.5** reveals that in the range of 2 ~ 110 K, the parameters M_0 , A , τ , and n changed drastically with increasing temperature. τ and n decreased with increasing temperatures, which suggests that energy barriers, which trap the system in its metastable state, are reduced at higher temperatures. When the temperature is higher than 110 K, the parameter M_0 still decreased with increasing temperature, indicating the polarization of spins in the Fe_{0.17}ZrSe₂ crystals is weaker at higher temperature. However, the Fe_{0.17}ZrSe₂ still exhibits slow relaxation behavior for $T > 110$ K and parameters A , τ , and n did not show obvious changes with temperature, consistent with the existence of a glassy phase at high temperature. We note that the fitting equation is not useful when T is higher than the freezing temperature, and relaxation curves at high temperature are noisy, making it challenging to extract precise relaxation parameters. Nevertheless, these fits provide some general characterization of the magnetic relaxation at high temperatures.

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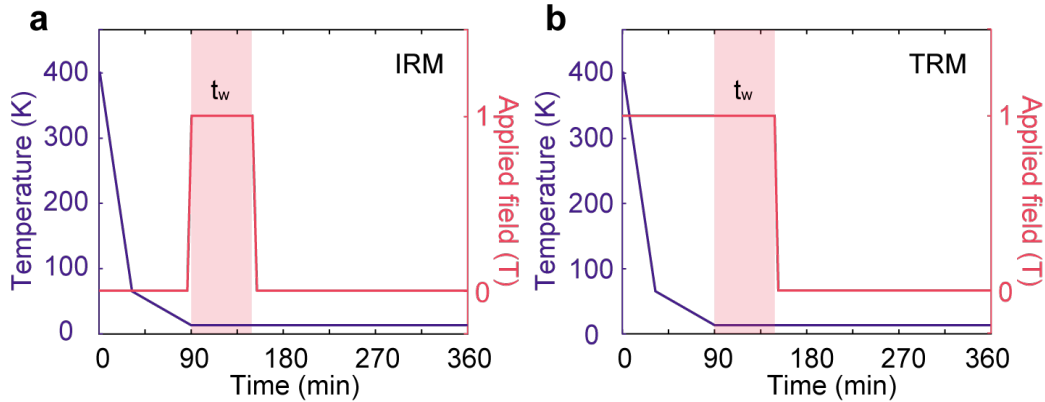


Figure 2.19. Illustration of isothermal remanent magnetization (IRM) measurements (a) and thermoremanent magnetization (TRM) measurements (b). The material was first fast-cooled from 400 K to 60 K by 10 K/min and then slow-cooled from 60 K to 2 K by 1 K/min under zero field (a) or under a 1 T applied field zero field (b) and held in applied field 1 T for a designated wait time, t_w , at 2 K, the field was then removed and the TRM or IRM data were collected.

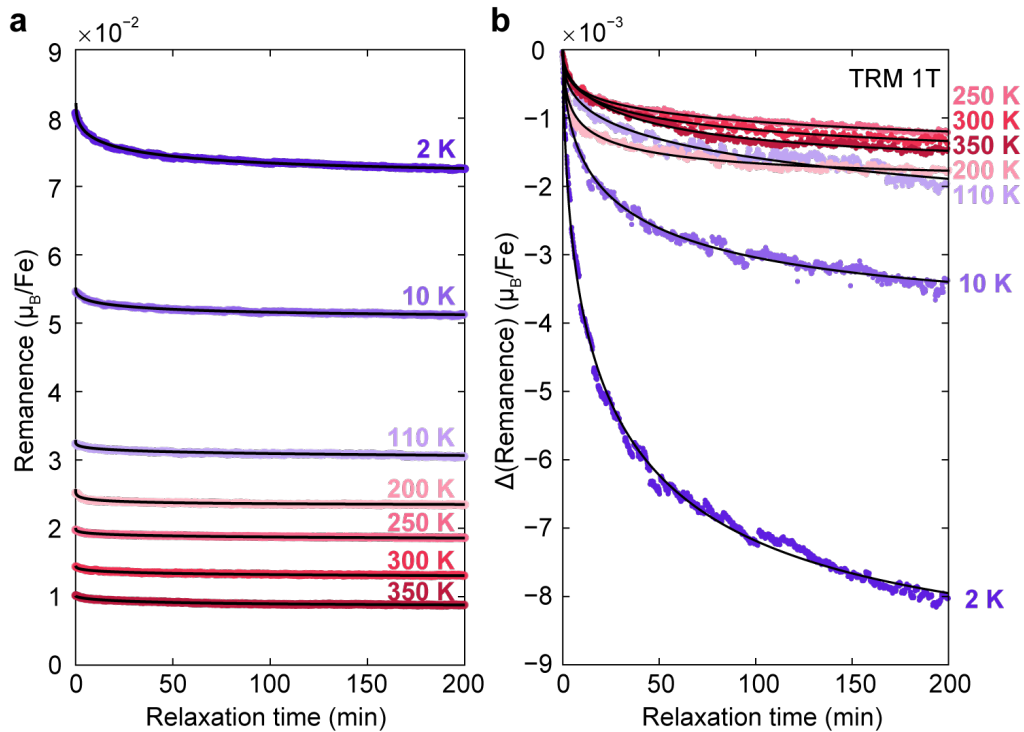


Figure 2.20. (a) The raw TRM curves at different temperature were obtained by FC in a 1 T magnetic field to the target temperature, waiting 60 min, removing this field, and finally measuring the variation in magnetization over 200 min. The TRM data plotted here are after field removal. (b) Change in TRM in (a) determined by subtracting the remanence at $t = 0$ min for all the TRM data (colored dots) and their corresponding fits (black lines).

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Table 2.5. Temperature dependence of TRM relaxation fitting results

$$M_R(t) = M_0 + A \exp[-(t/\tau)^{1-n}]$$

Temp (K)	M_0 (μ_B/Fe)	A (μ_B/Fe)	τ (min)	n
2	0.07127	0.0104	32.74	0.5997
10	0.05078	0.004411	28.9	0.5866
110	0.03072	0.001706	26.1	0.4184
200	0.02328	0.002122	13.55	0.6517
250	0.01843	0.001949	14.06	0.7214
300	0.01271	0.002835	12.31	0.7707
350	0.008366	0.002811	16.73	0.7509

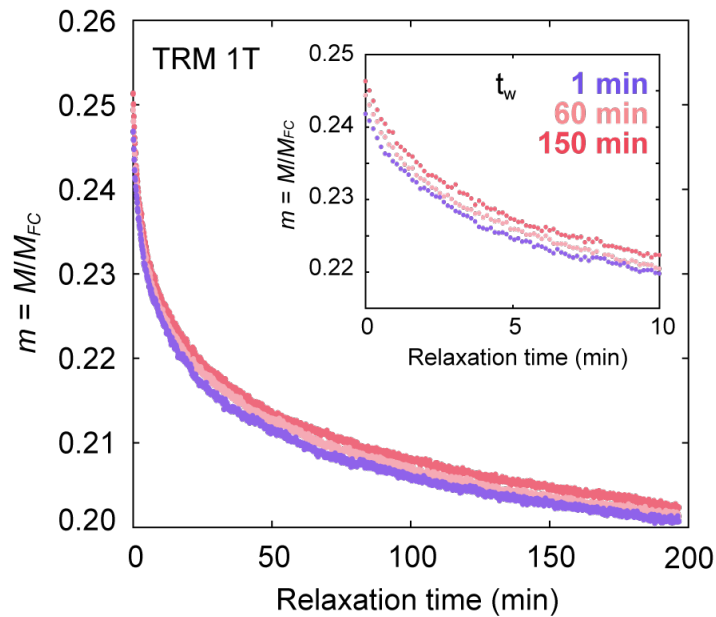


Figure 2.21. TRM data with different wait times. Inset: zoom in on the relaxation time ranging from 0 to 10 min. Magnetization increases with longer wait times, indicating the magnetic aging characteristic of spin glasses.

2.5.18. Variable temperature magnetization data as a function of field

The temperature-dependent magnetization versus applied magnetic field scans were performed in the range of -12 T to 12 T. Zoomed in plots of FC magnetization sweep in the field range of -0.2 T to 0.2 T are presented in the main text. The side-by-side comparison of ZFC and FC plots are shown below, with zoomed-in plots in the range of -0.2 T to 0.2 T (**Figure 2.22**) and full range plots in the range of -12 T to 12 T (**Figure 2.23**).

Figure 2.24 shows the cooling field-dependent magnetization versus field scans performed at 2 K. The zoom-in plots of magnetization sweep in the field range of -0.2 T to 0.2 T were presented in the main text. The sample was field cooled down from 400 K to 2 K under the applied field and then the applied field was set from the cooling field to 12 T. All loops were taken from $+12$ T to -12 T and back to $+12$ T.

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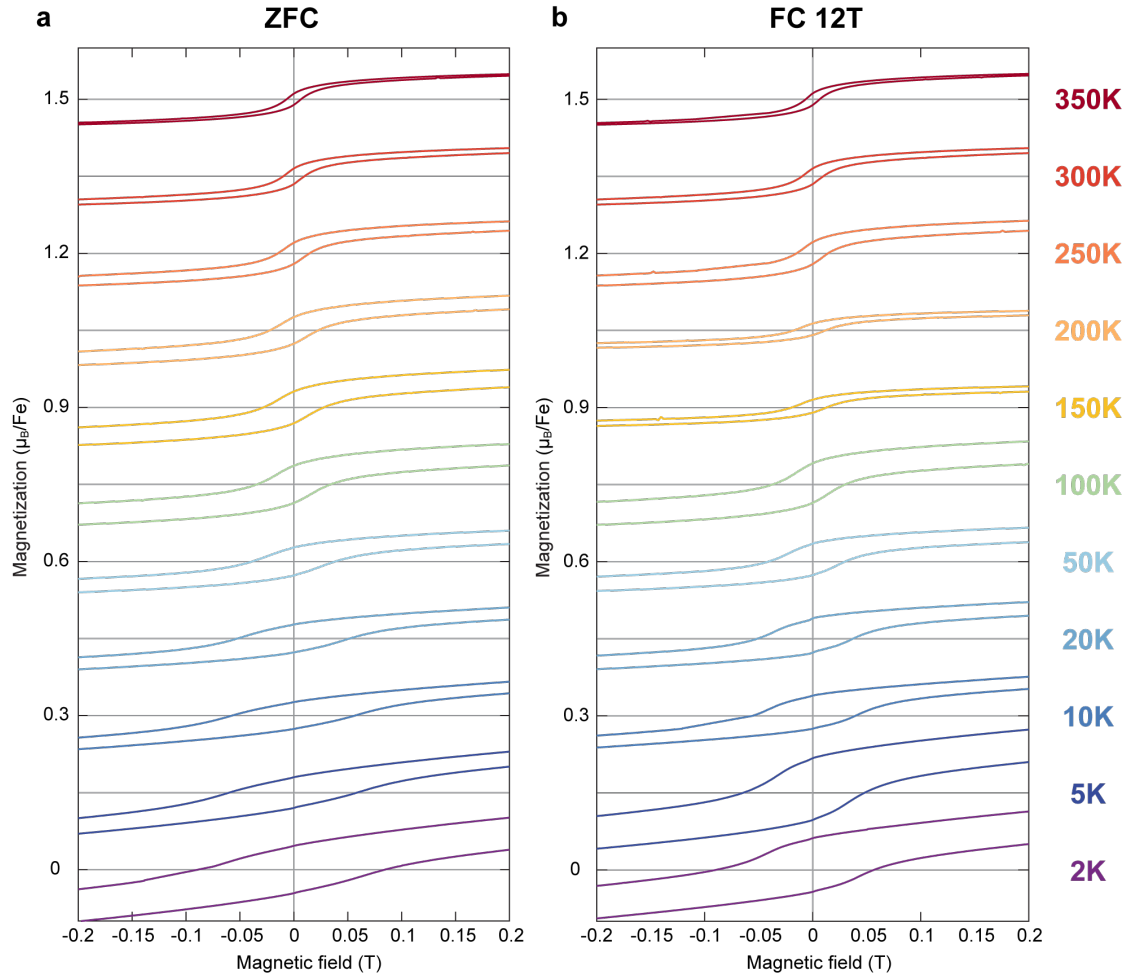


Figure 2.22. Magnetization versus magnetic field measurements at different temperatures. (a) ZFC and (b) FC under a 12 T external field and then sweep field from +12 T to -12 T back to +12 T. The applied field range of -0.2 T to 0.2 T is presented here. Each loop is offset on the y-axis by 0.15 μ_B/Fe . The magnetic field was applied along the c-axis of the samples.

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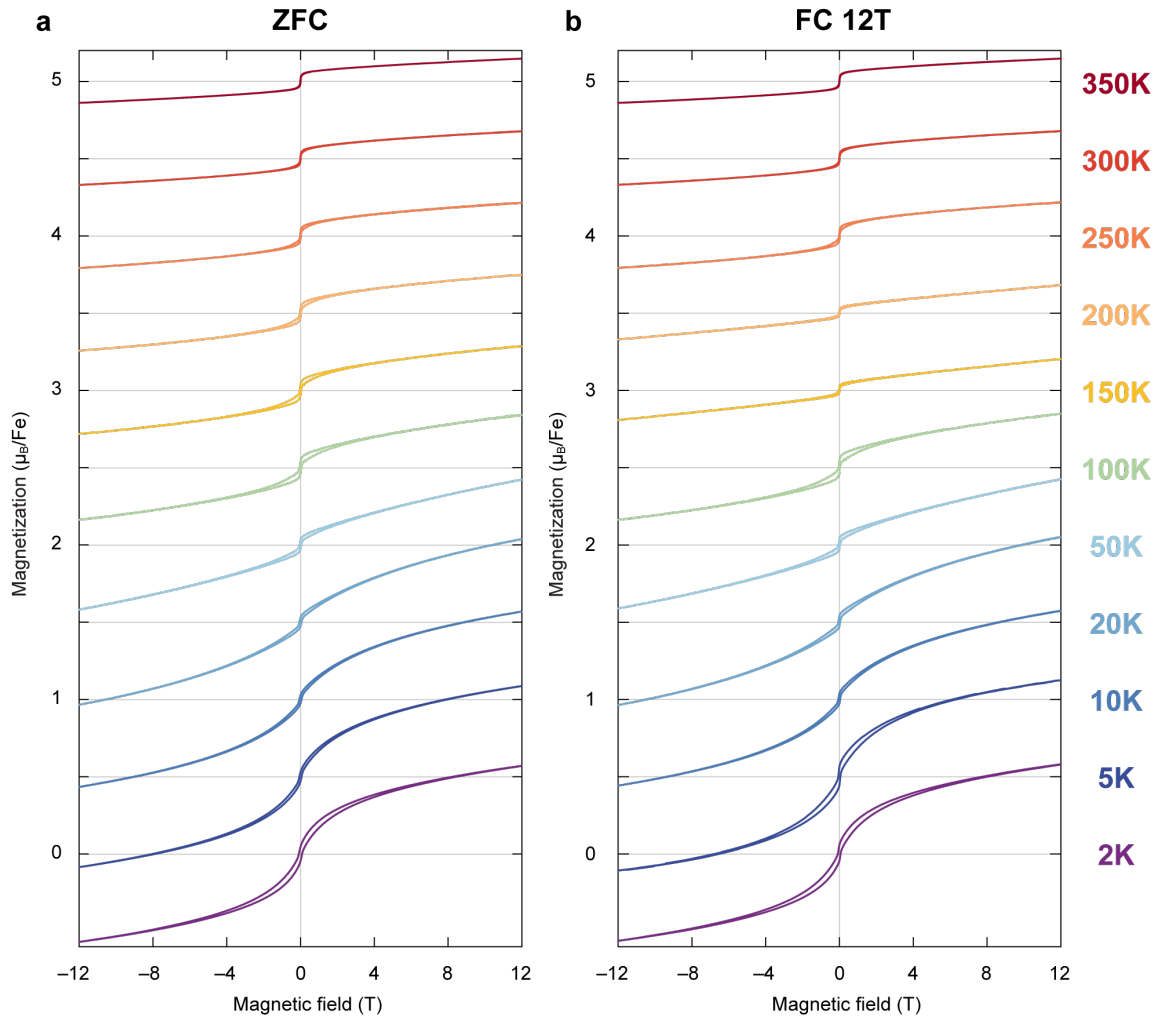


Figure 2.23. Magnetization versus magnetic field measurements at different temperatures. Same as Figure 2.22 but presented with the full range of applied field. Each loop is offset on the y-axis by 0.5 μ_B/Fe .

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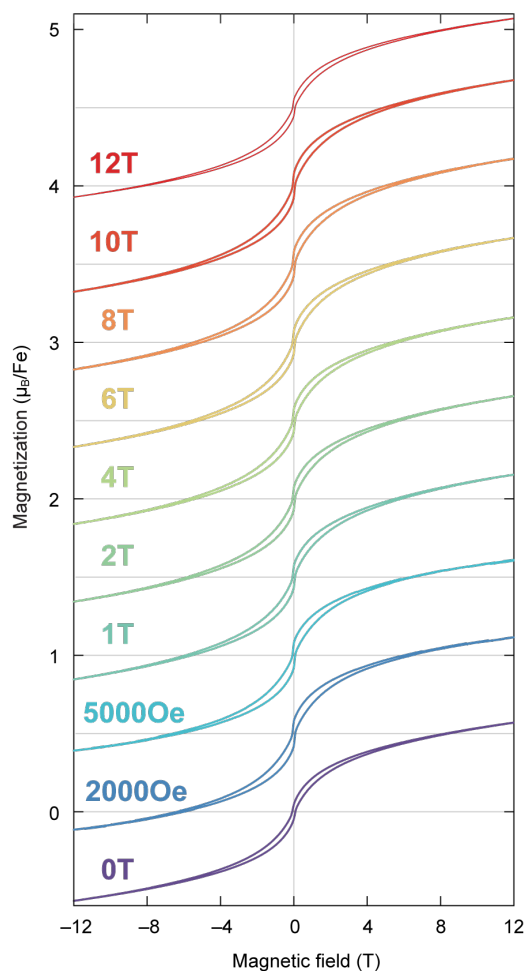


Figure 2.24. Magnetization versus magnetic field measurements at 2K with sample cooled down in different cooling fields. Each loop is offset on the y-axis by 0.5 μ_B/Fe . The magnetic field was applied along the c-axis of the samples.

2.5.19. Steric effect on the occupation of Fe in vdWs gap

To gain insights into the impact of steric effects on complex stability, we compare the sizes of octahedra and tetrahedra in iron selenide compounds and Fe-intercalated TMDs. We examined the reported crystal structures for FeSe_x compounds and Fe_xMSe₂ (*M* = transition metal) and extracted the Se–Se distances of octahedra (**Table 2.6**) and tetrahedra (**Table 2.7**). Compositions without published crystal structures are marked with a “–”. The extracted Se–Se distances of octahedra are plotted in **Figure 2.25b** and those of tetrahedra are presented in **Figure 2.25c**.

This simple analysis shows that the sizes of the FeSe₆ octahedra in Fe_xMSe₂ compounds are within the range of those found in FeSe_x compounds. However, we find that the sizes of the FeSe₄ tetrahedra in Fe_xMSe₂ compounds are consistently smaller than those found in FeSe, but Fe_xZrSe₂ possesses the FeSe₄ tetrahedron that is closest to that found in FeSe. This comparison hints to the reason why Zr-based TMDs are uniquely capable of accommodating a significant fraction of Fe intercalated in tetrahedral sites. Further theoretical investigations are required to gain a deeper understanding of the influence of steric effects on the preferred intercalation sites of Fe.

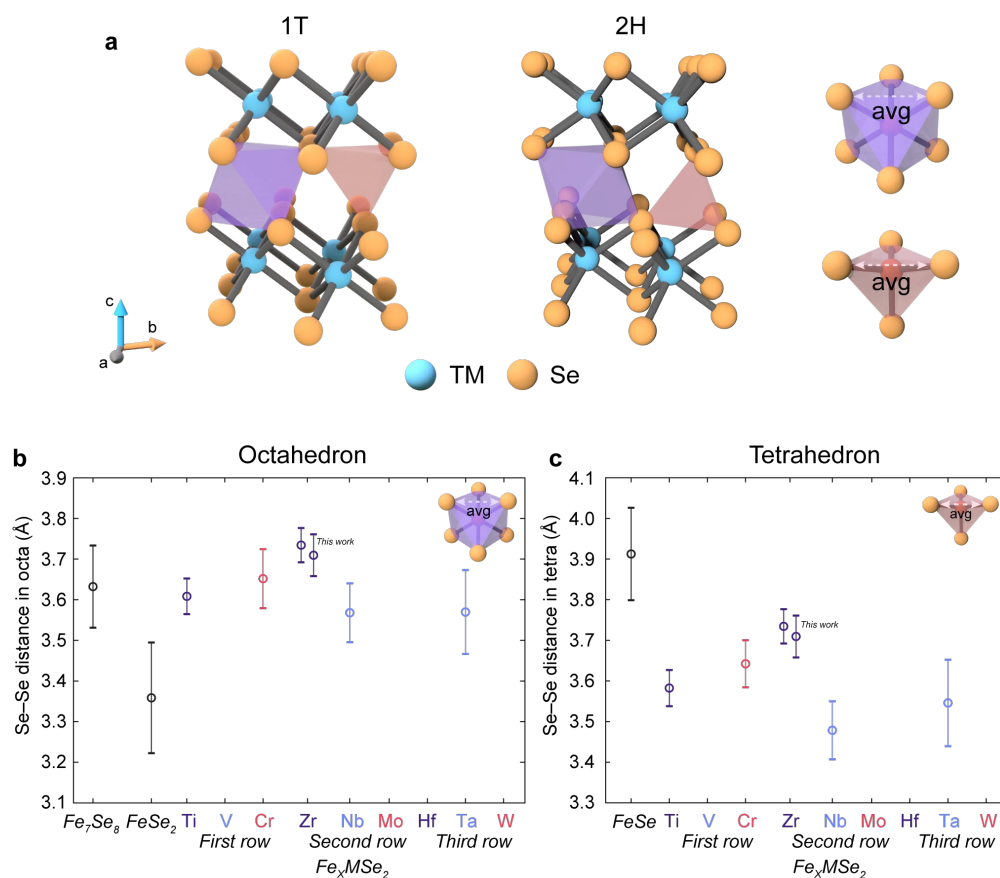


Figure 2.25. The comparison of Se–Se distances for FeSe₄ tetrahedra and FeSe₆ octahedra in FeSe_x compounds versus in Fe intercalated TMDs.

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Table 2.6. Se–Se distance for FeSe₆ octahedra

	Average Se–Se distance (Å)	Standard deviation Se–Se distance (Å)	ref
FeSe ₂	3.36	0.14	106-111
Fe ₇ Se ₈	3.63	0.10	112
Fe _x TiSe ₂	3.61	0.04	113-116
Fe _x VSe ₂	–	–	
CrSe ₂	3.65	0.07	117-119
Fe _x ZrSe ₂	3.73	0.04	120-121
Fe _x NbSe ₂	3.57	0.07	78
Fe _x MoSe ₂	–	–	
Fe _x HfSe ₂	–	–	
Fe _x TaSe ₂	3.57	0.10	122
Fe _x WSe ₂	–	–	
Fe _x ZrSe ₂ (This work)	3.71	0.05	

Table 2.7. Se–Se distances in FeSe₄ tetrahedra

	Average Se–Se distance (Å)	Standard deviation Se–Se distance (Å)	ref
FeSe	3.91	0.11	123-130
Fe _x TiSe ₂	3.58	0.04	113-116
Fe _x VSe ₂	×	×	
Fe _x CrSe ₂	3.64	0.06	117-119
Fe _x ZrSe ₂	3.73	0.04	120-121
Fe _x NbSe ₂	3.48	0.07	78
Fe _x MoSe ₂	×	×	
Fe _x HfSe ₂	×	×	
Fe _x TaSe ₂	3.55	0.11	122
Fe _x WSe ₂	×	×	
Fe _x ZrSe ₂ (This work)	3.71	0.05	

2.5.20. The contextualization of representative exchange bias systems

Table 2.8. Representative exchange bias systems

Structure	Materials	Magnetic phase	largest H_{EB}	Temp (largest H_{EB})	ref
Intrinsic exchange bias	YbFe ₂ O ₄	AFM/FM two magnetic sublattices	19 kOe	5 K	131
	Aurivillius oxides Bi ₁₀ Fe _{6+y} Ti _{3-y} O _{30+δ}	coupling between AFM and spin glass	38 Oe	300 K	132
	Fe _x NbS ₂ (x = 0.30, 0.35)	coupling between AFM and spin glass	30 kOe	1.8 K	28
	Mn ₃ (C ₆ S ₆)	Geometric frustrated spin glass	1625 Oe	2 K	29
	Fe _{0.17} ZrSe ₂	Structural disorder induced spin glass	166 Oe	2 K	This work
heterostructure	Co/CoO	Ferromagnet/ Ferromagnet	9500 Oe	4-10 K	4
	Co/CoN		3200 Oe	4-10 K	
	Ni/NiO	Ferromagnet/ antiferromagnet	400 Oe	4-10 K	
	Fe/Fe ₃ O ₄	Ferromagnet/ Ferrimagnet/	120 Oe	4-10 K	
	Fe/Fe ₂ N	Ferromagnet/ Ferromagnet	300 Oe	4-10 K	
	Co/CuMn	Ferromagnet/spin glass	85 Oe	2 K	22

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Chapter 3

Tunable intrinsic exchange bias in an Fe_xZrSe_2 ($x = 0.25, 0.33$) spin glass

3.1 Introduction

Transition metal dichalcogenides (TMDs) intercalated with open-shell first-row transition metals offer versatile platforms for designing magnetic materials with diverse properties: ferromagnetism observed in $\text{Fe}_{1/4}\text{TaS}_2$ ¹⁻⁴, antiferromagnetism in $\text{Fe}_{1/3}\text{NbS}_2$ ⁵⁻⁷, spin glass behavior in Fe_xNbS_2 ($x = 0.30$ and 0.35)⁸ and $\text{Fe}_{0.17}\text{ZrSe}_2$ ⁹, chiral magnetic textures in $\text{Cr}_{1/3}\text{TaS}_2$ and $\text{Cr}_{1/3}\text{NbS}_2$ ¹⁰⁻¹². The varied magnetic behaviors of T_xMCh_2 compounds can be precisely tailored by controlling the choice of host lattice, intercalant identity, and stoichiometry of the resulting T_xMCh_2 compound¹³.

In Chapter 2, it is demonstrated that Fe-intercalated ZrSe_2 , where Fe atoms occupy both tetrahedral and octahedral sites distributed in a disordered fashion between transition metal dichalcogenide (TMD) layers, exhibits spin glass behavior. Fe_xZrSe_2 not only provides novel design strategies for magnetic film interfaces by leveraging materials with inhomogeneous microscopic environments to induce frustration and support exchange bias, but also underscores the potential of intercalated TMDs like $\text{Fe}_{0.17}\text{ZrSe}_2$ for spintronics technologies operating near room temperature.

In this work, we explore the effect of intercalant amount on the magnetic phases and the exchange bias behaviors of Fe intercalated ZrSe_2 . For Fe_xZrSe_2 , localized moments interact indirectly by polarizing the itinerant holes, establishing short-range magnetic interactions. Adjusting the amount of intercalated Fe in Fe_xZrSe_2 can impact its magnetic behavior in three key aspects. Firstly, the quantity of intercalant influences the number of electrons transferred from intercalated Fe to the host lattice (**Figure 3.1a**), thereby altering the carrier density in ZrSe_2 . The critical temperature (T_C) in this system, as described by the sp-d Zener kinetic exchange model, strongly depends on the host compound and the concentration of free holes (p_h)¹⁴⁻¹⁷. An empirical relation $T_C \sim p_h^{1/3}$ has been established^{18,19}. Secondly, the intercalant amount affects the spacing between localized spin moments (**Figure 3.1b**). According to Ruderman–Kittel–Kasuya–Yosida (RKKY) theory, the interaction between two localized moments oscillates

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between ferromagnetic (FM) and antiferromagnetic (AFM) on the length scale of the hole's Fermi wavelength²⁰⁻²². Thirdly, a higher quantity of intercalated Fe ($x > 0.3$) might lead to the formation of an ordered superlattice in Fe_xZrSe_2 materials. The structure of Fe_xZrSe_2 closely resembles that of Fe_xZrS_2 .²³ It has been reported that in Fe_xZrS_2 , broad superlattice peaks in selected area electron diffraction begin to appear when x ranges between 0.3 and 0.5, indicating the presence of short-range order among the Fe atoms.²⁴ The establishment of Fe ordering in the materials may promote a magnetic phase characterized by long-range magnetic ordering, which can interact with the spin glass phase. The coupling between the ordered phase and the disordered spin glass could contribute to an enhanced exchange bias⁸. Consequently, adjusting the amount of intercalated Fe offers an effective means to control the exchange interactions and magnetic phases of the materials, potentially influencing the exchange bias behavior observed in Fe_xZrSe_2 .

Here, we synthesized Fe_xZrSe_2 ($x = 0.25, 0.33$) crystals and confirmed their compositions and structures. We confirmed the disorder fashion of intercalated Fe between ZrSe_2 host lattice layers. Magnetic characterization reveals spin frustration in both $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$

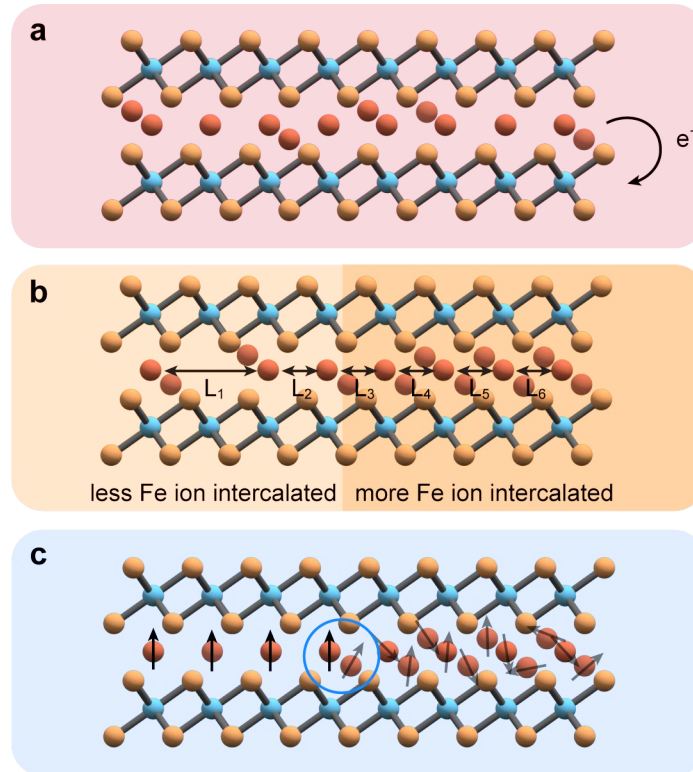


Figure 3.1. The effect of the intercalant amount of Fe ions on the exchange interactions in Fe_xZrSe_2 crystals. (a) The intercalated Fe ions donate electrons to the host lattice ZrSe_2 , leading to the change of carrier density. (b) The intercalated Fe concentration affects the spacing between magnetic moments, which in turn to affect the exchange interactions. (c) Ordered magnetic domains might emergent when the intercalant concentration is high and the coupling between coexisting ordered domain and spin-glass orders might enhance the exchange bias.

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crystals. Upon magnetic field cooling, Fe_xZrSe_2 displays a measurable, apparently intrinsic, exchange bias. Notably, $Fe_{0.33}ZrSe_2$ exhibit giant exchange bias, 3000 Oe at 100 K when cooling in 12 T, which shows strong potential in spintronic applications such as spin valves and magnetic tunnel junctions in high-density storages and magnetic switching for logic devices²⁵⁻³⁰. These results underscore the tight bond between the spin glass phase is and the exchange bias phenomenon and suggest a powerful strategy for designing highly tunable exchange bias systems with near-room temperature transition temperatures, which could have potential applications in future spintronics devices.

3.2 Results

Synthesis, Composition, and Structure of Fe-intercalated $ZrSe_2$

Single crystals of Fe_xZrSe_2 were synthesized using the same recipe in Chapter 2 using chemical vapor transport (CVT). A mixture of source materials Fe, Zr, Se in ratios of 0.6:1:2 (for $Fe_{0.33}ZrSe_2$) and 0.5:1:2 (for $Fe_{0.25}ZrSe_2$) with transport agent I_2 (1 mg/cm³) was loaded into an evacuated quartz ampoule and placed in a two-zone furnace with temperature set points of 900 °C and 1050 °C. After 15 days, hexagonal plate-shaped silver-black crystals with lateral dimensions of several millimeters were obtained. The crystals were thoroughly rinsed with toluene to remove the excess I_2 and stored in an argon-filled glove box.

To determine the composition of Fe_xZrSe_2 crystals, scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) was performed. Prior to SEM-EDS measurements, the as-grown crystals were cleaved with adhesive tape to expose a fresh surface. From the fitting of the EDS spectra (**Figure 3.2a**), the Fe:Zr:Se ratios of the two batches of

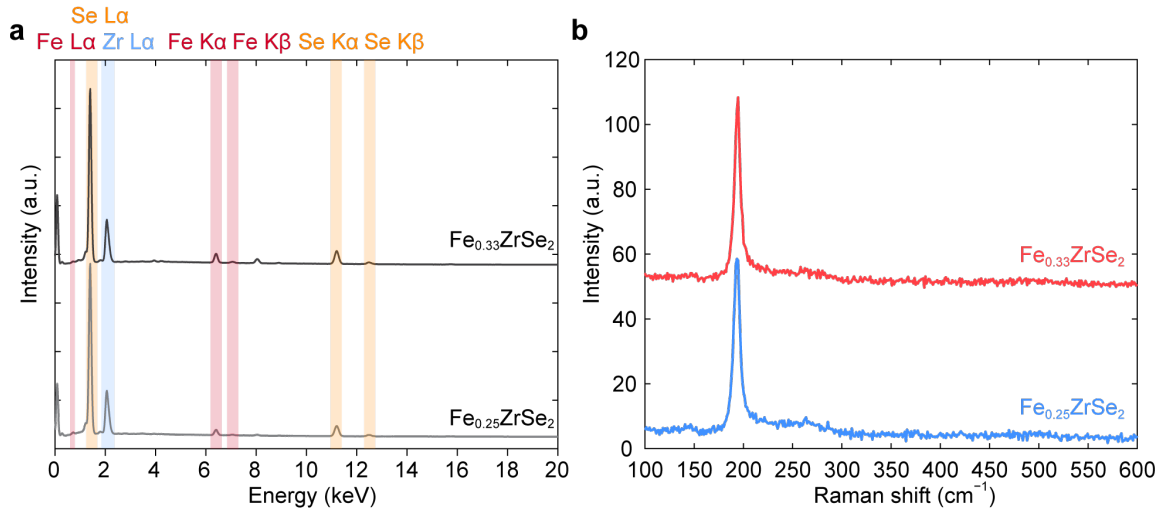


Figure 3.2. Compositional and structural characterization of $Fe_{0.33}ZrSe_2$ and $Fe_{0.25}ZrSe_2$. (a) SEM-EDX of $Fe_{0.33}ZrSe_2$ (top) and $Fe_{0.25}ZrSe_2$ (bottom). (b) Raman spectra of $Fe_{0.33}ZrSe_2$ (top red) and $Fe_{0.25}ZrSe_2$ (bottom blue) flakes with 532 nm excitation.

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crystals were 0.25:1:2 and 0.33:1:2.

Figure 3.3 presents Raman spectra of $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$ crystals obtained using 532 nm excitation. Both sample Raman spectra exhibit the characteristic phonon modes of the host lattice $1T\text{-ZrSe}_2$ ³¹, out-of-plane A_{1g} (194 cm^{-1}) and in-plane E_g (147 cm^{-1}) vibrations, providing the evidence that host lattice is preserved in the CdI_2 ($1T$) structure. The spectral features observed in $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$ were found at the same Raman shifts as those of ZrSe_2 and $\text{Fe}_{0.17}\text{ZrSe}_2$, reported in Chapter 2, indicating that the intercalation of Fe atoms did not break the crystal symmetry of host lattice $1T\text{-ZrSe}_2$.³² No Raman peaks corresponding to a superlattice were detected in $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$, suggesting that Fe centers might be disordered between the layers and no long-range superstructure is formed,³² or the superlattice peaks are too weak to be detected using Raman spectroscopy. Further characterization, such as selected area electron diffraction (SAED), should be done on both $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$ crystals to verify the absence of superlattice formation. Further structural characterizations, such as single crystal diffraction and X-ray absorption spectroscopy need to be done to verify the disorder fashion of Fe distribution between the vdWs gaps of $1T\text{-ZrSe}_2$.

Variable Temperature Magnetic Measurements of $\text{Fe}_{0.33}\text{ZrSe}_2$

Figure 3.3a depicts the zero-field cooled (ZFC) and field cooled (FC) dc magnetization under various applied fields ranging from 200 to 2000 Oe. These ZFC and FC curves bifurcate around 235 K, arising from irreversibility induced under different cooling protocols. Such bifurcation has been reported in spin-glass and superparamagnetic systems³³⁻³⁷. We observe that,

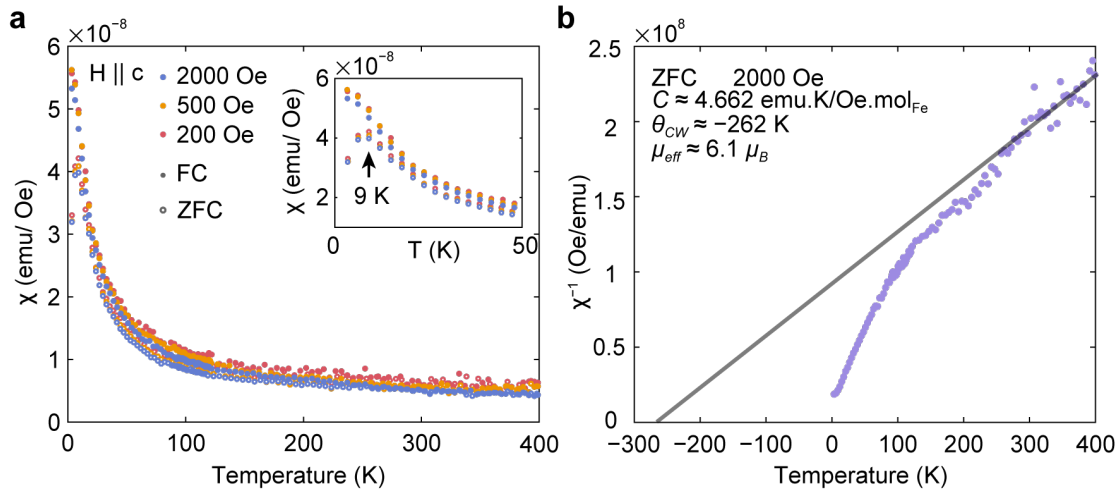


Figure 3.3. Temperature dependence of magnetic susceptibility of $\text{Fe}_{0.33}\text{ZrSe}_2$. (a) Temperature dependence out-of-plane zero-field-cooled (ZFC) and field-cooled (FC) DC magnetic susceptibility for an $\text{Fe}_{0.33}\text{ZrSe}_2$ single crystal under applied magnetic fields ranging from 200 to 2000 Oe. The ZFC and FC data at a given field are represented by open and closed symbols, respectively. Inset shows the expanded view of the region between 0 and 50 K. The peaks of ZFC curves for all the fields showed up at 9 K. (b) Inverse susceptibility as a function of temperature for $\text{Fe}_{0.33}\text{ZrSe}_2$ (purple dots). The data above 300 K was fitted to the Curie–Weiss model $\chi = C/(T - \theta_{CW})$ (black line).

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for all the magnetic fields, the ZFC curves increase with decreasing temperature followed by a downturn around 9 K, whereas the FC curves show continuously increasing moments. As a function of temperature, the magnetization of $\text{Fe}_{0.33}\text{ZrSe}_2$ between 300 and 400 K follows the Curie–Weiss law with $\chi = C/(T - \theta_{\text{CW}})$, where C and θ_{CW} are the Curie constant and Curie–Weiss temperature, respectively (**Figure 3.3b**). We find $\theta_{\text{CW}} = -262$ K, consistent with the predominance of antiferromagnetic exchange interactions in the high temperature regime. C is determined to be $4.662 \text{ emu K/mol}_{\text{Fe}} \cdot \text{Oe}$ and the calculated effective magnetic moment μ_{eff} of $6.1 \mu_B$ is close to the theoretical value of $4.90 \mu_B$ for high spin Fe^{2+} ions, assuming $g = 2$ and $S = 2$.

Relaxation of magnetization for the spin-glass phases of $\text{Fe}_{0.33}\text{ZrSe}_2$

A multivalley energy landscape arising from spin frustration emerges when cooling a spin glass through its freezing temperature^{34,36,38}. The non-ergodicity of the glass system in turn engenders complex magnetic relaxation processes that are apparent in thermoremanent magnetization (TRM) measurements as a slow relaxation of the magnetization over time. For the investigation of the slow relaxation dynamics of $\text{Fe}_{0.33}\text{ZrSe}_2$, TRM measurements were performed following the protocols outlined in **Figures 3.4a**. In short, TRM measurements were carried out by cooling down to target temperature in the presence of a field, holding at this applied field for t_w , removing the field, and then monitoring the change in magnetization as a function of time. **Figures 3.4b** show that the magnetization when holding the materials at 3 K for 90 min and then it relaxes in time upon removal of the applied field, a characteristic of glassy systems.

Magnetic hysteresis and giant exchange bias of $\text{Fe}_{0.33}\text{ZrSe}_2$

Measurements of magnetization as a function of applied field were performed at 5 K after zero-field cooling the sample. As depicted in **Figures 3.5a,b**, the magnetization of the system

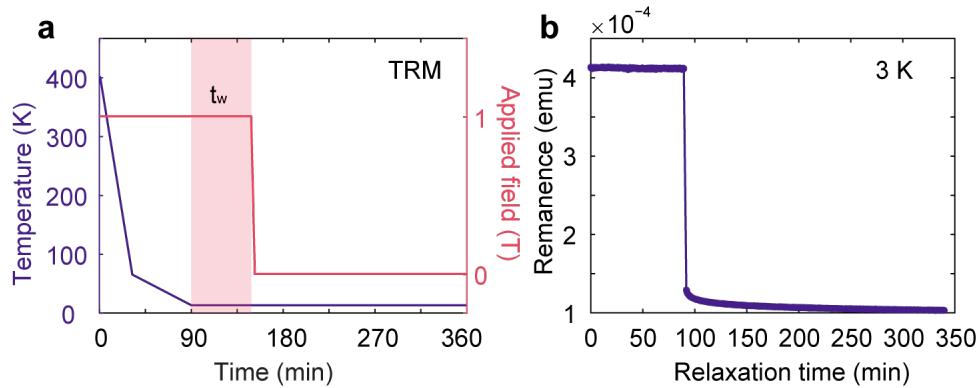


Figure 3.4. Slow magnetic relaxation behavior of $\text{Fe}_{0.33}\text{ZrSe}_2$. (a) Illustration of thermoremanent magnetization (TRM) measurements. The material was first fast-cooled from 400 K to 60 K by 10 K/min and then slow-cooled from 60 K to 3 K by 1 K/min under a 1 T applied field and held in applied field 1 T for a designated wait time, t_w 90 min, at 3 K, the field was then removed and the TRM data were collected. (b) A full TRM measurement is plotted from the start of wait time.

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exhibits a hysteresis loop with a coercive field, $\mu_0 H_c$, of 715 Oe. At the highest measured applied field of 12 T, the hysteresis loop does not fully saturate. Variable-field magnetization data were also collected at 5 K after cooling the sample under applied fields of +12 T and -12 T (**Figures 6a,b**), revealing hysteresis loops with distinct lateral shifts from near zero to ∓ 1380 Oe, respectively, accompanied by a shift along the vertical axis. Upon cooling in a positive (negative) field, the loop exhibited a bias in the negative (positive) direction, which is a signature of exchange bias^{39,40}. The magnitude of the exchange bias field, H_{EB} , was calculated as:

$$\mu_0 H_{EB} = (\mu_0 H_{int1} + \mu_0 H_{int2})/2$$

where $\mu_0 H_{int1}$ and $\mu_0 H_{int2}$ are the intercepts on horizontal axes. The magnitude of $\mu_0 H_c$ is defined as the half-width of the hysteresis loop at the average of the vertical intercepts, as depicted in the inset of **Figure 3.5a**.

Plots of $M(H)$ over a range of temperatures are shown in **Figure 3.5c** and the associated temperature-dependent evolution of exchange bias field $\mu_0 H_{EB}$ and coercive field $\mu_0 H_c$ for $\mu_0 H_{FC} = 12$ T (compared to the corresponding ZFC case) are presented in **Figures 3.5c,e**. Hysteresis curves of magnetization versus magnetic field measurements at different temperatures for $\text{Fe}_{0.33}\text{ZrSe}_2$ were showed in **Figure 3.6**. No zero-field-cooled exchange bias (ZEB) effect was observed. When cooling in the applied magnetic field, the value of $\mu_0 H_{EB}$ increases with increasing temperature from 9 to 100 K, while $\mu_0 H_{EB}$ decreases with increasing temperature from 100 to 300 K. A finite $\mu_0 H_{EB}$ persists up to at least 250 K, and at 300 K, the $\mu_0 H_{EB}$ decreases to $\mu_0 H_{EB}$ at zero-field cool level. Likewise, $\mu_0 H_c$ increases with increasing temperature from 15 to 100 K, and when temperature goes above 100 K, the $\mu_0 H_{EB}$ decreases with increasing temperature and hysteresis loop is completely closed at 250 K. Notably, both $\mu_0 H_{EB}$ and $\mu_0 H_c$ peak at 100 K. Further experiments for data points at 150 and 200 K need to be collected to better understand the trends of $\mu_0 H_{EB}$ and $\mu_0 H_c$ to temperature and their correlations to T_{irr} of $\text{Fe}_{0.33}\text{ZrSe}_2$.

The exchange bias behavior at 3 K was also probed at different cooling fields as shown in **Figures 3.5d,f**. Hysteresis curves of magnetization versus magnetic field measurements at different cooling fields for $\text{Fe}_{0.33}\text{ZrSe}_2$ were shown in **Figure 3.7**. $\mu_0 H_{EB}$ appears unchanged by increasing cooling fields from 2 to 10 T, and it oscillates within a range of 1450 and 1750 Oe. The value of $\mu_0 H_c$ stays stable within the cooling range from 2 to 8 T, but decreases by 1000 Oe when increasing $\mu_0 H_{FC}$ from 8 T to 10 T.

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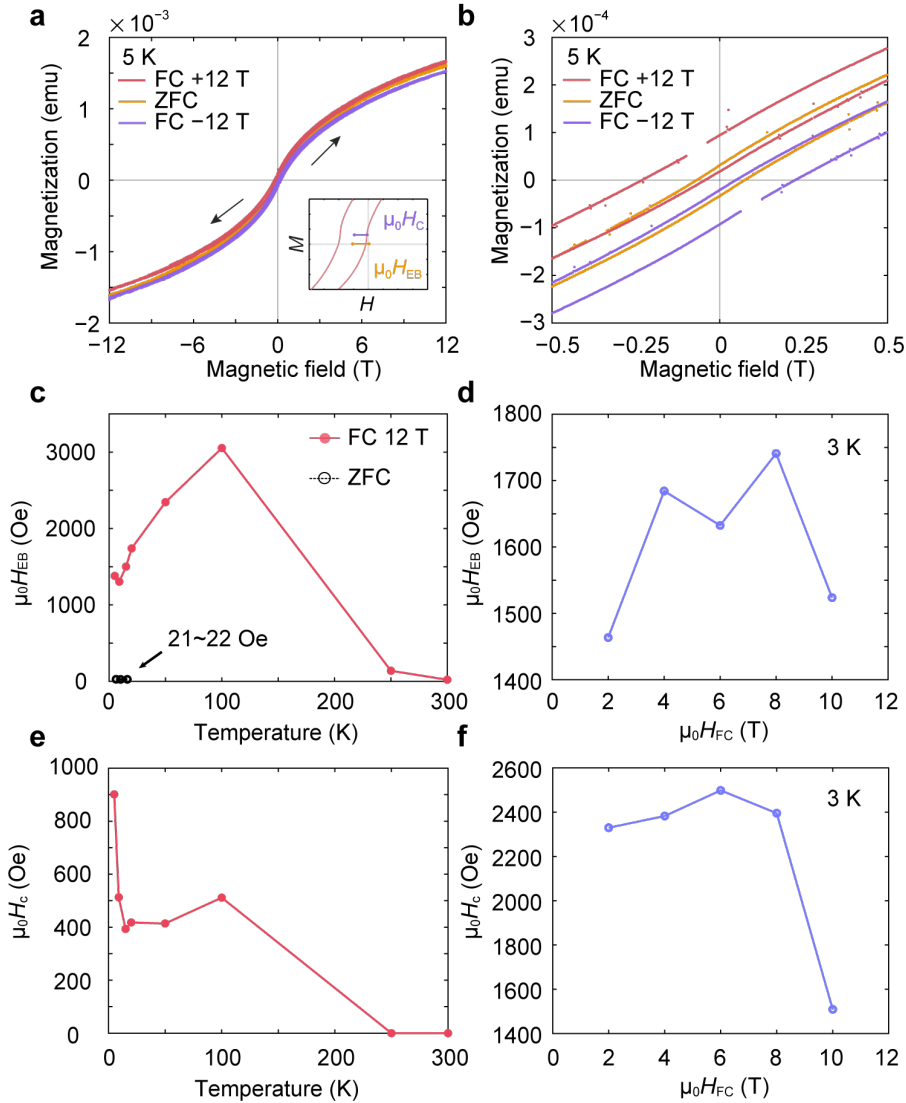


Figure 3.5. Exchange bias of $\text{Fe}_{0.33}\text{ZrSe}_2$. (a) Magnetic hysteresis loops measured after the samples are cooled under 12 T (red curve), -12 T (purple curve), and zero field (orange curve) from 400 K to 2 K. The inset in (a) demonstrates the definition of exchange bias field $\mu_0 H_{EB}$ (purple), and coercive field $\mu_0 H_C$ (orange). $\mu_0 H_{EB}$ was extracted from each loop by taking the average of the x intercepts, $\mu_0 H_{EB} = (\mu_0 H_{int1} + \mu_0 H_{int2})/2$; $\mu_0 H_C$ was calculated from the half-width of the hysteresis loop at the average of the y intercepts. (b) Expanded view of the region between -0.5 and 0.5 T in (a). The shifts of the hysteresis loops collected under applied fields are symmetrical relative to the zero-field loop. (c, e) Temperature dependence of the extracted (c) exchange bias field $\mu_0 H_{EB}$ and (e) coercive fields $\mu_0 H_C$ after cooling in a 12 T (red trace) and 0 T (black dotted trace) from 400 K. (d, f) Cooling field dependence of (d) $\mu_0 H_{EB}$ and (f) $\mu_0 H_C$ after cooling from 400 to 2 K. All the hysteresis loops were collected with the magnetic field applied along the c-axis of the samples. The solid lines are a guide to the eye.

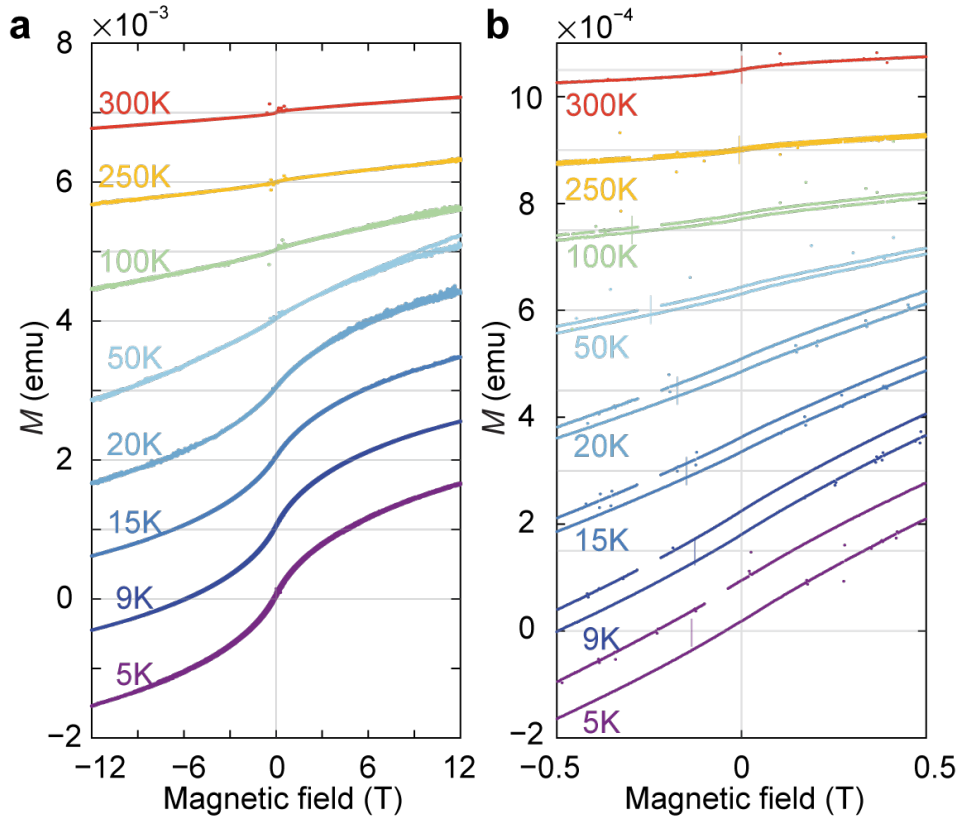


Figure 3.6. Magnetization versus magnetic field measurements at different temperatures for $\text{Fe}_{0.33}\text{ZrSe}_2$. (a) Magnetic hysteresis loops measured after the samples are cooled under 12 T to different temperatures and then sweep field from +12 T to -12 T back to +12 T. Each loop is offset on the y-axis by 1×10^{-3} emu. (b) Expanded view of the region between -0.5 and 0.5 T in (a). Each loop is offset on the y-axis by 1.5×10^{-4} emu. The solid lines showing the position of exchange bias field $\mu_0 H_{EB}$ are a guide to the eye.

Variable Temperature Magnetic Measurements of $\text{Fe}_{0.25}\text{ZrSe}_2$

Figure 3.8 depicts the zero-field cooled (ZFC) and field cooled (FC) dc magnetization under various applied fields ranging from 500 to 2000 Oe. These ZFC and FC curves bifurcate around 17 K, much lower than T_{irr} observed in $\text{Fe}_{0.17}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$. We observe that, with 500 Oe applied field, the ZFC curve increases with decreasing temperature followed by a plateau around 6 K, whereas the FC curve shows continuously increasing moments. Whereas with 2000 Oe applied field, both ZFC and FC curves increase with decreasing temperature.

As a function of temperature, the magnetization of $\text{Fe}_{0.25}\text{ZrSe}_2$ between 200 and 400 K follows the Curie–Weiss law with $\chi = C/(T - \theta_{\text{CW}})$, where C and θ_{CW} are the Curie constant and Curie–Weiss temperature, respectively (**Figure 3.8b**). We find $\theta_{\text{CW}} = -1790$ K, consistent with

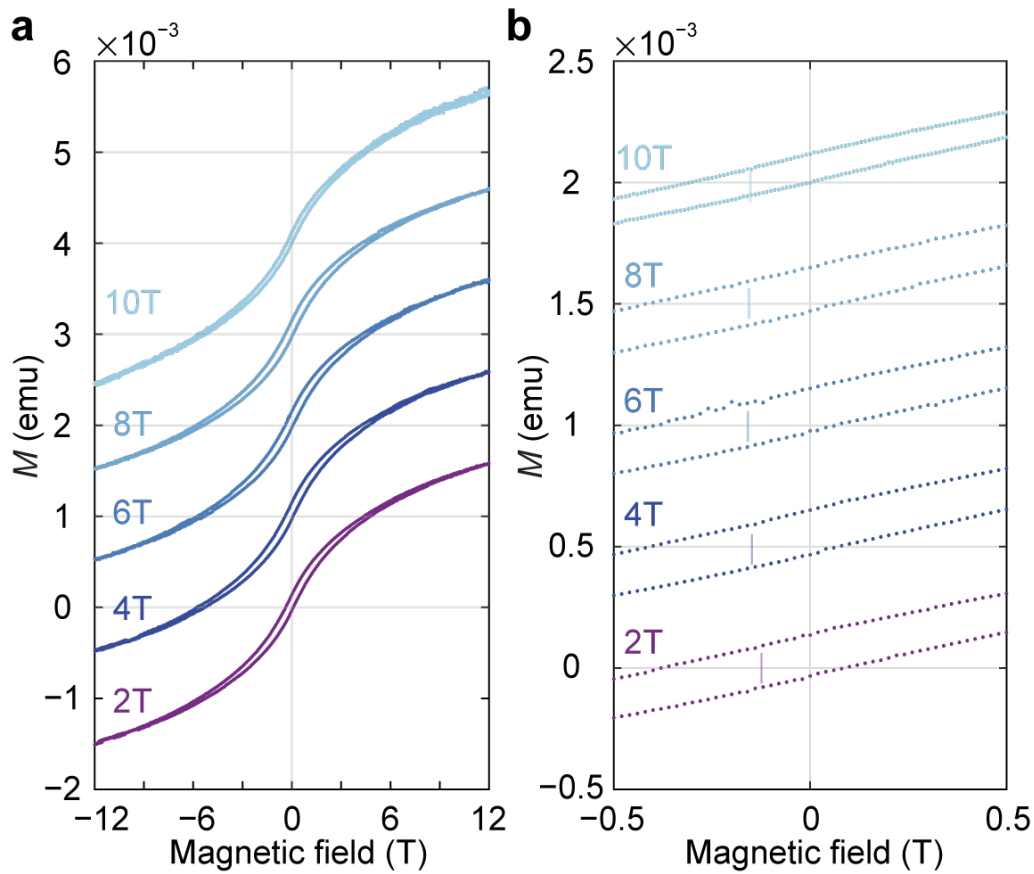


Figure 3.7. Magnetization versus magnetic field measurements under various cooling fields for $\text{Fe}_{0.33}\text{ZrSe}_2$. (a) Magnetization versus magnetic field measurements at 3 K with sample cooled down in different cooling fields. Each loop is offset on the y-axis by 1×10^{-3} emu. The magnetic field was applied along the c-axis of the samples. (b) Expanded view of the region between -0.5 and 0.5 T in (a). Each loop is offset on the y-axis by 5×10^{-4} emu. The solid lines showing the position of exchange bias field $\mu_0 H_{EB}$ are a guide to the eye.

the predominance of antiferromagnetic exchange interactions in the high temperature regime.

Magnetic hysteresis and exchange bias of $\text{Fe}_{0.25}\text{ZrSe}_2$

Measurements of magnetization as a function of applied field were performed at 5 K after zero-field cooling the sample. As depicted in **Figures 3.9a,b**, the magnetization of the system exhibits a hysteresis loop with a coercive field, $\mu_0 H_c$, of 375 Oe. At the highest measured applied field of 12 T, the hysteresis loop does not fully saturate. Variable-field magnetization data were also collected at 5 K after cooling the sample under applied fields of +12 T and -12 T (**Figures 3.9a,b**), revealing hysteresis loops with small lateral shifts from near zero to ± 105 Oe, respectively, accompanied by a shift along the vertical axis. The exchange bias field of

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$\text{Fe}_{0.25}\text{ZrSe}_2$ is much smaller than that of $\text{Fe}_{0.33}\text{ZrSe}_2$.

The associated temperature-dependent evolution of exchange bias field $\mu_0 H_{EB}$ and coercive field $\mu_0 H_c$ for $\mu_0 H_{FC} = 12$ T (compared to the corresponding ZFC case) are presented for $\text{Fe}_{0.25}\text{ZrSe}_2$ in **Figures 3.9c,e**. No zero-field-cooled exchange bias (ZEB) effect was observed. When cooling in the applied magnetic field, the value of $\mu_0 H_{EB}$ increases with increasing temperature from 9 to 50 K, while $\mu_0 H_{EB}$ decreases with increasing temperature from 50 to 300 K and at 300 K, the $\mu_0 H_{EB}$ decreases to $\mu_0 H_{EB}$ at zero-field cool level. However, $\mu_0 H_c$ decreases with increasing temperature from 5 to 300 K. Further experiments for data points at more temperatures need to be collected to better understand the trends of $\mu_0 H_{EB}$ and $\mu_0 H_c$ to temperature and their correlations to T_{irr} of $\text{Fe}_{0.25}\text{ZrSe}_2$. The exchange bias behavior at 3 K for $\text{Fe}_{0.25}\text{ZrSe}_2$ was also probed at different cooling fields as shown in **Figures 3.9d,f**. $\mu_0 H_{EB}$ increases with increasing cooling fields from 2 to 12 T, and the value of $\mu_0 H_c$ stays within the range of 1150 and 1300 Oe. Further experiments for data points at more cooling fields should be

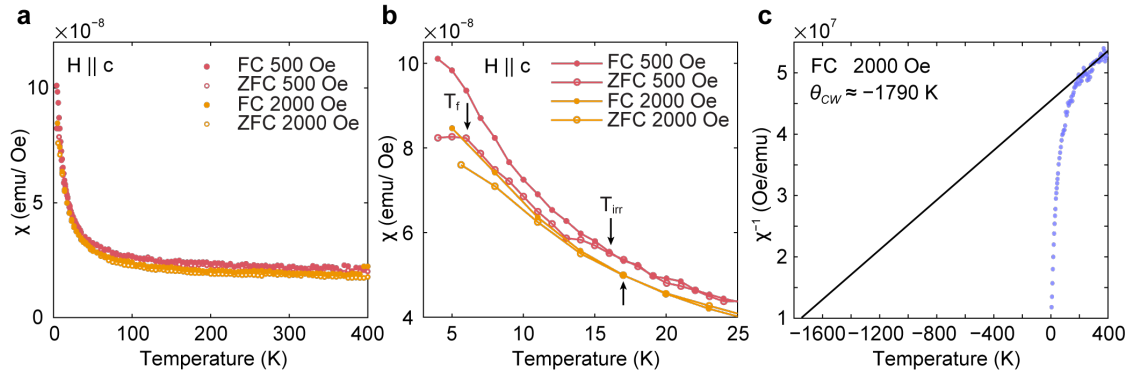


Figure 3.8. Temperature dependence of magnetic susceptibility of $\text{Fe}_{0.25}\text{ZrSe}_2$. (a) Temperature dependence out-of-plane zero-field-cooled (ZFC) and field-cooled (FC) DC magnetic susceptibility for an $\text{Fe}_{0.25}\text{ZrSe}_2$ single crystal under applied magnetic fields ranging from 500 to 2000 Oe. The ZFC and FC data at a given field are represented by open and closed symbols, respectively. (b) The expanded view of the region between 3 and 25 K. (c) Inverse susceptibility as a function of temperature for $\text{Fe}_{0.25}\text{ZrSe}_2$ (purple dots). The data above 200 K was fitted to the Curie–Weiss model $\chi = C/(T - \theta_{CW})$ (black line).

collected for better understanding the exchange bias behavior of $\text{Fe}_{0.25}\text{ZrSe}_2$.

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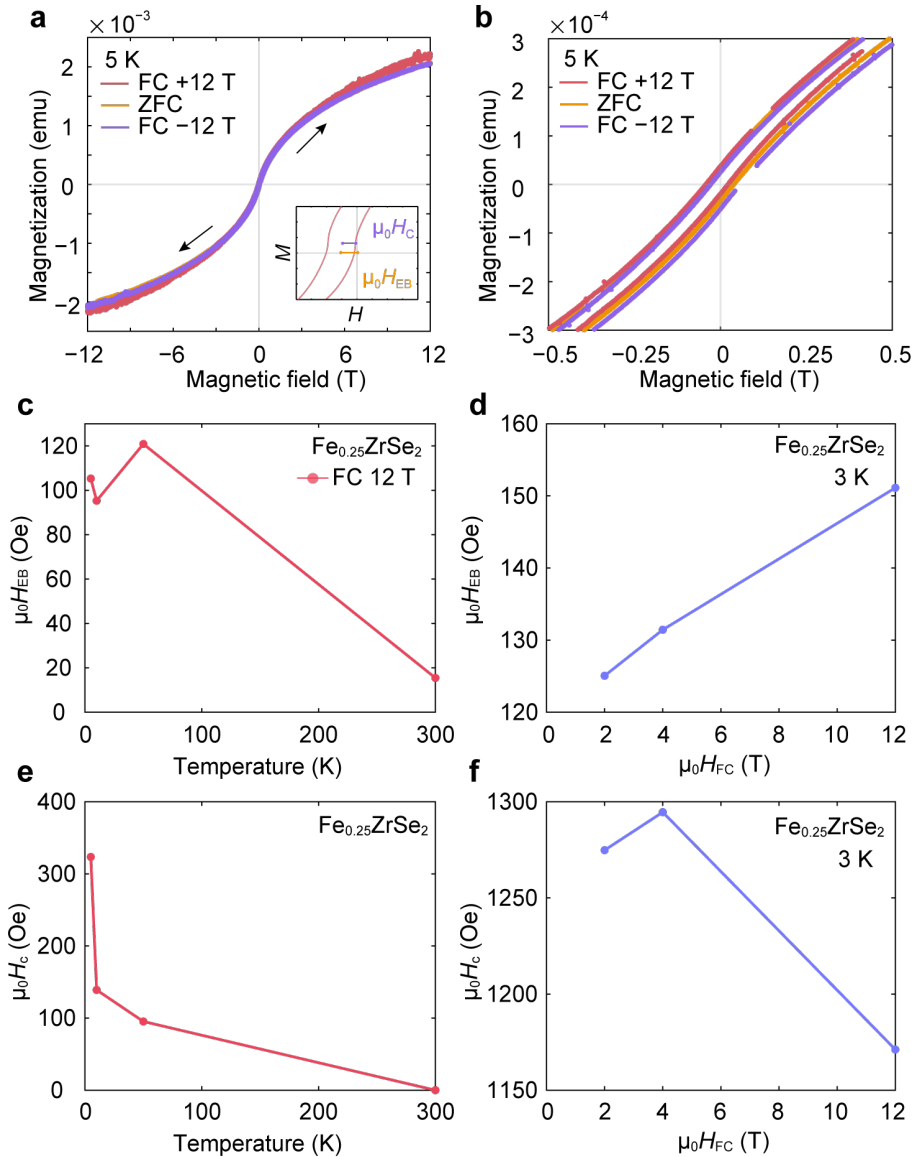


Figure 3.9. Exchange bias of $\text{Fe}_{0.25}\text{ZrSe}_2$. (a) Magnetic hysteresis loops measured after the samples are cooled under 12 T (red curve), -12 T (purple curve), and zero field (orange curve) from 400 K to 2 K. The inset in (a) demonstrates the definition of exchange bias field $\mu_0 H_{EB}$ (purple), and coercive field $\mu_0 H_C$ (orange). $\mu_0 H_{EB}$ was extracted from each loop by taking the average of the x intercepts, $\mu_0 H_{EB} = (\mu_0 H_{int1} + \mu_0 H_{int2})/2$; $\mu_0 H_C$ was calculated from the half-width of the hysteresis loop at the average of the y intercepts. (b) Expanded view of the region between -0.5 and 0.5 T in (a). The shifts of the hysteresis loops collected under applied fields are symmetrical relative to the zero-field loop. (c, e) Temperature dependence of the extracted (c) exchange bias field $\mu_0 H_{EB}$ and (e) coercive fields $\mu_0 H_C$ after cooling in a 12 T (red trace). (d, f) Cooling field dependence of (d) $\mu_0 H_{EB}$ and (f) $\mu_0 H_C$ after cooling from 400 to 2 K. All the hysteresis loops were collected with the magnetic field applied along the c-axis of the samples.

3.3 Discussion

Spin glass behavior

For both $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$, their magnetic susceptibility data (**Figure 3.3 and Figure 3.8**) display a bifurcation in FC and ZFC measurements at a temperature, T_{irr} . The T_{irr} of $\text{Fe}_{0.33}\text{ZrSe}_2$ is around 240 K, which is close to that of $\text{Fe}_{0.17}\text{ZrSe}_2$, which is around room-temperature. However, for $\text{Fe}_{0.25}\text{ZrSe}_2$, its T_{irr} appeared around 17 K, which is much lower than those of $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$. The splitting between ZFC and FC magnetization shown in Fe_xZrSe_2 is typical feature for spin-glass- or cluster-glass-like states^{41,42}. As mentioned in chapter 2, for glassy systems, the T_{irr} depends on magnetic field—a phenomenon typically attributed to the freezing of moments^{43,44}. This freezing occurs when the crystalline anisotropy of small domains overcomes thermal fluctuations, which leads spins to freeze in random directions. To further analyze the glassy nature of the system, we need to study the dependence of T_{irr} on the applied magnetic field. If it shows that the system follows the Almeida–Thouless (AT) line with $T_{\text{irr}} \propto H^{2/3}$, then the system can be considered as spin glass system. However, the magnetic susceptibility data for both $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$ we collected so far is not enough for the AT fitting. Thus, more ZFC and FC at different applied fields with high signal to noise ratio need to be collected to study the magnetic phase of the Fe_xZrSe_2 . Moreover, for $\text{Fe}_{0.25}\text{ZrSe}_2$, a broad ZFC “blocking peak” at a freezing temperature T_f appeared around 9 K, which might correspond to a broad size distribution of magnetic entities. Another possible reason is that the applied field 500 Oe might be so strong that it forces the spins to align. Further experiments collecting ZFC and FC at lower applied fields need to be done for us to determine if the ZFC has broad blocking peak or not. Measurements of magnetization over time reveal slow spin relaxation dynamics at 3 K in $\text{Fe}_{0.33}\text{ZrSe}_2$ crystals, which is another characteristic feature for glassy magnetic materials. Further experiments collecting IRM and TRM and AC susceptibility need to be collected for $\text{Fe}_{0.25}\text{ZrSe}_2$ $\text{Fe}_{0.33}\text{ZrSe}_2$ to confirm their spin glass behavior.

Exchange bias effect

Measurements of magnetization as a function of magnetic field for both $\text{Fe}_{0.33}\text{ZrSe}_2$ (**Figure 3.5**) and $\text{Fe}_{0.25}\text{ZrSe}_2$ (**Figure 3.9**) display magnetic hysteresis with a finite coercivity, $\mu_0 H_c$, a behavior that is commonly associated with ferromagnetic systems. However, it is important to note that the opening of hysteresis loops has also been reported in several spin glass materials^{45–47}. **Figure 3.5** also shows that when cooled in an applied field, $\text{Fe}_{0.33}\text{ZrSe}_2$ exhibits a robust exchange bias. The interesting phenomenon is the synchronization of the dependence of coercive field $\mu_0 H_c$ and the exchange bias field $\mu_0 H_{\text{EB}}$ on the temperature from 20 to 300 K, where they increase upon increasing temperature from 20 to 100 K, whereas decrease with increasing temperature from 100 to 300 K. Similar phenomenon has been reported in the spin glass/ferromagnet bilayer systems⁴⁸, however, the mechanism still needs further study. One possible explanation is that there is the coexistence of spin glass phase and antiferromagnetic phase in the $\text{Fe}_{0.33}\text{ZrSe}_2$. Furthermore, the onset of exchange bias field $\mu_0 H_{\text{EB}}$ around 250 K coincides with T_{irr} around 240 K. $\text{Fe}_{0.33}\text{ZrSe}_2$ shows the giant exchange bias up to 3053 Oe after field cooled at applied magnetic field 12 T to 100 K.

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To evaluate the potential applicability of the exchange bias phenomenon in $\text{Fe}_{0.33}\text{ZrSe}_2$, we position this system within the context of representative exchange bias systems, as outlined in **Table 2.8**. The observed exchange bias in $\text{Fe}_{0.33}\text{ZrSe}_2$, measured at 3053 Oe at 100 K, exceeds the exchange bias field values observed in various canonical heterostructure systems. Additionally, the operating temperature of 100 K for the giant exchange bias effect in $\text{Fe}_{0.33}\text{ZrSe}_2$ is significantly higher compared to the temperatures typically observed in these systems (4 ~ 10 K), indicating the high potential of $\text{Fe}_{0.33}\text{ZrSe}_2$ for spintronic applications at room temperature.

Figure 3.10 shows the comparison of T_{irr} and largest exchange bias fields for Fe_xZrSe_2 . The T_{irr} for $\text{Fe}_{0.25}\text{ZrSe}_2$ is around 17 K, which is much lower than that of $\text{Fe}_{0.17}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$. Even though all the Fe_xZrSe_2 show robust exchange bias behaviors, however, the $\text{Fe}_{0.33}\text{ZrSe}_2$ show the giant exchange bias, which is much higher than Fe_xZrSe_2 with lower x . It would be interesting to do more structural characterization on the materials and correlate their structure with their magnetic phases and exchange bias behavior.

3.4 Conclusions

Combined compositional, structural characterization reveals that $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$ crystals exhibit high crystallinity of the 1T-ZrSe₂ host lattice, while Fe atoms

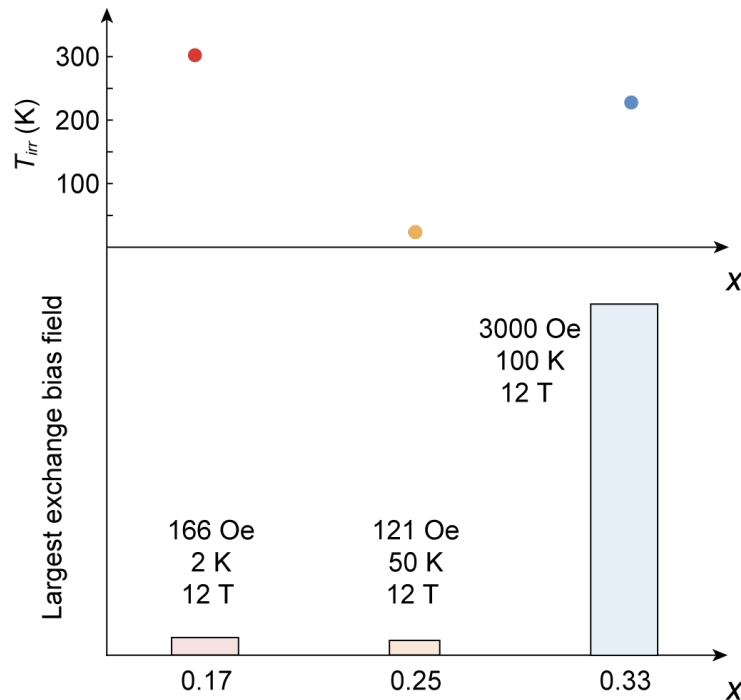


Figure 3.10. The contextualization of Fe_xZrSe_2 with different x . The irreversible temperature and largest exchange bias field of Fe_xZrSe_2 ($x = 0.17, 0.25, 0.33$). The conditions of the largest exchange bias field for each system are labelled next to the column.

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distributed in a disordered fashion between TMD layers. Magnetometry measurements of $\text{Fe}_{0.33}\text{ZrSe}_2$ demonstrate magnetic irreversibility under zero-field cooling (ZFC), slow relaxation dynamics. These findings indicate a frustrated, and multi-degenerate ground state in $\text{Fe}_{0.33}\text{ZrSe}_2$ single crystals. Interestingly, a robust giant exchange bias is observed at 100 K in $\text{Fe}_{0.33}\text{ZrSe}_2$. All Fe_xZrSe_2 ($x = 0.17, 0.25, 0.33$) crystals with different Fe amounts exhibit both spin glass and exchange bias behavior, which emphasizes the correlation between spin disorder and exchange bias behavior. Exploring exchange bias in systems like Fe_xZrSe_2 offers valuable insights into the role of disorder and frustration in magnetic materials more widely, including prototypical metallic magnetic multilayers. Our results highlight the potential of intercalated TMDs like Fe_xZrSe_2 for spintronics technologies that can operate near room temperature. And the intercalant amount is a powerful tuning knob for achieving Fe_xZrSe_2 materials with designed magnetic properties. This work also opens doors to new design strategies for magnetic film interfaces that leverage materials with inhomogeneous microscopic environments to induce frustration and support exchange bias.

There are a lot of experiments that need to be done to fully understand how the structures of the Fe_xZrSe_2 affect its magnetic behaviors. Selected area electron diffraction (SAED) and X-ray absorption spectroscopy (XAS) are essential to determine the formation of superlattice in $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$. To study the magnetic phase of the Fe_xZrSe_2 , temperature dependence of magnetic susceptibility at various cooling fields with high signal to noise ratio need to be collected along with the temperature dependence of spin relaxation. As for the exchange bias, the magnetic hysteresis loops need to be collected to study the effect of the temperature and cooling field on the exchange bias, which allows us to obtain the roadmap to designing exchange bias of Fe_xZrSe_2 .

3.5 Experimental

3.4.1 Chemicals

Unless otherwise stated, all materials and reagents were used as received.

The following chemicals were used for the chemical vapor transport (CVT) growth of crystalline iron intercalated zirconium diselenide (Fe_xZrSe_2). Iron powder (spherical, $<10\text{ }\mu\text{m}$, purity $>99.9\%$, metal basis), and selenium powder (200 mesh, purity 99.999% , metals basis) were purchased from Alfa Aesar (Ward Hill, MA, USA). Zirconium pellets (catalog # ZR39X88-10G, purity $>99.9\%$) was purchased from R.D. Mathis Co. (Long Beach, CA, USA). Iodine (catalog # 229695-20G, purity $>99.999\%$, trace metals basis) was purchased from Sigma Aldrich Co., LLC. (St. Louis, MO, USA). ZrSe_2 single crystals were purchased from HQ graphene (Groningen, The Netherlands). The as-grown Fe_xZrSe_2 flakes were washed using toluene in an Ar-filled glove box. Glassware was oven-dried at a temperature of $150\text{ }^\circ\text{C}$ for $\geq 4\text{ h}$ and allowed to cool in an evacuated glove box antechamber prior to use. Anhydrous toluene was stored over 3- or 4-Å molecular sieves prior to use.

3.4.2 Chemical vapor transport growth of Fe_xZrSe_2

Fe_xZrSe_2 was synthesized following procedures reported previously.⁴⁹ Table 3.1 shows the precursors and transport agents used in the CVT growth of $\text{Fe}_{0.25}\text{ZrSe}_2$ and $\text{Fe}_{0.33}\text{ZrSe}_2$. A mixture of zirconium pellet, selenium powder, Fe powder along with transport agent I_2 was loaded into 40 cm long quartz ampoule in atmospheric conditions. The ampoule was then evacuated to 1×10^{-2} Torr. The contents of ampoule were then cooled using liquid nitrogen to minimize the vaporization of I_2 . When the pressure dropped below 1×10^{-4} Torr, the ampoule was sealed, and placed in a 3-zone furnace. The temperature for hot zone is 950 °C and for cold zone is 800 °C. The heating and cooling rate was around 55 °C/h.

Table 3.1 Precursors and transport agents for the CVT growth of Fe_xZrSe_2

	Fe powder	Zr pellet	Selenium powder	Transport agent (I_2)
$\text{Fe}_{0.25}\text{ZrSe}_2$	37.5 mg (0.670 mmol)	116.0 mg (1.273 mmol)	210 mg (2.658 mmol)	50.2 mg (0.197 mmol)
$\text{Fe}_{0.33}\text{ZrSe}_2$	44.6 mg (0.797 mmol)	120.4 mg (1.321 mmol)	207.8 mg (2.630 mmol)	50.8 mg (0.200 mmol)

3.4.2 Magnetometry measurements

DC magnetization measurements as a function of temperature and applied field were carried out in a Quantum Design Physical Property Measurement System (PPMS) Dynacool equipped with a 12 T superconducting magnet using the Vibrating Sample Magnetometer (VSM) option, with a detection limit of 10^{-6} emu. For out-of-plane measurements, one Fe_xZrSe_2 crystal of approximately 0.5 mg was loaded into a straw sample holder.

3.6 References

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CHAPTER 3. TUNABLE INTRINSIC EXCHANGE BIAS IN AN Fe_xZrSe_2 ($x = 0.25, 0.33$)
SPIN GLASS

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Chapter 4

Li intercalation in Fe_xZrSe_2 : In situ observation of its dynamics and tuning optical and electrical properties

4.1 Introduction

New technologies based on nanoscale systems hold tremendous potential for drastically lowering the energy costs of data storage schemes because in such systems multiple correlated physical processes define the exhibited magnetic state.¹ These competing correlated processes open a window to exploiting alternative mechanisms for switching magnetization that are many orders of magnitude more energy efficient.¹ The control of spin by an electric field as opposed to the typical magnetic field^{2,3} is one such possibility, which would represent a critical step towards taking full advantage of spin-based electronics, since an electrostatic handle for spin polarization would permit more rapid storage/retrieval of data with minimal power consumption.^{3,4}

Semiconductors, which exhibit tunable electrical transport, and magnets, characterized by tunable spin configurations, underpin numerous information technologies.⁵ A longstanding challenge has been to develop materials that combine and interconnect these distinct properties. Two-dimensional (2D) semiconducting materials provide an avenue to achieve this goal. 2D van der Waals (vdW) materials are particularly promising for electrostatic field control owing to their atomic-scale thickness, rendering them highly responsive to surface perturbations.^{6,7} Additionally, their vdW surfaces facilitate their seamless integration into conventional circuits.⁸ Magnetic semiconductors are an attractive platform for the electrical control of both charge and spin degrees of freedom.⁵ The recent discovery of magnetic order in atomically thin magnetic semiconductors, including CrI_3 ⁹⁻¹², CrBr_3 ¹² and $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (CGT)¹³, has led to the study of magnetoelectric phenomena such as ferromagnetic–antiferromagnetic switching^{11,14}, tunable magnetization loops¹⁵, enhanced tunnelling magnetoresistance¹⁶ and magnon-assisted tunnelling¹⁴. These capabilities could be used to develop novel spintronic devices. Yet existing approaches to obtain 2D vdW materials are focusing on the isolation of constituent sheets of magnetic van der Waals (vdW) materials that are already known to be magnetic in bulk form.

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However, a converse approach involves the bottom-up design of 2D magnetic layers through the intercalation of chemical species bearing unpaired spins into the vdW interface, e.g. Fe or Ni intercalated ZrS_2 and ZrSe_2 ¹⁷. This route offers the benefit of providing control over intrinsic magnetic properties with a chemical knob—the extent of intercalation—in addition to external (e.g. electrostatic and mechanical) stimuli. In principle, each discrete intercalation compound would represent a new magnetic material. The project highly enlarges the 2D magnet library.

Similar to DMSs where magnetism is established upon magnetic impurity doping of intrinsically non-magnetic semiconductor host, the magnetism in transition metal intercalated semiconducting TMDs is established by the intercalation of paramagnetic ions into non-magnetic host, ZrS_2 and ZrSe_2 . Magnetic ground state can be modulated by both intercalate density and electrostatic doping. For $\text{Fe}_{0.17}\text{ZrSe}_2$, localized moments interact indirectly by polarizing the itinerant holes, establishing a long-range magnetic order. According to the widely accepted sp-d Zener kinetic exchange model, critical temperature T_C depends strongly on the host compound and the free hole concentration, p_h .¹⁸⁻²¹ For the latter, an empirical relation $T_C \sim p_h^{1/3}$ has been found.^{22,23} According to Ruderman–Kittel–Kasuya–Yosida (RKKY) theory, the interaction between two localized moments depends on their separation, oscillating between FM and AFM on the length scale of the hole’s Fermi wavelength.²⁴⁻²⁶ Charge modulation is, thus, an effective tool to controlling the exchange interactions.

$\text{Fe}_{0.17}\text{ZrSe}_2$ features a large interlayer spacing (~ 0.61 nm)¹⁷ and octahedral coordination environment²⁷ between its layers, facilitating the intercalation of alkali metal ions such as Li^+ . Recent research has highlighted the electrochemical intercalation and deintercalation of Li^+ as effective methods to manipulate and optimize the optical and electrical properties of two-dimensional layered semiconductors, with demonstrated reversibility of the intercalation process.²⁸⁻³¹ Electrochemical intercalation enables much higher doping levels in layered materials compared to electrical gating, unlocking novel physics such as superconductivity.³²

In this study, we demonstrate successful Li^+ intercalation into $\text{Fe}_{0.17}\text{ZrSe}_2$ thin films without inducing wrinkling or structural distortion. The presence of Fe ions between the ZrSe_2 layers likely plays a crucial role in maintaining lattice integrity and mitigating structural deformation. Through subtle electrochemical control, we show that the structural, optical, and electrical properties of $\text{Fe}_{0.17}\text{ZrSe}_2$ can be drastically modified in a reversible manner. The reversible ion intercalation and de-intercalation observed in $\text{Fe}_{0.17}\text{ZrSe}_2$ establish a solid

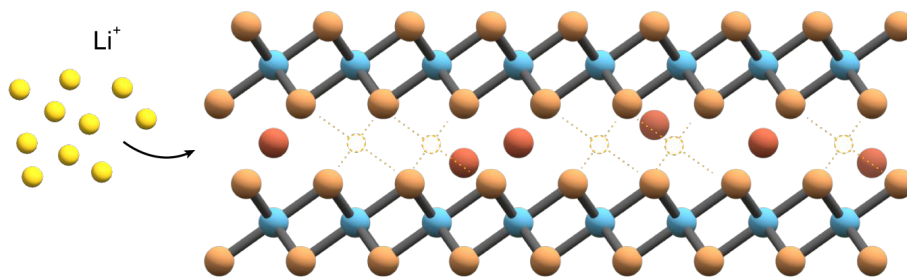


Figure 4.1. Fe_xZrSe_2 crystals have vacant octahedral sites within vdWs gap, which allows for the intercalation of Li ions.

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foundation for future investigations into electrostatic control over spin polarization, which enables rapid data storage and retrieval with minimal power consumption.

4.2 Results and discussion

Optical measurements during Li electrointercalation

Figure 4.2 illustrates the schematic of the mesoscopic electrochemical cell, which allows us to characterize the optical properties of $\text{Fe}_{0.17}\text{ZrSe}_2$ flake while we perform Li intercalation. Mechanically exfoliated $\text{Fe}_{0.17}\text{ZrSe}_2$ flake was transferred onto SiO_2/Si substrates with prepatterned bottom contacts, and then covered by Li electrolyte (LiTFSI/PEO). To perform electrochemical intercalation, a bias voltage was applied between the $\text{Fe}_{0.17}\text{ZrSe}_2$ working electrode and Au counter electrode (see Section 4.4.6 for additional experimental details and **Figure 4.10** for set-up).

Figure 4.3a top shows the protocol used for Li intercalation that we swept the potential between the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake working electrode and Au counter electrode at a rate of approximately 1 mV/s increasing the from 0 to the target voltage 1V at a temperature of 65 °C and then holding the V_{CE} for 5 min. With no changes in optical contrast, the V_{CE} was then increased to the next target voltage (1.5, 2, 2.5, 3 V) and repeated the same steps until the change of optical contrast was observed.

After holding V_{CE} at 3.5 V for 8 min, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake became darker, which indicates the Li intercalation (**Figure 4.3a, 3.5V_8min in purple box**). Continuing holding V_{CE} at 3.5 V for 20 min, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake became even darker compared to 3.5V_8min. However, holding V_{CE} at 3.5 V for extended time (**Figure 4.3b, 3.5V_30min, 3.5V_40min**) did not yield any additional darkening of the material. This observation suggests a potential saturation or equilibrium in the darkening process under $V_{\text{CE}} = 3.5$ V. The deintercalation of this $\text{Fe}_{0.17}\text{ZrSe}_2$ flake can be achieved by gradually ramping down the applied voltage bias V_{CE} from 3.5 V to 3.0 V with scanning rate 1 mV/s and holding at $V_{\text{CE}} = 3.0$ V, the color of the flake became lighter quickly (**Figure 4.3b 3.0V_3min in green box**). During a 10-minute interval of maintaining V_{CE}

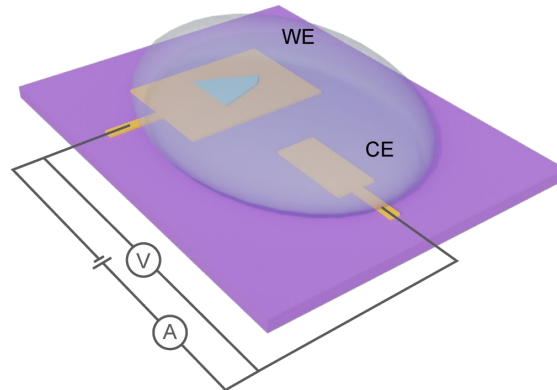


Figure 4.2. Schematic of the mesoscopic electrochemical cell for the optical experiment.

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at 3.0 V, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake exhibited a gradual lightening over time. Subsequently, there were no significant further alterations observed in the coloration of the flake. Notably, during the

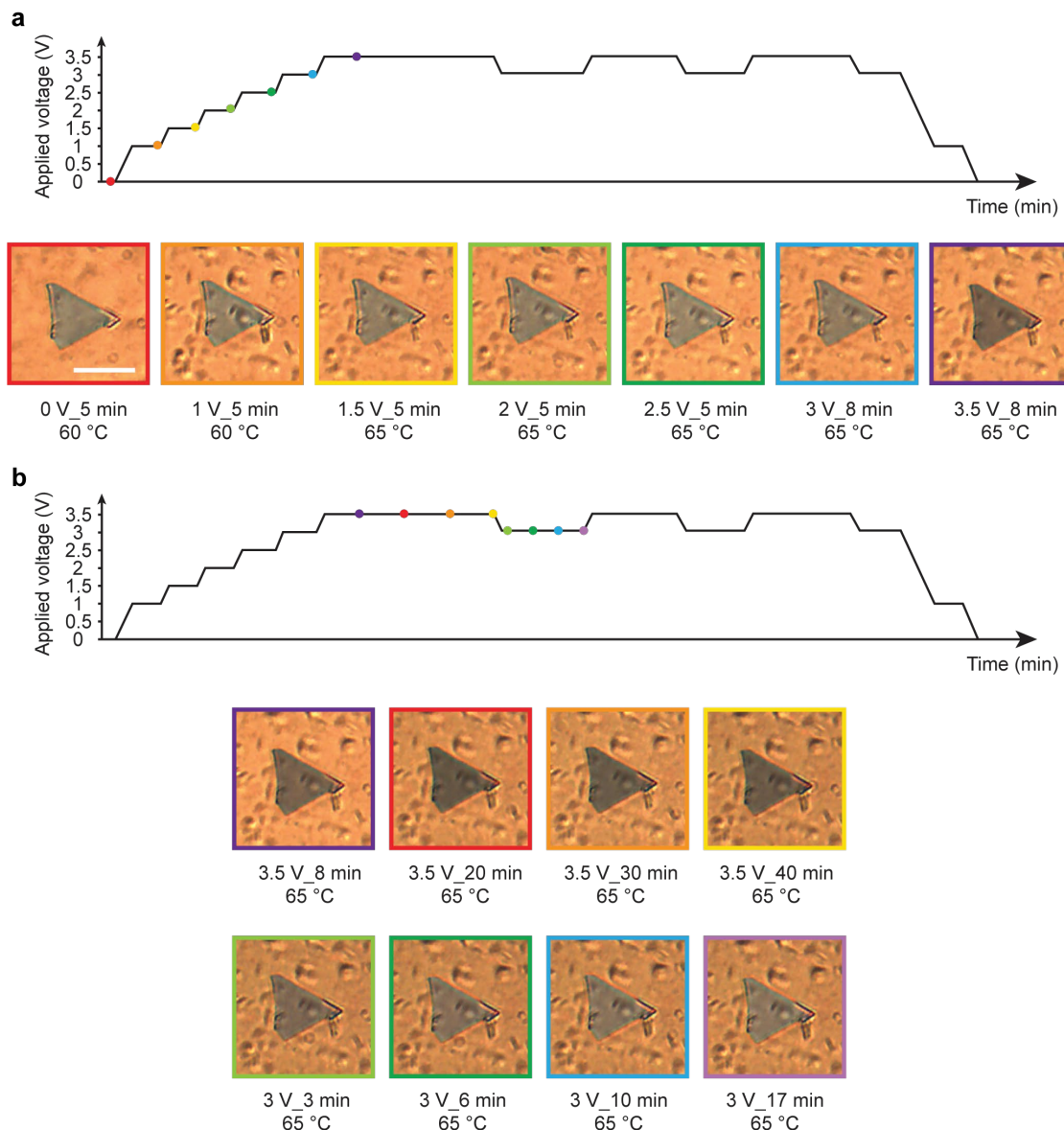


Figure 4.3. Optical micrographs of a $\text{Fe}_{0.17}\text{ZrSe}_2$ flake on an on-chip electrochemical cell for optical measurements during the Li intercalation and deintercalation process. (a) Optical images of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake when ramping up the V_{CE} from 0 to 3.5 V. When the potential V_{CE} is lower than 3 V, no visible changes were observed even after extended periods of time, 5 min. While V_{CE} was increased to 3.5 V, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake became darker. (b) Optical images of the same $\text{Fe}_{0.17}\text{ZrSe}_2$ flake during the Li intercalation when holding V_{CE} at 3.5 V and during the deintercalation process when holding V_{CE} at 3.0 V. At 3.0 V, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake became lighter and almost went back to its original color. The scale bar: 100 μm .

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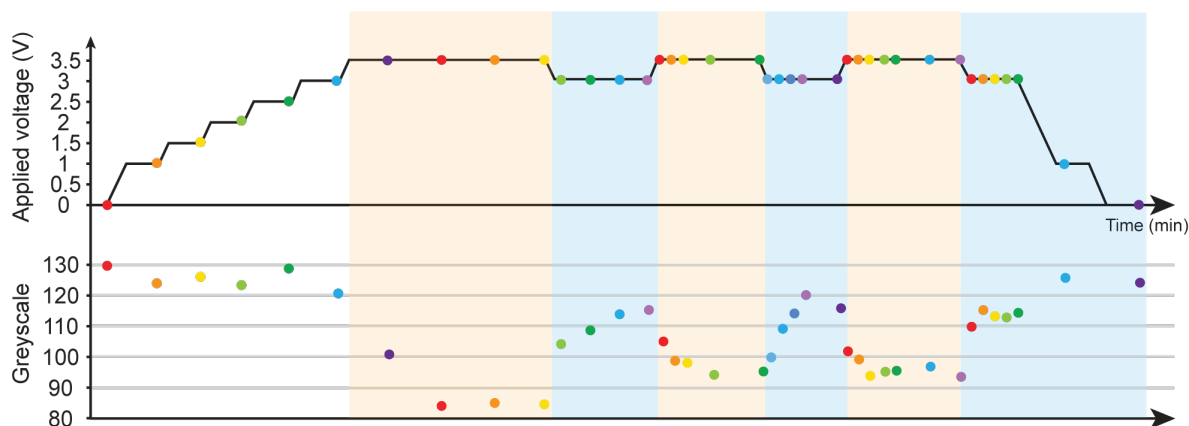


Figure 4.4. The gray scale change of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake during the intercalation cycles. Li intercalation process is shaded in orange and deintercalation process is shaded in the blue.

cycle, the flake changed color uniformly, with no marked distinction between the edge and the center. To test the reversibility of the Li intercalation process, we repeated the V_{CE} sweep cycle in the described above for 2 more cycles (see Section 4.4.6, **Figure 4.11**). To provide a more straightforward demonstration of the reversibility of intercalation, we measured gray scale of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake across three intercalation cycles. (**Figure 4.4**). The grey scale optical contrast was determined by averaging the grey scale values across the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake. Initially, the grey scale registered at a high value of 130 and remained within the range of 120 to 130 when the V_{CE} was below 3.0 V. Upon increasing the V_{CE} to 3.5 V, the grey scale markedly decreased, stabilizing around 85. Subsequent cycles exhibited consistent patterns, with low grey scale values indicating intercalation of $\text{Fe}_{0.17}\text{ZrSe}_2$ and high values signifying deintercalation. The grayscale intensities of intercalated and deintercalated states exhibit remarkable similarity across different cycles, respectively, which underscores the high reversibility of the discharge/charge cycle.

In-situ Raman measurements during Li electrointercalation

To investigate the structural changes in the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake during the Li intercalation and deintercalation cycles, we performed in-situ Raman spectroscopy of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake during Li intercalation.

Figure 4.5a illustrates the schematic representation of the mesoscopic electrochemical cell used for in-situ Raman spectroscopy and optical property measurements. In **Figure 4.5b**, optical images of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes under different applied voltages are presented. Lighter coloration of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes was observed when V_{CE} was below 3.3 V, while the flakes exhibited darkening at $V_{\text{CE}} = 3.3$ V, consistent with the optical trends observed in the previous section. **Figure 4.5c** depicts the corresponding Raman spectra of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake corresponding to the optical images in **Figure 4.5b**. All Raman spectra acquired at different V_{CE} values exhibit characteristic phonon modes of $\text{Fe}_{0.17}\text{ZrSe}_2$, including out-of-plane A_{1g} vibrations

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($\sim 194 \text{ cm}^{-1}$) and in-plane E_g vibrations ($\sim 147 \text{ cm}^{-1}$), consistent with previously reported values,¹⁷ which implied that the host lattice ZrSe_2 stays at 1T phase throughout the cycles. At $V_{\text{CE}} = 3.3 \text{ V}$, the Raman spectrum at $V_{\text{CE}} = 3.3 \text{ V}$ exhibits a decrease in the intensity of A_{1g} mode, suggesting the dissociation of interlayer bonding due to influx of Li^+ ions. Additionally, a broadening of line width of A_{1g} mode indicates increased impurity scattering and structural defects.²⁹ Similar observations of the reduction and broadening of the A_{1g} phonon have been reported in other transition metal dichalcogenide (TMD) materials, such as MoS_2 .^{33,34}

Figure 4.5d illustrates zoom-in spectra of the A_{1g} region from **Figure 4.5c**, where the dots represent collected data points, the lines denote the fitted curves to the data, and vertical lines highlight the A_{1g} peaks. A_{1g} modes exhibit a red shift with an increase in applied bias from 0 to 3.3 V, indicating a weakening of interlayer interactions due to intercalated Li^+ .²⁹ This weakening may result from two factors, the expansion of interlayer distance caused by intercalated Li^+ , as well as the charge transfer from Li to conduction band of $\text{Fe}_{0.17}\text{ZrSe}_2$, which leads to the occupation of antibonding orbitals in the frontier molecular band of $\text{Fe}_{0.17}\text{ZrSe}_2$, similar phenomenon reported previously in molecules.³⁵

However, after maintaining the applied bias at 3.3 V for an hour, A_{1g} modes exhibited a blue-shift and a clear damping in intensity, consistent with findings in previously reported literature.^{36,37} The underlying mechanism behind this phenomenon remains unresolved. However, it has been demonstrated in some TMDs and graphene that two main factors may contribute: lattice expansion leading to a red shift and changes in phonon self-energy induced by doping.^{29,38}

Upon deintercalation of $\text{Fe}_{0.17}\text{ZrSe}_2$ by reducing V_{CE} to 0 V, the optical contrast (**Figure 4.5b**, purple box), along with the position and intensity of the A_{1g} and E_g peaks in the Raman spectrum (**Figure 4.5c,d**, purple box) of the flake, reverted to their non-intercalated states. This observation underscores the high reversibility of both the structural and optical properties of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake throughout the intercalation cycles.

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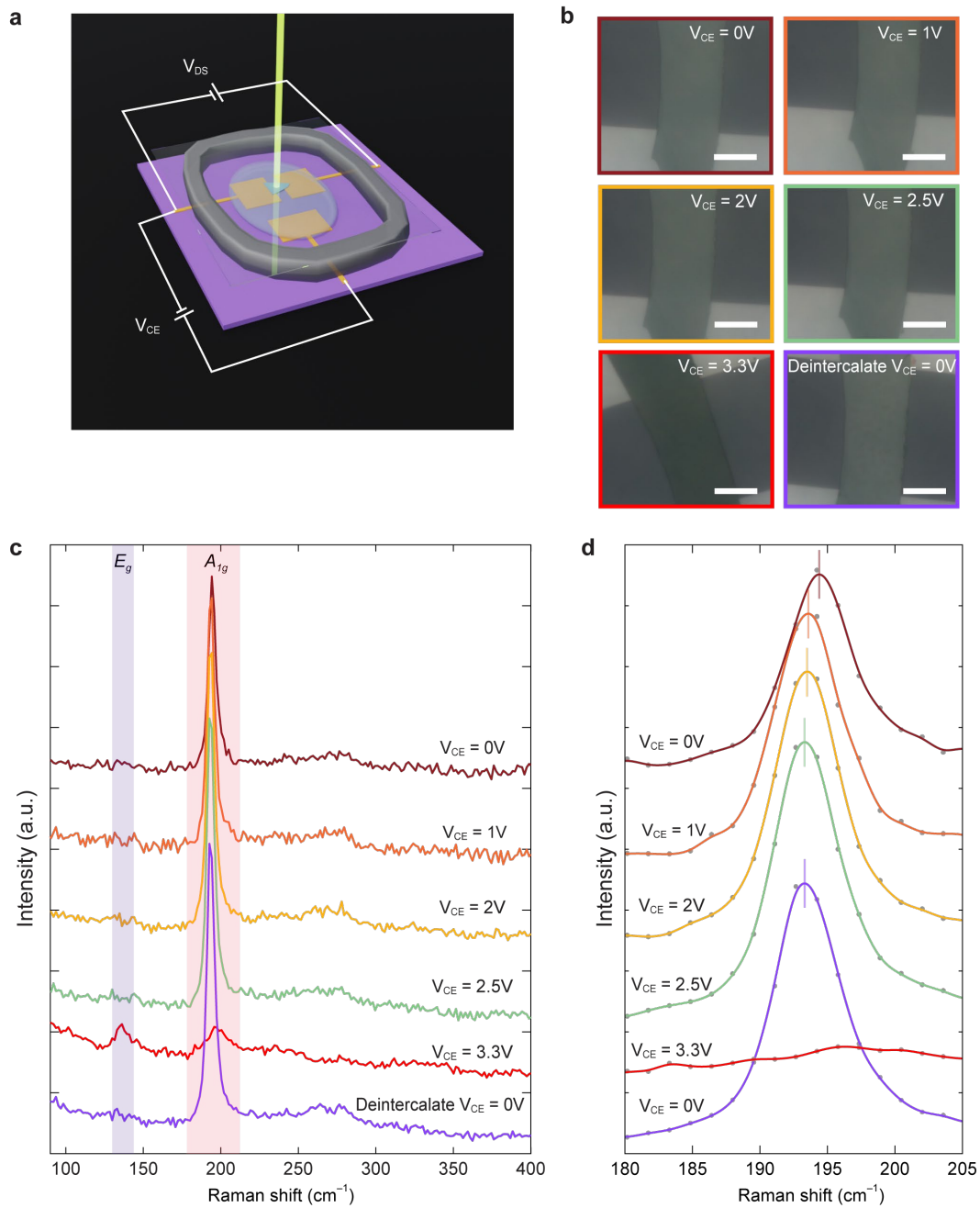


Figure 4.5. Cycling effects on the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake and Raman spectroscopy. (a) Schematic of the mesoscopic electrochemical cell for the Raman experiment. (b) Optical images of the $\text{Fe}_{0.17}\text{ZrSe}_2$ during the Li intercalation cycles. (c) The Raman spectroscopy using 633 nm excitation of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake at different V_{CE} corresponding to the optical image in (b). The locations of characteristic phonon modes of the host lattice $\text{Fe}_{0.17}\text{ZrSe}_2$ E_g (shaded in purple) and A_{1g} (shaded in red) are labeled in graph. (d) The zoom-in Raman spectra of A_{1g} mode from (c). The scale bar: 2 μm .

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Significantly, the consistent color uniformity and Raman spectra across various locations on the flake throughout the entire intercalation process suggest a homogeneous distribution of Li intercalation across the entire $\text{Fe}_{0.17}\text{ZrSe}_2$ flake (see Section 4.4.8 for details)

Reversible control of optical and electrical properties

The in-situ optical microscopy and Raman spectroscopy results presented in this study illustrate the remarkable reversibility and stability of Li intercalation within the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake. Next, we brought the device into glovebox and performed Li intercalation and at the same time characterize optical and electrical properties of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake in situ to show the highly tunable electrical properties via ion intercalation.

The optical contrast change of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake was evident, as the flake got intercalated (deintercalated), it became darker (lighter) (**Figure 4.6a**). In the depicted two-contact device (**Figure 4.6a**), the drain-to-source voltage (V_{SD}) was maintained at 50 mV, and the drain-to-source current (I_{SD}) was recorded while scanning the V_{CE} at 65 °C. **Figure 4.6b** illustrates the dependence of source-drain current (I_{SD}) on V_{CE} during the second intercalation/deintercalation cycle. During intercalation, V_{CE} was swept from 0 V to 2.5 V at a rate of 1 mV/s, followed by an increase from 2.5 to 3.3 V with a voltage increment of 0.1 V and a sweep rate of 0.5 mV/s; the voltage was then held until I_{SD} stabilized. For deintercalation, V_{CE} was decreased from 3.3 V to 0 V at a rate of 0.5 mV/s. Once the desired potential was attained, the system temperature was swiftly reduced to 30 °C at a rate of 20 °C/min, causing the polymer electrolyte to solidify and halting any ongoing electrochemical processes. Subsequently, current-voltage (I - V) curves were acquired (see Section 4.4.9 for details).

The I_{SD} exhibited a notable increase as V_{CE} was continuously swept from 2.8 V to 3.3 V, indicating enhanced conductivity due to Li intercalation. Conversely, during the decrease of V_{CE} from 3.3 V to 0 V, the current gradually decreased, reflecting Li extraction. Analysis of the resistance extracted from the I - V curve (**Figure 4.6c**) revealed a 27-fold decrease after Li intercalation, followed by a return to the original resistance level post-deintercalation, suggesting the restoration of the semiconducting phase in the deintercalated $\text{Fe}_{0.17}\text{ZrSe}_2$ flake. Similar conductivity enhancements post-Li intercalation, without host lattice phase transformation, have been observed in other TMDs such as ZrS_2 , ZrSe_2 ,³⁶ likely attributable to the doping effect arising from charge transfer between Li ions and the host lattice. The process of charge transfer necessitates a disparity in the chemical potential between the host 2D material and the intercalant, alongside the presence of empty bands capable of accepting electrons or holes.³⁹ With an exceedingly low electrode potential (−3.04 V vs. standard hydrogen electrode),⁴⁰ lithium ions emerge as highly efficient electron donors. During intercalation, TMDs only function as electron acceptors, potentially attributed to the bonding between the transition metal and chalcogens, leading to the formation of a negatively charged chalcogen layer.^{39,41}

No wrinkling or structural distortion was observed during the intercalation and deintercalation cycles, indicating the robustness of the $\text{Fe}_{0.17}\text{ZrSe}_2$ structure. This robustness lays a solid foundation for the high reversibility of the optical and electrical properties of $\text{Fe}_{0.17}\text{ZrSe}_2$ during the cycles. Similar ultralong cyclic stabilities for Li intercalation and Na intercalation have been reported in Fe doped $\text{NbS}_x\text{Se}_{2-x}$,⁴² which lead to the conjecture that the reversible

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intercalation in the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake might be attributed to the presence of Fe ions between the host lattice layers. The Fe forming covalent bonds with surrounding Se atoms made the lattice mechanically inextensible and naturally control intercalation homogeneity. This contrasts with intercalation into layered materials lacking Fe ions between host lattice layers, where ions may flood into open van der Waals gaps, potentially leading to less controlled intercalation.

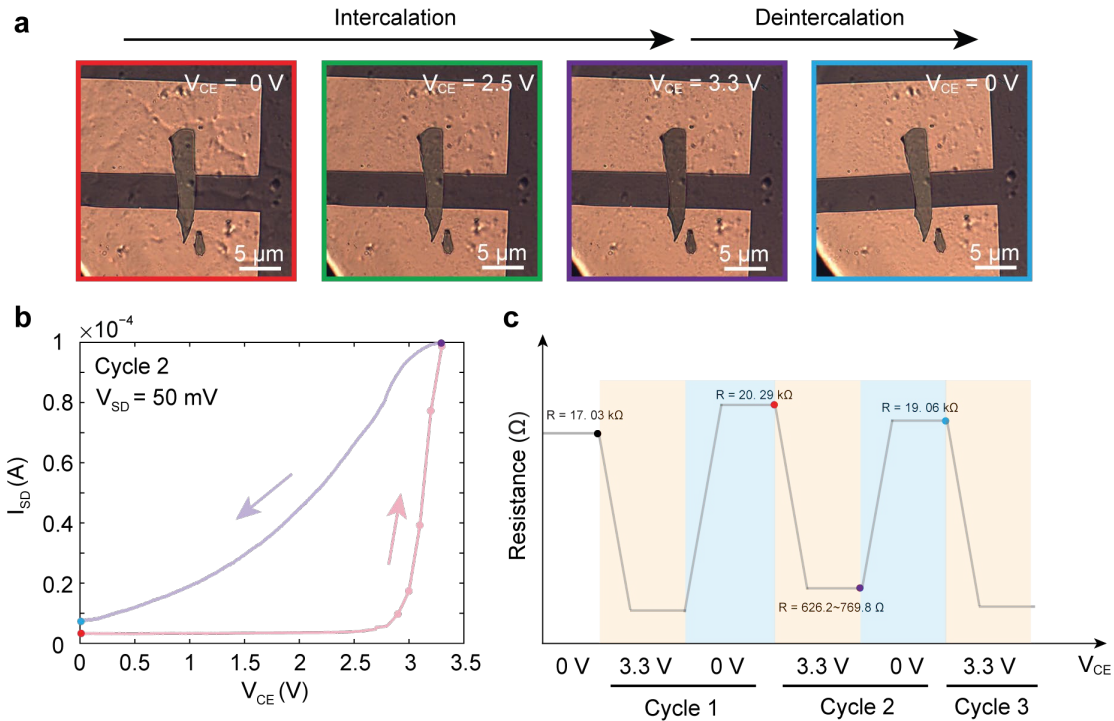


Figure 4.6. Reversible control of optical and electrical properties of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake via Li^+ intercalation. (a) In situ optical microscopy images show uniform color change of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake upon Li^+ intercalation and de-intercalation. Scale bar, 5 μm . (b) The potential dependence V_{CE} of source-drain current I_{SD} in intercalation/deintercalation cycle 2. The bias between source and drain was $V_{\text{SD}} = 50$ mV. The V_{CE} applied on $\text{Fe}_{0.17}\text{ZrSe}_2$ was swept from 0 V to 3.3 V and back to 0 V for three cycles. The red and purple arrows indicate the sweeping directions. (c) The potential dependence V_{CE} of the $\text{Fe}_{0.17}\text{ZrSe}_2$ resistance calculated from the I–V curve. The intercalation and deintercalation part in a cycle are shaded with yellow and blue box, respectively. The color dots in (b) and (c) are corresponding to the color box in (a).

Li ion diffusion measurements via optical microscopy through edge intercalation

To estimate the diffusion coefficient of Li^+ ions within $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes and investigate the intercalation mechanism, we developed an electrolyte transfer method that facilitated edge intercalation experiments. This method enables precise deposition of electrolyte at predetermined

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positions on the flake. By leaving the top surface uncovered, we can readily observe the color change of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake during the intercalation process.

The assembly of the electrolyte stamp is inspired by PDMS stamps used for stacking flakes. In this method, the electrolyte is carefully dispensed or painted onto a PDMS-coated glass slide using a fine needle (**Figure 4.7a**), and the electrolyte solidifies as the solvent evaporates (**Figure 4.7b**). The stamp is loaded onto a home-built transfer stage, and then positioned so that the electrolyte can contact both the flake's edge, the working electrode, and the counter electrode (**Figure 4.7c**). The stamp is gently lowered until the electrolyte lightly touches the substrate. Subsequently, increasing the temperature of the stage from room temperature to 55 °C causes the electrolyte to melt and detach from the stamp, thereby depositing onto the substrate.

We fabricated a two-electrode on-chip electrochemical cell, ensuring precise positioning of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes at the edge of the working electrode, with the electrolyte in direct contact with the flakes' edges (**Figure 4.7d,e**). No optical contrast change occurred when the applied potential between the $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes and the counter electrode remained below 4.5 V for an extended duration.

As the applied voltage bias was increased beyond 4.5 V, observable changes in optical contrast across the flakes could be observed, which showed that Li^+ ions intercalated into and diffused through the $\text{Fe}_{0.17}\text{ZrSe}_2$ lattice from the edge to the basal area. **Figure 4.7f** shows a series of optical microscope images taken over a period of 60 min as under a bias of 4.5 V at 65 °C. These images clearly display the movement of the diffusion front with time, which was indicated in the **Figure 4.7f** with white arrows. As the applied voltage bias was increased beyond 4.5 V, noticeable changes in optical contrast across the flakes indicated the intercalation and diffusion of Li^+ ions within the $\text{Fe}_{0.17}\text{ZrSe}_2$ lattice, starting from the edge and progressing towards the basal area. **Figure 4.7f** presents a series of optical microscope images captured over a 60-minute period under a bias of 4.5 V at 65 °C. These images clearly illustrate the temporal movement of the diffusion front, indicated by white arrows in **Figure 4.7f**. The intercalated area was extracted from each image at different time points (see Section 4.4.11 for details), allowing for the estimation of the diffusion coefficient, D , of Li^+ ions in $\text{Fe}_{0.17}\text{ZrSe}_2$ through line regression analysis of the temporal evolution of the intercalated area (**Figure 4.7g**), using a simplified continuum model reported previously.^{43,44}

$$D = \frac{\Delta A}{4\Delta t}$$

where ΔA is the change in area and Δt is the diffusion time.

We observed that the threshold voltage required for edge intercalation of Li into the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake is higher than the intercalation voltage reported in previous sections, where the onset voltage bias for Li intercalation was around 3.3 ~ 3.5 V. Furthermore, the intercalation timescale (~60 min for complete intercalation) is longer compared to the timeframe reported in the previous section, which was around 20 min. The higher onset voltage and longer intercalation time for edge intercalation suggest that the Li intercalation observed previously likely involves both top and edge intercalation processes.

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Considering the intercalation phenomena observed in previous sections, characterized by a uniform color change across the entire flake, top intercalation may be predominant. The extended intercalation time could be attributed to a limited interacting area available at each edge or slower diffusion of Li ions from the edge compared to diffusion from the top surface of the flake. Further experiments focusing on intercalation kinetics are essential for a comprehensive understanding of the intercalation process.

We observed reversible intercalation in both $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes, evidenced by color change after setting V_{CE} back to 0 V, suggesting that the edge intercalation process is reversible. (see Section 4.4.10 for details).

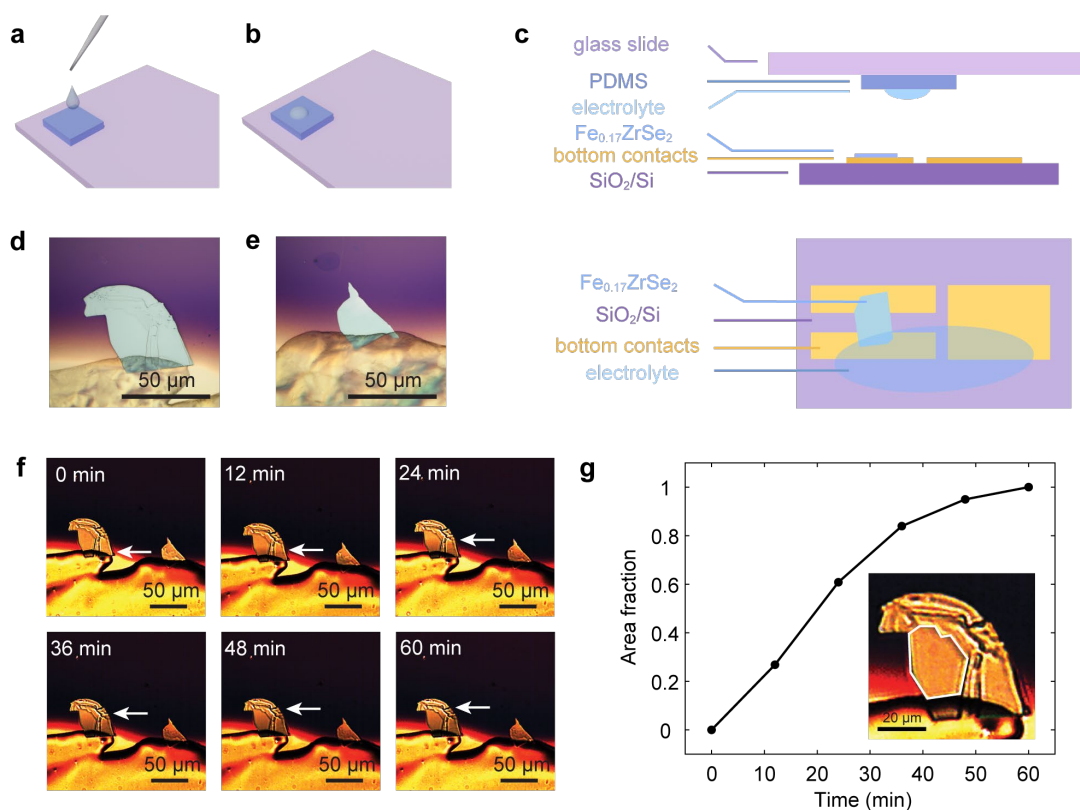


Figure 4.7. Li ion diffusion measurements in $\text{Fe}_{0.17}\text{ZrSe}_2$ through edge intercalation. (a,b) The formation of the electrolyte stamp on PDMS/glass. Li electrolyte was dropped onto PDMS/glass using fine tip and the electrolyte became solid after the solvent evaporated. (c) The top figure shows the sideview of the process transferring electrolyte from the stamp onto the device. The bottom figure shows the top view of the device with transferred electrolyte. The electrolyte needs to cover the edge of the flake and the working electrode, and the counter electrode. (d,e) The optical micrographs of the two $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes with edge touching the electrolyte. (f) The optical micrographs of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake in (d,e) taken over a time period of 60 min after application of a potential of 4.5 V, showing the movement of the diffusion front during intercalation, which is labelled out using white arrow. (g) Temporal evolution of the intercalated area fraction at 4.5 V and 65 $^{\circ}\text{C}$.

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The electrolyte transfer method we developed enables precise placement of electrolyte at desired locations, facilitating the study of edge intercalation processes and diffusion coefficients of intercalated ions. This method holds promise for broader applications requiring exposure of the top surface of the thin films, such as transmission electron microscopy (TEM).

4.3 Conclusions

In summary, we demonstrate the electrochemical intercalation of Li ions into $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes with high reversibility and stability, characterized through in situ structural, optical, and electrical property analysis. The unique structure of $\text{Fe}_{0.17}\text{ZrSe}_2$, with Fe ions situated between the layers of the host lattice ZrSe_2 , likely contributes to the robustness of the flakes during the intercalation process. This Li intercalation resulted in a significant 27-fold increase in electrical conductivity of $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes, establishing a solid foundation for electrostatic control over spin polarization. The capability to reversibly engineer the physical properties of $\text{Fe}_{0.17}\text{ZrSe}_2$ opens exciting opportunities in optoelectronics and rapid data storage and retrieval with minimal power consumption.

4.4 Experimental

4.4.1. Materials and instruments

Unless otherwise stated, all materials and reagents were used as received.

Methyl methacrylate (MMA) (Model: MMA(8.5)MAA EL6, Lot number: 18070609, and Poly(methyl methacrylate) (PMMA) (Model: 495 PMMA A6) were purchased from MICRO CHEM (Westborough, MA, USA). Anhydrous acetonitrile, polyethylene oxide (PEO) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSi) for Li electrolyte were purchased from Alfa Aesar (Ward Hill, MA, USA). Poly(Bisphenol A carbonate) (PC) (average $M_w \sim 45000$) for making transfer stamps was purchased from Sigma Aldrich (St. Louis, MO, USA)

Blue tape (lot # 1090980) was purchased from Ultron System Inc. (Moorpark, CA, USA). PDMS GEL film (PF-40/17-X4) was purchased from Gel-Pak (Hayward, CA, USA).

Si wafer with 285 nm oxide layer was purchased from Nova (Flower Mound, TX, USA).

For cleaning substrates, UV-ozone cleaner (model # PSDP-UV) was purchased from Novascan Technologies, Inc. (Boone, IA, USA) and plasma system was purchased from Plasma Etch Inc. (Carson City, NV, USA)

4.4.2. Device fabrication

For the device fabricated for optical contrast experiment, thin strips of aluminum foil were taped across SiO_2/Si chips to create exposed stripes. Thermal evaporation was used to deposit Cr/Au (5 nm/100 nm) in the exposed areas to create Au electrodes.

For the device fabricated for in-situ Raman and magnetoresistance experiments, the

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MMA:PMMA bilayer electron beam resist system was used to produce nanoscale structures with clean edges via lift-off. In a typical experiment, the substrate was placed upon the spin coater (Model WS-650MZ-23NPPB, Laurell Technologies corporation, Lansdale, PA, USA) and an aliquot (100 μL for each 0.5 in^2 of substrate area) of MMA was dispensed on top of it. The assembly was then spun at 300 rpm for 5 s and then at 4000 rpm for 60 s. After the spin coat, the MMA-coated substrates were annealed on a hot plate (Model C-MAG HS 7, IKA Works, Inc., Wilmington, NC, USA) at 130 $^\circ\text{C}$ for 3 min in air to remove the solvent. Same process for the second resist layer PMMA.

Then, electron-beam lithography (EBL) (Model: Cabl-9510CC, CRESTEC Corporation, Tokyo, Japan) was used to define the device pattern, followed by development in a cold 3:1 v/v mixture of IPA:DI water at room temperature for 90 s. To clean the substrates and enhance the interaction between evaporated metal and substrate SiO_2/Si , the chips were O_2 plasma cleaned (Model: PK-12 RIE, Plasma-Therm, LLC, North Saint Petersburg, FL) with 40 sccm O_2 (with pressure 60 mTorr) at power 35 W for 15 s. Right after the plasma cleaning, the chips were loaded into electron beam evaporation (Electron Beam 10 kW 4-pocket Evaporator) chamber in 2 min, which was pump down for 1 hr to 6×10^{-6} Torr. After reaching the target pressure, the chips were evaporated with metal layers based on different devices, followed by overnight liftoff in acetone.

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4.4.3. Mechanical exfoliation

$\text{Fe}_{0.17}\text{ZrSe}_2$ thin films were obtained following procedures reported in published papers.^{45,46}

SiO_2/Si was cut into $1\text{ cm} \times 1\text{ cm}$ and cleaned by UV ozone cleaner at $200\text{ }^\circ\text{C}$ for 30 min. Note that O_2 plasma cleaning of substrate is not recommended here since the oxygen radical decorated on the surface of the SiO_2/Si substrate leads to the degradation of $\text{Fe}_{0.17}\text{ZrSe}_2$ flakes. The exfoliation was carried out inside an Ar-filled glovebox. Bulk crystals were tessellated using blue tape and PDMS. First, prepare a piece of 20 cm long blue, reduced-residue tape and fold the two ends to make non-stick handholds. With fine-tip tweezers, pick out 5 single pieces of $\text{Fe}_{0.17}\text{ZrSe}_2$ crystal ($\sim 1\text{ mm} \times 1\text{ mm}$) and place on the tape. Slowly fold the tape in half and pull apart, repeat folding until TMDs micro-flakes are spread across the tape surface. Cut the PDMS gel (Lot #: GP013345, Gel-Pak, Hayward, CA) into $1\text{ cm} \times 3\text{ cm}$ rectangle and place it onto a glass slide. Then in order to transfer flakes from blue tape to PDMS, we mount the blue tape with flakes on the PDMS/glass slide with flakes facing PDMS and press the two layers together with fingers for 5 min to promote adhesion and generate a static charge. After that, we slowly pull tape layers apart in one direction, almost parallel to one another. (**Figure 4.8a**). To find the flakes for the device, we scanned the flake/PDMS/glass slide under Optical microscopy (OM) (Nikon Eclipse LV 150N upright microscope, Nikon Metrology, Inc., Irvine, CA, USA) equipped with a CCD camera. and cut the PDMS grid out with the flake with the desired thickness, which were identified by optical contrast (**Figure 4.8b**).

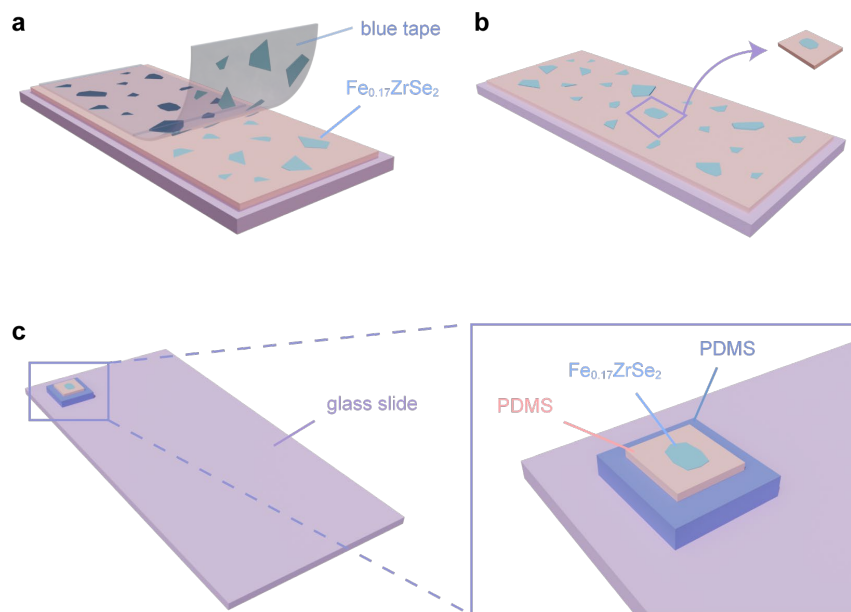


Figure 4.8. Schematic of mechanical exfoliation of $\text{Fe}_{0.17}\text{ZrSe}_2$ crystals and assembly of flake/PDMS/PDMS/glass slide stamp.

4.4.4. Transfer of exfoliated flakes onto devices using dry transfer strategy

To make the transfer stamp, we cut PDMS gel with thickness of 2 mm from gel box into $0.5 \text{ cm} \times 0.5 \text{ cm}$, placed it at the top left corner of the glass slide and transfer the flake/PDMS onto PDMS/glass slide using a tweezer. (**Figure 4.8b**). We completed the transfer of flakes onto the devices using a home-built micro-manipulation stage in an argon glovebox. **Figure 4.9** shows the benefit of making stamps using a thick PDMS. With the thick PDMS, the stamp can touch the chip without damaging contacts and wire bonds.

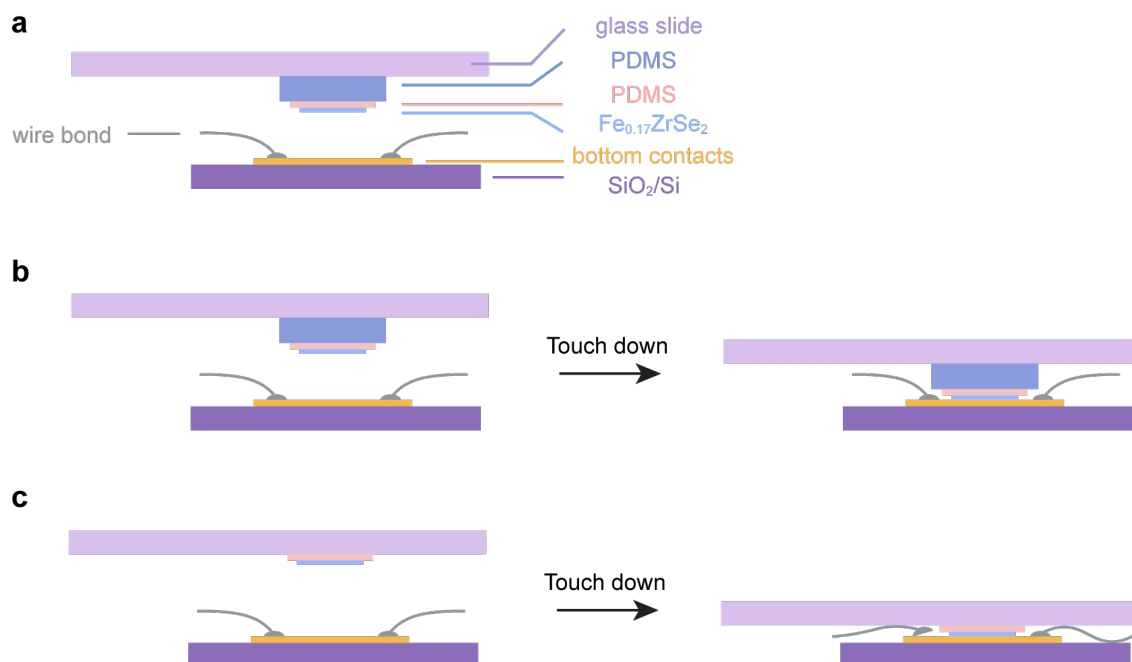


Figure 4.9. Schematic of using different stamps. (a) The side view of the flake/PDMS/PDMS/glass. (b) The transfer process of using flake/PDMS/PDMS/glass stamp prevents the damage of bonds and the bottom contacts. (c) The transfer process of using flake/ /PDMS/glass stamp usually cause damages.

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4.4.5. Electrolyte preparation for electrochemical intercalation of lithium

A mesoscopic polymer electrolyte is prepared following procedures reported in our published paper.⁴⁵

In an argon glovebox, 3.7 mL of anhydrous acetonitrile (dried with 3 Å molecular sieves) is added to 0.3 g of polyethylene oxide (PEO) and 50 mg of lithium bis(trifluoromethylsulfonyl)imide (LiTFSi) and stirred overnight. After stirring overnight, a 10–15 μl droplet of this electrolyte solution was dropcast onto the SiO_2/Si substrate possessing the electrically contacted the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake, such that the droplet encompassed both the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake, source and drain and the counter electrodes. Rapid evaporation of the acetonitrile solvent yielded a solid polymer electrolyte for electrochemical studies. Additional extraneous solvent was removed by vacuum-drying the electrolyte overnight.

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4.4.6. Set-up for optical contrast measurement

Figure 4.10a shows the setup for the optical contrast measurement. The chip with Au strips was affixed to a glass slide using Kapton double-sided tape, along with two Si strips coated with Cr (5 nm)/ Au (100 nm). Subsequently, the sample chip was wire-bonded to Au/Si strips using wire bonder (Model: HB05 Wire Bonder TPT Wire Bonder GmbH & Co. KG, Munich, Germany) with approximately 10 wires on each pad, facilitating a robust and reliable connection. Following this, the sample were transferred onto the chip and the Li electrolyte was drop cast using the BD PrecisionGlide Needle from BD 1 mL TB Syringe (Becton, Dickinson and Company, Franklin Lakes, NJ, USA) onto the chip to cover both flake and electrodes. Since the measurement was taken place in the Ar glovebox, not further sealing was needed. **Figure 4.10b** shows the OM image (Nikon Eclipse LV 150N upright microscope, Nikon Metrology, Inc., Irvine, CA, USA) of $\text{Fe}_{0.17}\text{ZrSe}_2$ flake transferred onto Au bottom contacts. **Figure 4.10c** is the image of the optical contrast experiment setup. The glass slide was placed under the transfer stage microscope lens and was secured on the stage because of the vacuum chuck. The Au strips were clamped with the alligator clips, which were attached to the voltage source Keithley (Model 2400 SourceMeter, Tektronix, Inc. Beaverton, OR, USA) to control the potential between the two electrodes. **Figure 4.10d-f** are the connections from the devices inside the glovebox to the Keithley outside the glovebox, which might be useful for labmates who want to do similar experiments in the future. The optical image of flakes during the intercalation were obtained using a microscope attached to the home-built transfer stage in the Ar glovebox.

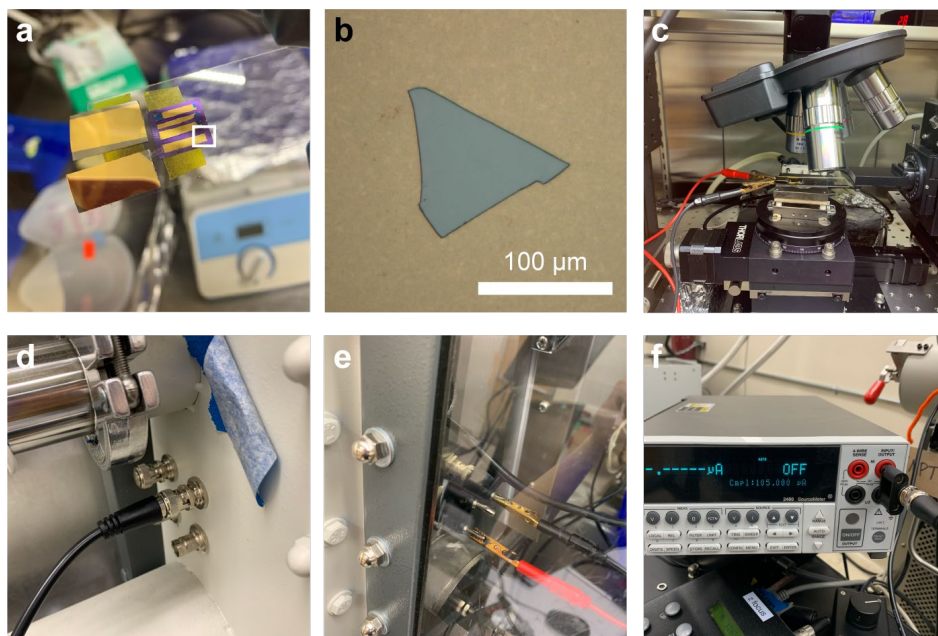


Figure 4.10. Setup of optical contrast device. (a) The device with Cr/Au strip contacts is wired bonding to the Au strips. Both Au strips and device are affixed to glass slide. (b) Zoomed-in OM image of white box area in (a), a $\text{Fe}_{0.17}\text{ZrSe}_2$ flake on the Au strip. (c) The image of the optical experiment setup. (d-f) Connection from inside the glovebox to outside.

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Figure 4.11a shows the optical contrast change of the first cycle of Li intercalation and deintercalation. We carried out Li intercalation by sweeping the potential between the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake working electrode and Au counter electrode at a rate of approximately 1 mV/s increasing the from 0 to the target voltage 1V at a temperature of 65 °C and then holding the V_{CE} for 5 min. With no changes in optical contrast, the V_{CE} was then increased to the next target voltage (1.5, 2, 2.5, 3 V) and repeated the same steps until the change of optical contrast was observed. After holding V_{CE} at 3.5 V for 8 min, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake became darker, which indicates the Li intercalation. After holding V_{CE} at 3.5 V for 20 min, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake became even darker compared to 3.5V_8min. However, holding V_{CE} at 3.5 V for extended time (3.5V_30min, 3.5V_40min) did not yield any additional darkening of the material. This observation suggests a potential saturation or equilibrium in the darkening process under $V_{\text{CE}} = 3.5$ V. When we gradually deintercalated this $\text{Fe}_{0.17}\text{ZrSe}_2$ flake by ramping down its potential V_{CE} from 3.5 V to 3.0 V with scanning rate 1 mV/s and holding at $V_{\text{CE}} = 3.0$ V, the color of the flake became lighter quickly (Figure 4.11a 3.0V_3min in green box). During a 10-minute interval of maintaining V_{CE} at 3.0 V, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake exhibited a gradual lightening over time. Subsequently, there were no significant further alterations observed in the coloration of the flake. **Figure 4.11b and c** shows the optical contrast change of the third cycle and V_{CE} back to 0 V after 3 cycles. The optical contrast change of the $\text{Fe}_{0.17}\text{ZrSe}_2$ in the third cycle is still consistent with that of the first cycle, indicating the robust reversibility of the intercalation and deintercalation process.

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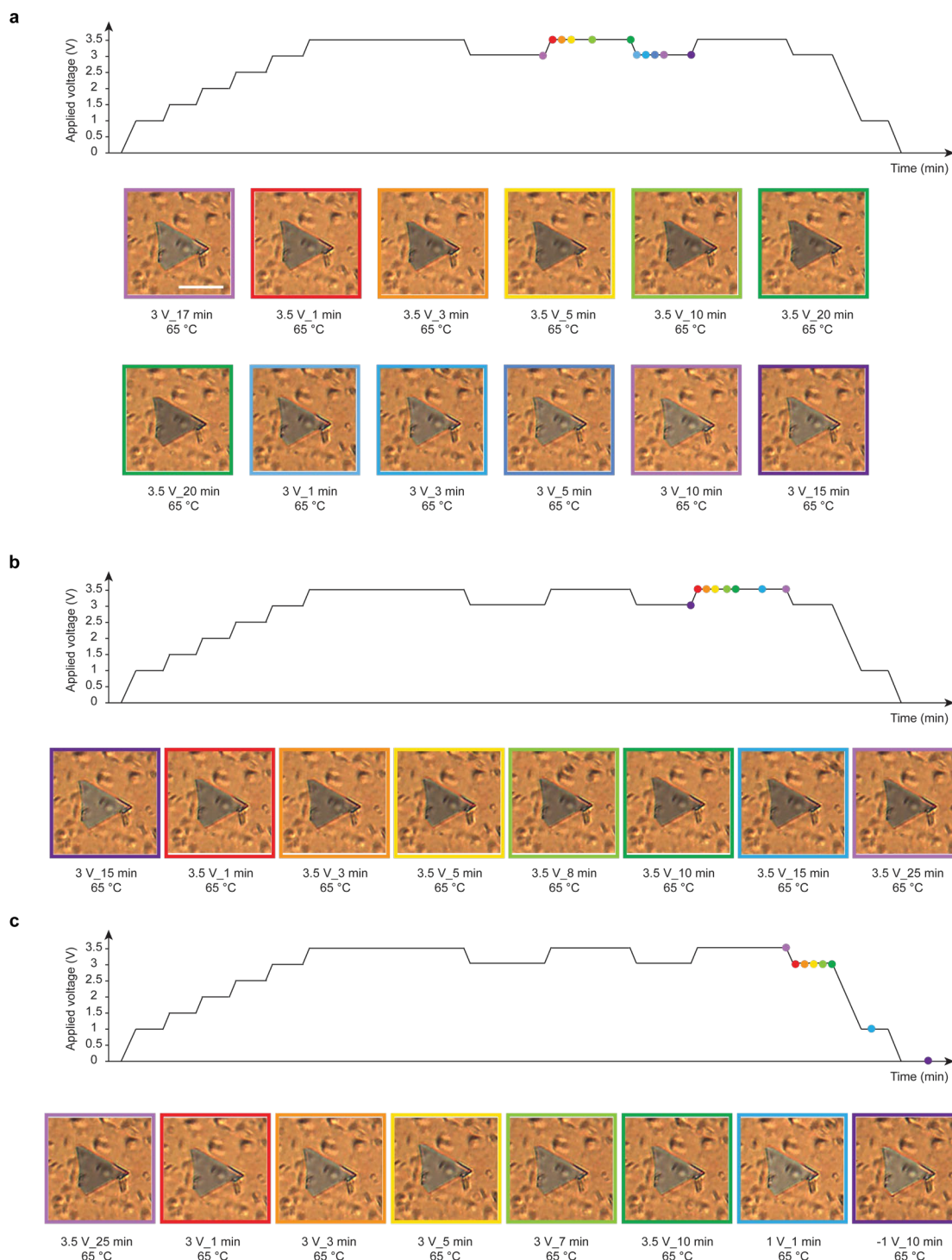


Figure 4.11. Optical contrast changes upon V_{CE} scan. (a-c) Optical image change of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake in the 2nd intercalation cycle (a), in the intercalation process of the 3rd cycle (b), and in the deintercalation process of the 3rd cycle. The scale bar: 100 μm .

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4.4.7. Set-up for in-situ Raman spectroscopy experiments

Raman spectra were acquired with a HORIBA LabRAM Evo Raman spectrometer using a 532 nm wavelength laser source. A 100 $\times$ (NA = 0.9) objective (M Plan Achromat lens, Olympus Corporation) was used with a laser spot size of $\sim 1\ \mu\text{m}$ and a laser power of $\sim 200\ \mu\text{W}$. Spectra were acquired with a grating of 600 grooves/mm, 1 s acquisition times, and 20 accumulations in ambient conditions (room temperature, 1 atm pressure). Higher laser powers ($> 200\ \mu\text{W}$) and longer acquisition times ($> 5\ \text{s}$) were found to lead to sample degradation. The applied laser power is higher than that for bare $\text{Fe}_{0.17}\text{ZrSe}_2$, since the coverslip and electrolyte will dissipate the laser power that actually hit the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake.

The set up for the in-situ Raman spectroscopy experiments is similar to that of optical contrast change experiments. Cr 5nm/Pt 70nm were deposited onto the chip. The contact pads at the termination of each extended contact consisted of Cr (5 nm)/ Au (100 nm). The chip in **Figure 4.12a** was affixed to a glass slide using Kapton double-sided tape, along with four Si strips coated with Cr (5 nm)/ Au (100 nm). Subsequently, the sample chip was wire-bonded to Au/Si strips with approximately 10 wires on each pad, facilitating a robust and reliable connection. Following this, the sample and Li electrolyte were successively transferred onto the

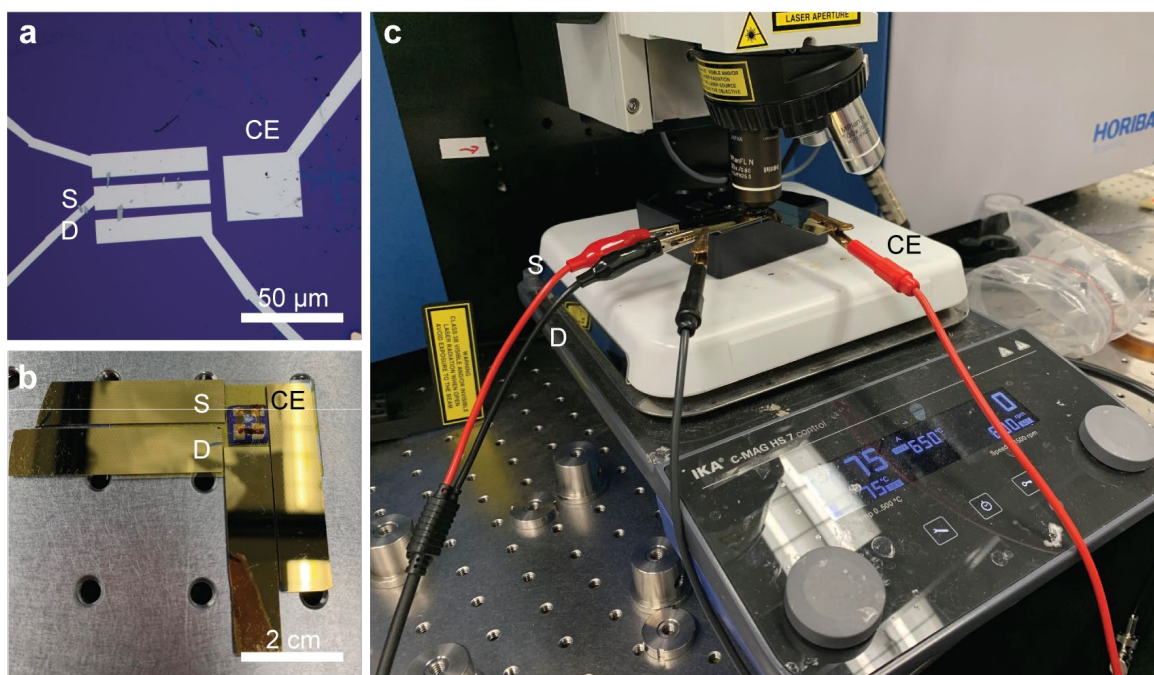


Figure 4.12. Set-up for in-situ Raman spectroscopy experiments. (a) The optical image of the device on the SiO_2/Si substrate. (b) The layout of the chip and the Au strips on the glass slide. The chips contact pads are wired to the Au strips. (c) The set-up for obtaining in-situ Raman spectra of $\text{Fe}_{0.17}\text{ZrSe}_2$ flake upon Li intercalation and deintercalation. The set-up in (b) was placed on the heat conductive hold and right underneath the Raman objective lens. The alligator clamps were connecting the Au strips and the Keithley, which control the voltage sweep V_{CE} and V_{SD} during the intercalation and deintercalation.

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chip. To ensure hermeticity, H vacuum grease (Apiezon Vacuum Products, Manchester, UK) was applied around the device on the chip, and a cover slip was positioned atop to seal it (**Figure 4.12b**).

The setup for in-situ Raman spectroscopy experiments was established as shown in **Figure 4.12c**. A hot plate was utilized to elevate the electrolyte temperature to 75°C promote ion mobility (due to the heat dissipation of the set-up, the hot plate temperature was set to be higher than the optical experiments and electrical experiments). A metal holder was strategically positioned between the experimental device and the hot plate to ensure that the sample reached the appropriate working distance of the Raman lens, while preventing the alligator clamps from making contact with the hot plate.

4.4.8. Uniform intercalation of Li over the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake

Figure 4.13 shows the optical images and the Raman spectra of different spots on $\text{Fe}_{0.17}\text{ZrSe}_2$ flake at $V_{\text{CE}} = 2, 3.3, 0 \text{ V}$, respectively. The uniformity of color and the consistency of the Raman spectra across various spots on the flake suggest uniform Li intercalation throughout the flake.

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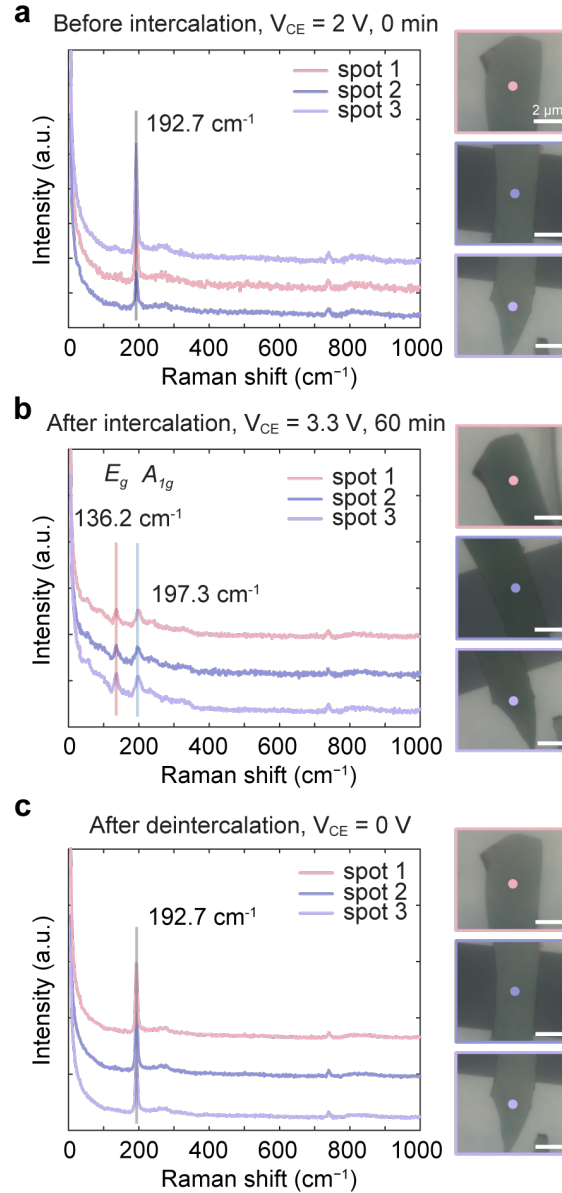


Figure 4.13. Uniform intercalation of Li over the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake. (a-c) The Raman spectra and optical images of different spots on the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake at $V_{\text{CE}} = 2$ V, before intercalation (a); at $V_{\text{CE}} = 3.3$ V, after intercalation (b); and at $V_{\text{CE}} = 0$ V, after deintercalation (c). The dot in each optical image indicates the location of the Raman scan. The scale bar: 2 μm .

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4.4.9. Set-up for in-situ electrical transport measurements

The same device of Raman spectroscopy experiment was used for electrical transport measurement. The I-V curves for calculating the resistance of Li intercalated $\text{Fe}_{0.17}\text{ZrSe}_2$ reported in **Figure 4.6** are plotted below.

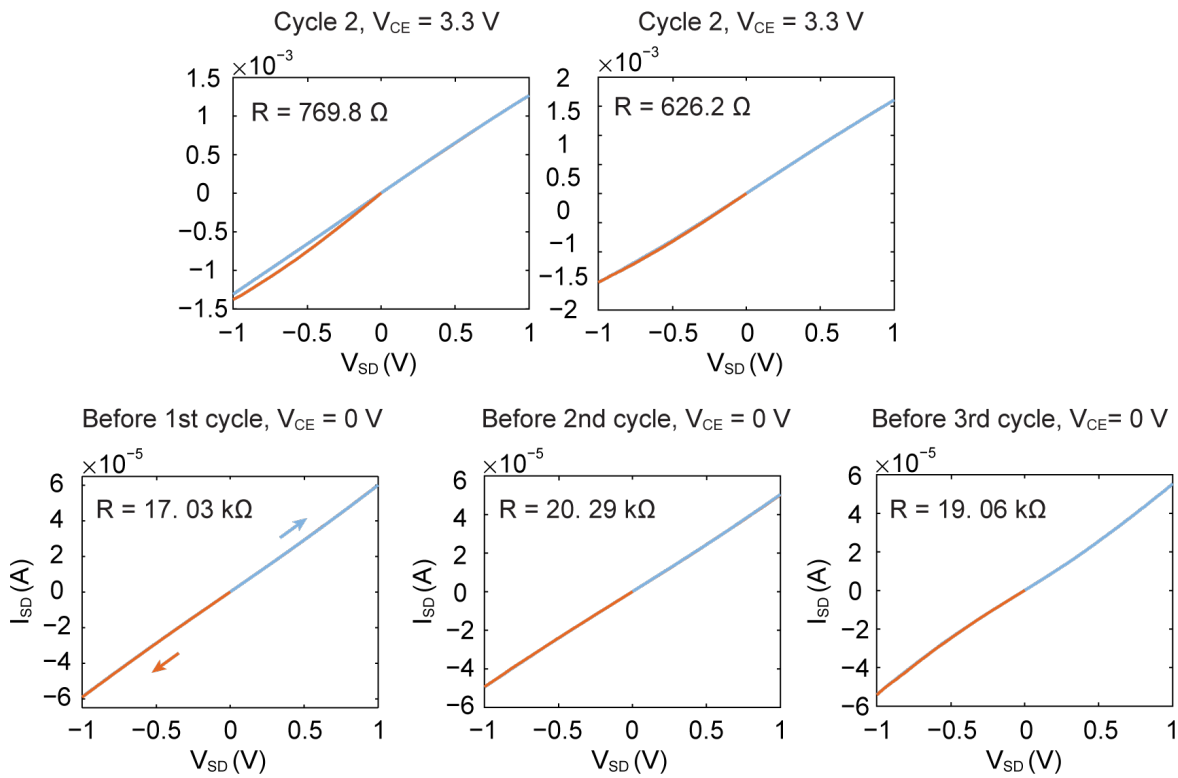


Figure 4.14. The I-V curves for the Li intercalated $\text{Fe}_{0.17}\text{ZrSe}_2$.

4.4.10. Reversibility of the edge intercalation

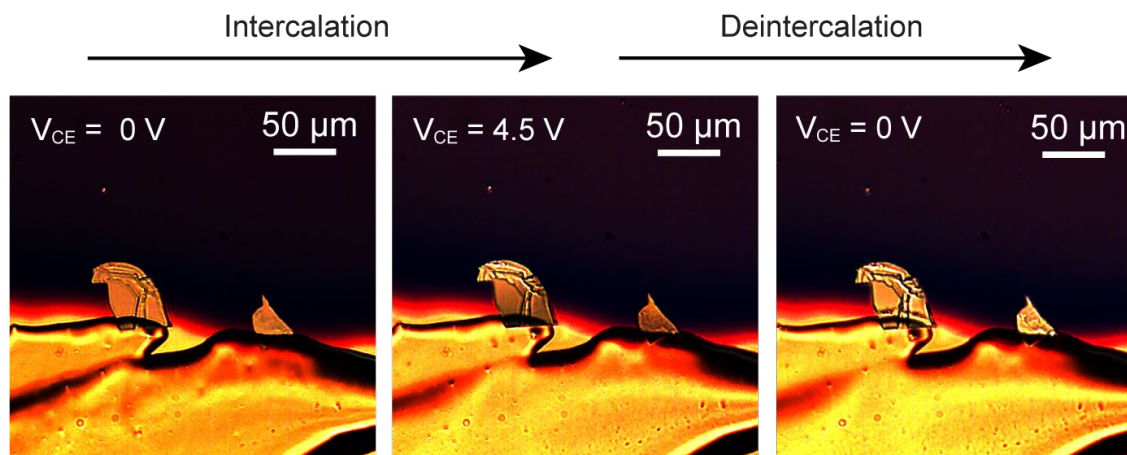


Figure 4.15. The reversibility of the edge intercalation. The color of the flake started as pale at $V_{\text{CE}} = 0 \text{ V}$, and became darker when increasing the V_{CE} to 4.5 V . After decreasing the V_{CE} to 0 V , the color of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake returned to pale, which indicating the reversibility of the edge intercalation.

4.4.11. Diffusion study of Li^+ intercalation from the $\text{Fe}_{0.17}\text{ZrSe}_2$ edge into its bulk

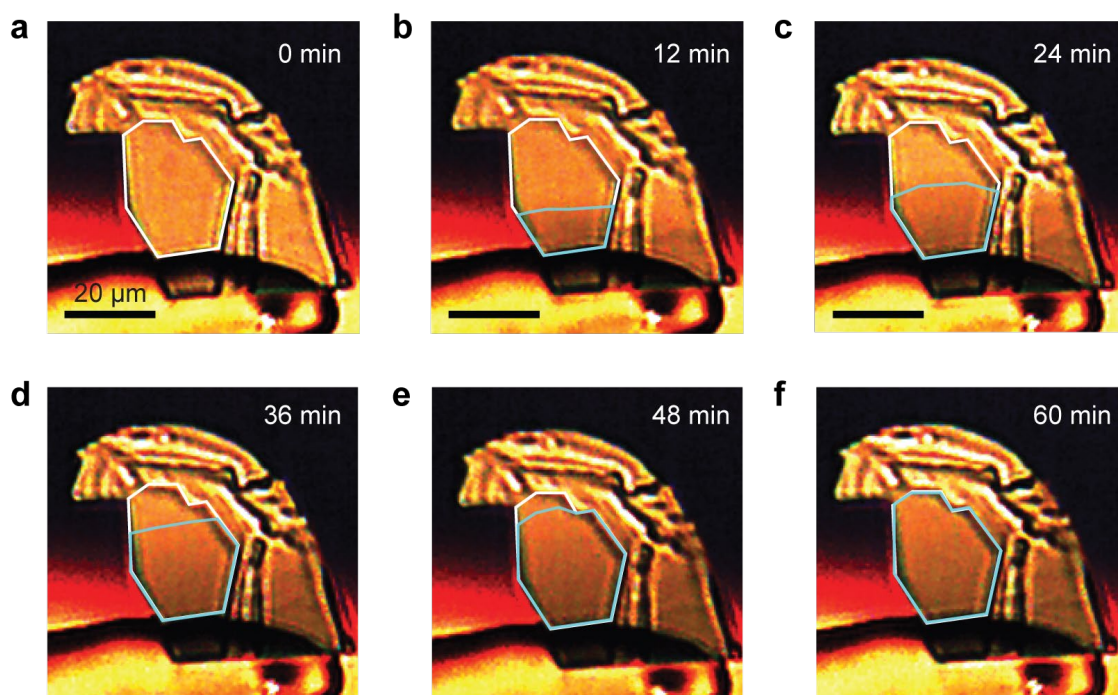


Figure 4.16. Diffusion study of Li^+ intercalation into $\text{Fe}_{0.17}\text{ZrSe}_2$. (a-f) Optical micrograph of $\text{Fe}_{0.17}\text{ZrSe}_2$ flake. The total area is marked with the white line while the intercalated area is marked in the blue line.

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4.4.12. The conditions to destroy the flake

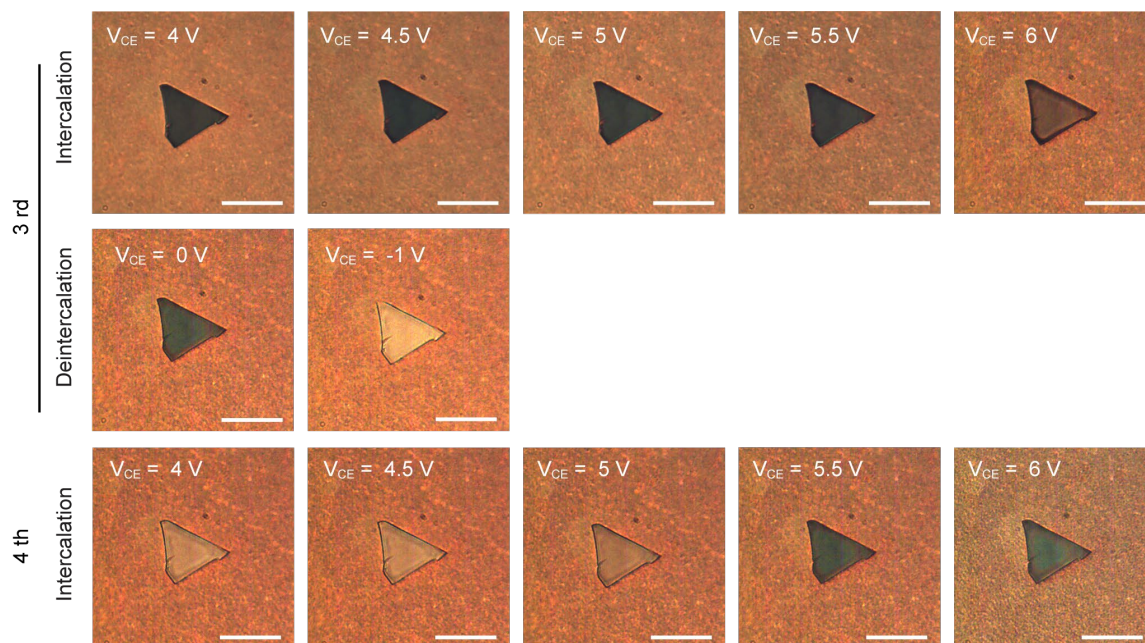


Figure 4.17. Over intercalation of $\text{Fe}_{0.17}\text{ZrSe}_2$ flake. The optical images of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake sweeping V_{CE} from 4 to 6 V and then decrease V_{CE} to 0 and -1 V in the 4th cycle. Afterwards, in 5th cycle, the V_{CE} was increased to 6 V again and the optical contrast at 6 V is different from that in the 3rd cycle, which indicates the irreversibility of the intercalation process. The scale bar: $100 \mu\text{m}$.

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Chapter 5

Effect of magnetic disorder from spin glass $\text{Fe}_{0.17}\text{ZrSe}_2$ on spin current

5.1 Introduction

Spintronics leverages the quantum spins of electrons for information storage and processing. The utilization of pure spin current, manifesting itself as a flow of spin angular momentum without simultaneous charge transport, presents a promising alternative to traditional charge-based electronic devices in alignment with Moore's law. Unlike spin-polarized charge currents, a pure spin current can be achieved when spin-up and spin-down electrons move in opposite directions, resulting in a net charge current of zero. This unique property enables pure spin currents to mitigate challenges associated with charge currents, such as electromigration and Joule heating, thereby offering improved energy efficiency, reduced heat generation, and enhanced operational speed.

Generation and manipulation of spin-polarized current effectively are essential for spintronic devices. In the recent years, spin fluctuations have been discovered to play an important role for the effective enhancement of the spin current.²⁻⁴ Spin fluctuations typically occur when magnetic materials transition from a long-range ordered magnetic state to a disordered state. Numerous studies have observed enhancements in spin currents around the magnetic phase transition temperature, coinciding with the onset of spin disorder, in various systems, such as ferromagnetic (FM) metal;⁵⁻⁷ the antiferromagnetic (AFM) metal^{8,9}; the AFM insulators.¹⁰⁻¹² To investigate the potential impact of spin fluctuations on spin-current enhancement, spin-glass (SG) systems present a promising candidate. Spin glasses, characterized by correlated spin disorder, exhibit significant short-range order that enables the induction of large fluctuations, making them valuable for exploring spin-current enhancements.

Fe intercalated ZrSe_2 has been reported to be a versatile spin glass systems where the spin density and magnetic ordering can be precisely controlled through the choice of the host lattice, intercalant, and stoichiometry of the resulting Fe_xZrSe_2 compound.^{13,14} And also Fe_xZrSe_2 is a semiconductor, which permits the strong modulation of their charge carrier densities electrostatically¹⁵⁻¹⁷ or electrochemically,¹⁸ offering the possibility of achieving electrically

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controlled magnetism. To investigate the interplay between spin currents and the spin glass semiconductor system Fe_xZrSe_2 , we utilize the interface of the spin glass with heavy metals such as Pt to measure spin-Hall magnetoresistance and proximity-induced magnetization.^{19,20} Pt, a nonmagnetic heavy metal with strong spin-orbit coupling (SOC), is capable of converting a charge current into a spin current and plays a pivotal role in generating and detecting pure spin currents.¹⁹

In this work, we demonstrate the tuning of magnetic properties in Pt thin films fabricated on SiO_2/Si substrates. By attaching spin glass $\text{Fe}_{0.17}\text{ZrSe}_2$ on the Pt thin film, the anomalous Hall effect (AHE) and spin hall effect (SHE) emerges in the initially nonmagnetic Pt. Surprisingly, the AHE observed in the $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ thin film is quite similar to that in Pt thin films grown on Bi-doped YIG substrates. The magnetization control by spin glass sheds light on the novel physical characteristics and functionalities of Pt as an exchange-enhanced magnetic material.

5.2 Results and discussion

Fabrication of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ device

The experimental geometry for our Hall-bar magnetotransport measurements is shown **Figure 5.1** shows the schematic and optical image of Pt Hall bar device for transport measurements, a Hall bar configuration was fabricated using electron beam lithography (EBL) techniques. A 6 nm thick Pt thin film was deposited on a SiO_2/Si substrate via electron beam evaporation. Additionally, extended contacts were defined using EBL, followed by the deposition of Cr (5 nm)/Au (100 nm) onto the substrate (refer to Experimental **Figure 5.6** for the

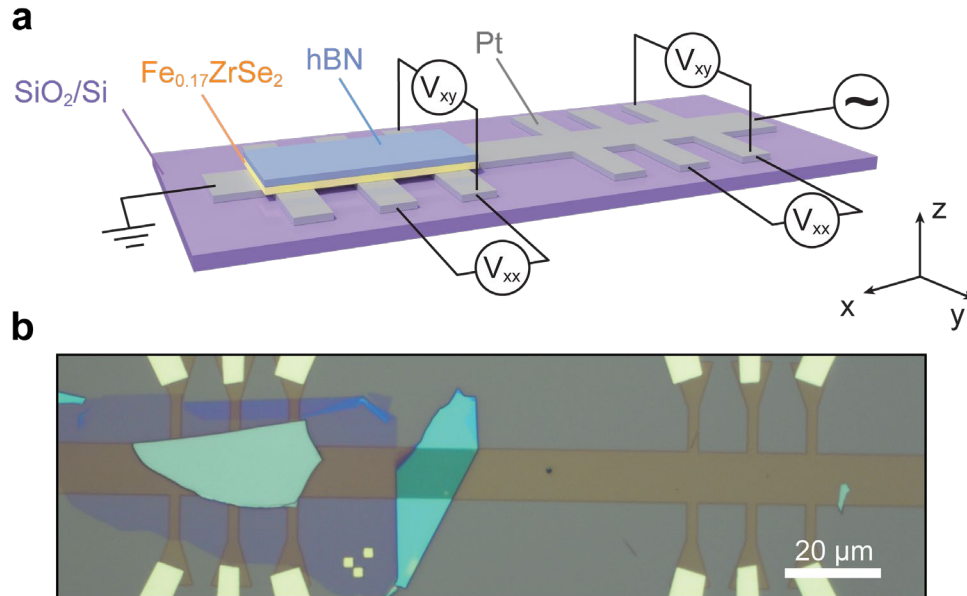


Figure 5.1. Pt Hall bar device. (a) Schematic illustration of the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake is transferred onto the top of Pt Hall bar and encapsulated with hBN. (b) The optical image of the measured Hall bar device.

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pattern design). After the liftoff process, the substrate underwent O_2 plasma cleaning to eliminate polymer residue from the metal contacts and to enhance the adhesion of the Pt thin film to the $\text{Fe}_{0.17}\text{ZrSe}_2$ layer (refer to Experimental **Figure 5.7** for the AFM image of the Pt thin film). $\text{Fe}_{0.17}\text{ZrSe}_2$ was exfoliated using blue tape and transferred onto PDMS in argon glovebox. Subsequently, the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake was carefully dropped from the PDMS onto the Pt Hall bar. To secure the flake and protect it from degradation upon exposure to air, a hBN flake was transferred onto the substrate to encapsulate the $\text{Fe}_{0.17}\text{ZrSe}_2$ flake in the air-free environment.

Anomalous Hall effect (AHE) of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ device

Figure 5.2 depicts the temperature dependencies of Hall resistivity (R_{xy}) observed in Pt and $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$. In **Figure 5.2a**, the Hall resistivity of pure Pt shows a linear dependence on the magnetic field (H). The Hall coefficient remains essentially temperature-independent, consistent with expectations for paramagnetic metals²¹. In contrast, completely different Hall results have been observed in $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$, exhibiting both an ordinary Hall effect and an anomalous Hall effect (AHE) as shown in **Figure 5.2b** where the latter is a key FM characteristic. The relationship between R_{xy} and the applied magnetic field becomes highly nonlinear. When T is higher than 90 K, we observed that the downward bending of R_{xy} for increasing H , whereas the curvature was changed to upward bending upon cooling. Furthermore, the curves sweeping in forward and backward overlapped with each other and no hysteresis in R_{xy} was observed. Similar nonlinear Hall curve of R_{xy} has been reported for $\text{Bi:YIG}/\text{Pt}$,^{19,22} which led to the conclusion that insulating spin glass $\text{Fe}_{0.17}\text{ZrSe}_2$ might induce local magnetic moment at the interface of Pt due to magnetic proximity effect.

Figure 5.3 shows the magnetoresistance (MR) data change of the Pt and $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ as a function of the amplitude of the magnetic field H . The magnitude of $\Delta R_{xx}/R_0$ is defined as the change of resistivity divided by the resistivity at zero field. In the experiment, the external magnetic field H was applied perpendicular to the Pt film plane and the electric-current direction.

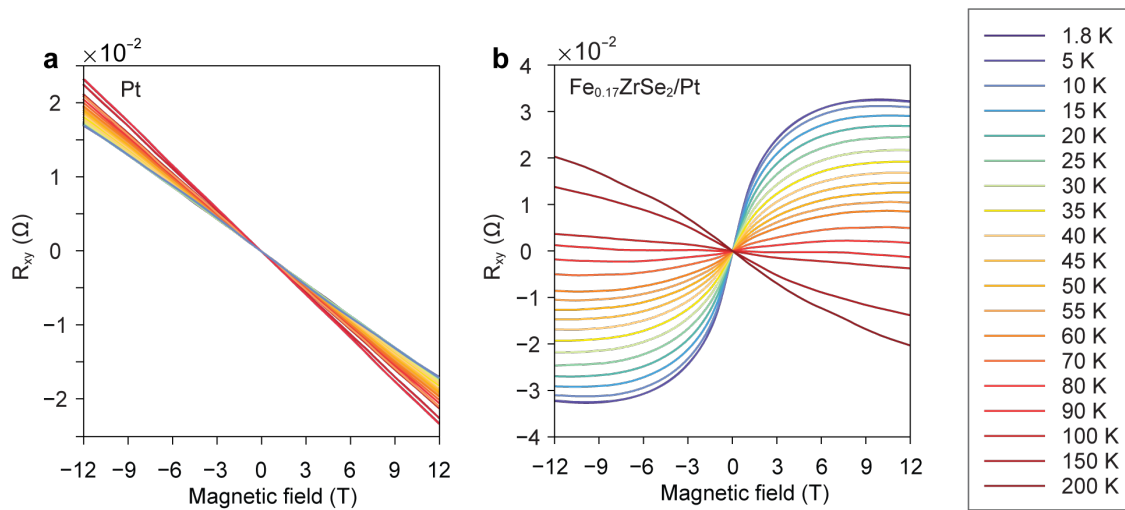


Figure 5.2. Temperature dependence of Hall resistance R_{xy} . Hall effect in Pt (a) and in $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ (b) at different temperatures.

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As shown in **Figure 5.3a**, at 200 K, the resistance of Pt shows very weak dependence on H in the present field range, however, the $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ exhibits a clear resistance change, where the resistance increases when increasing H from $H = 0$ to ± 12 T. Magnetoresistance of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ at 1.8 K showed no hysteresis (**Figure 5.3b**) and the difference in the magnetic responses between $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ and Pt-only showed that the magneto-transport in Pt was induced by magnetic proximity effect. **Figure 5.3d** shows the MR results of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ exhibit a pronounced anisotropic MR (AMR) behavior. Magnetoresistance of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ increased with temperature and the sign changed at 20 K. Since Pt is near the Stoner ferromagnetic instability, it is possible that the ferromagnetism might be induced in the Pt layer by the equilibrium proximity to spin glass $\text{Fe}_{0.17}\text{ZrSe}_2$, leading to and the AMR^{19,20,23,24}. It has been reported that Pt atoms that are very close to the interface in FM/Pt films will develop a finite magnetic moment due to a static proximity effect^{1,23}.

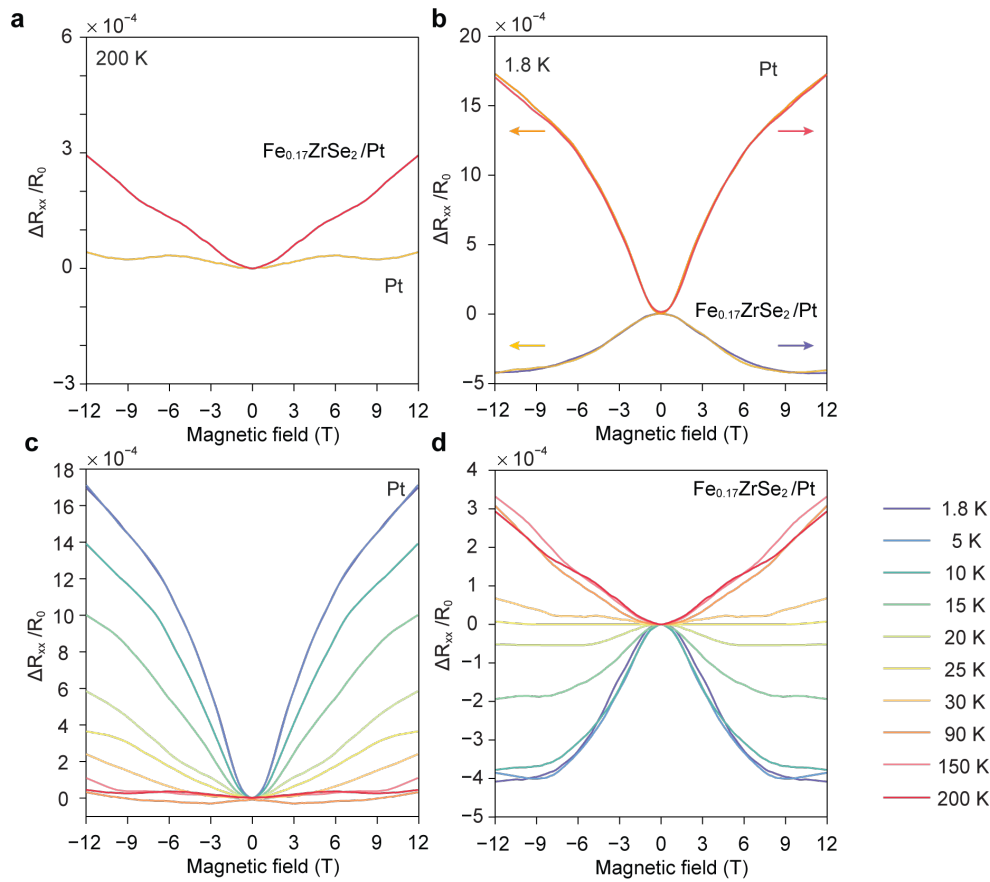


Figure 5.3. Magnetoresistance resistances of Pt and $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ at different temperatures with out-of-plane magnetic field H_z . (a,b) Magnetoresistance resistances of pure Pt (upper curves) and $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ (lower curves) at 200 K (a) and 1.8 K (b) for magnetic field sweeps in positive (Pt, red; $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$, violet) and negative (Pt, orange; $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$, yellow) directions. Magnetoresistance of Pt (c) $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ (d) at different temperatures.

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Spin Hall MR of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ device

To further study the magnetoresistance behavior of this $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ heterostructure device, we also measure the magnetoresistance of the same pre-patterned Pt Hall bar device with the magnetic field applied in different directions (**Figure 5.4**). H_z indicates the applied magnetic field that is perpendicular to the Pt thin film. H_x and H_y are in-plane applied magnetic fields. H_x indicates that the magnetic field is applied along the current direction, while H_y indicates the magnetic field is applied perpendicular to the current direction. For all the applied field, the $\Delta R_{xx}/R_0$ was smaller at lower temperature and $\Delta R_{xx}/R_0$ increase with increasing temperature. With different directions, the sign change of $\Delta R_{xx}/R_0$ is at different temperature, where for in-plane applied field (H_x and H_y), the transition temperature is 15 K and for out-of-plane applied field (H_z), the transition temperature is 25 K.

The difference in the R_{xx} with different directions of the applied magnetic field might be induced by spin hall effect. **Figure 5.5a** shows the initial setup for a Pt thin film, a freestanding metallic thin film with strong spin-orbit Interaction (SOI). When an electric current (J_e) flows along the film plane, it induces a spin current (J_s) perpendicular to the film surface due to Spin Hall Effect (SHE) in Pt. This spin current carries spin polarization σ parallel to the surface. **Figure 5.5b** shows that at the surface of the film, a portion of the spin current is reflected into the bulk part of the film. This reflection process in actual Pt films leads to a non-equilibrium spin accumulation near the surface (**Figure 5.5f**) and subsequent spin diffusion.

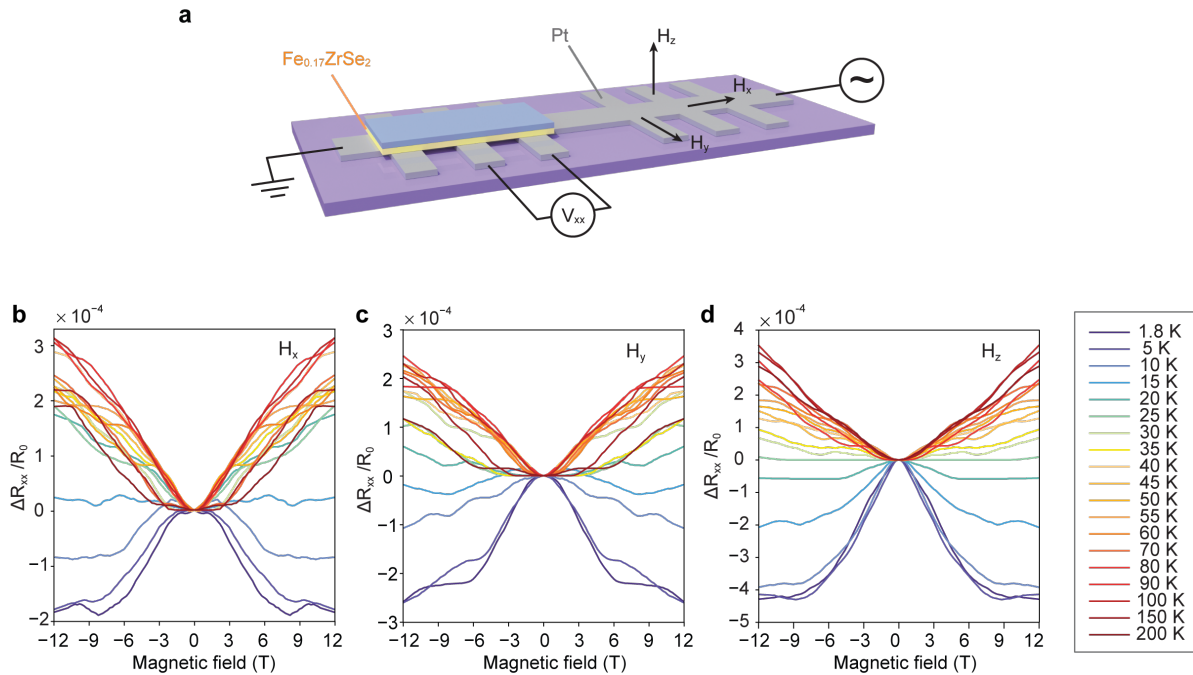


Figure 5.4. Magnetoresistance resistances of Pt and $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ at different temperatures with different directions of applied magnetic field. (a) The schematic of measured device. (b-d) Magnetoresistance resistances of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ with H_x (b), H_y (c) and H_z (d).

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Additionally, Inverse Spin Hall Effect (ISHE) in Pt converts the reflected spin current into an electric current (**Figure 5.5c**) generating an electromotive force along the film plane. This additional electric current, resulting from the combined effects of SHE and ISHE, always aligns parallel to the original one. Hence, measurements of electric currents in thin films with spin-orbit interaction inevitably include this supplementary contribution. By introducing an electrically insulating magnet onto the Pt surface, it is possible to manipulate this process. This setup fosters interfacial spin mixing between the $\text{Fe}_{0.17}\text{ZrSe}_2$ and Pt, involving exchange of spin-angular momentum between magnetization (M) in interfacing material and conduction-electron spin polarization in Pt. Spin-flip scattering is triggered when σ and M are not aligned, affecting the behavior of the spin current and its interaction with the magnetization, depicted in **Figure 5.5c** and **Figure 5.5d**.

A portion of the spin current is absorbed by the magnetization, generating a spin-transfer torque, even at the interface with a magnetic insulator. This absorption is maximal when $M \perp \sigma$ and minimal when $M \parallel \sigma$. Consequently, the conductivity enhancement resulting from SHE and ISHE is maximized (minimized) when M is perpendicular (parallel) to J_e , as J_e is perpendicular to σ . The resistance of the Pt film is consequently influenced by the direction of magnetization in the material $\text{Fe}_{0.17}\text{ZrSe}_2$, leading to the emergence of Spin Hall Magnetoresistance (SMR).

While a complete consensus is still lacking, the anisotropic MR (AMR) and spin Hall MR (SMR) are possible underlying mechanisms. To study the contribution of AMR and SMR, we will perform both the field dependent magnetoresistance (FDMR) measurements and angle-

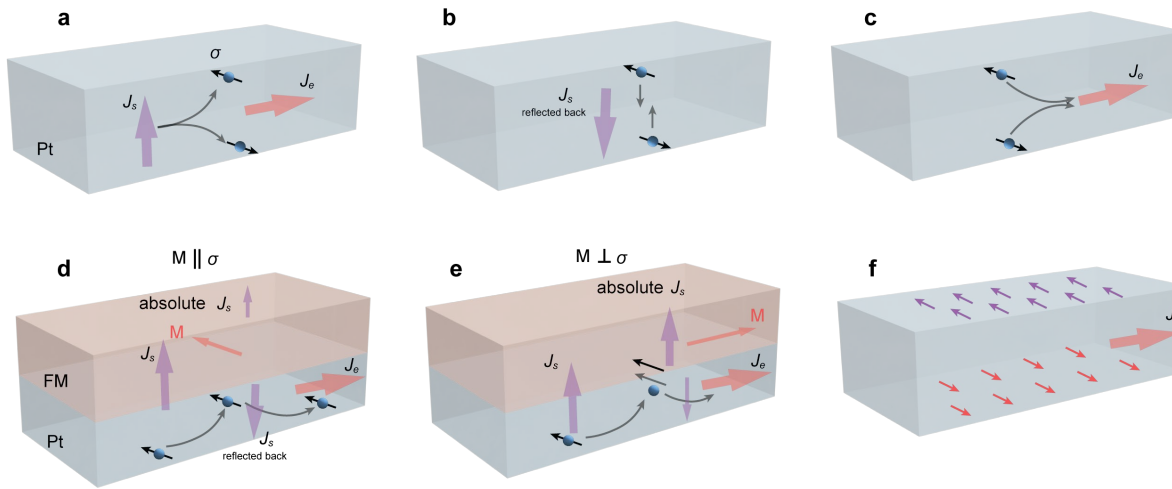


Figure 5.5. Illustrations of spin Hall effects (SHE) and inverse spin Hall effects (ISHE) and in Pt/FM insulator and geometry effect. (a-c) Illustrations of the magnetic modulation of conductivity attributed to SHE and ISHE in a Pt thin film coupled with a ferromagnetic insulator (FM). (d-e) Depiction of the geometric relationship between electron flow and accumulated spins within Pt, juxtaposed with the magnetization orientation in the magnetic insulator. (f) Representation of spin accumulation engendered by non-equilibrium proximity, stemming from SHE in Pt. Spin accumulation at Pt interfaces is contingent upon the direction of its spin polarization. Adapted from ref. 1

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dependent magnetoresistance (ADMR) measurements on the $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ bilayer.

5.3 Conclusions

Combined electrical measurement showed that the Pt thin film behaves as a nonmagnetic material, however, the spin glass on the top of the Pt thin film induced the AHE, which is quite similar to that in Pt thin films grown on ferromagnet Bi-doped YIG substrates. Furthermore, the spin glass $\text{Fe}_{0.17}\text{ZrSe}_2$ also leads the SHE in the Pt thin film, which indicates the equilibrium spin accumulation near the surface of Pt thin film and subsequent spin diffusion. In order to study the contribution of AMR and SMR to the magnetoresistance, we need to study the magnetic field orientation dependence of the magnetoresistance since AMR and SMR differ in the angle dependence of the magnetic fields. Notably, we found out that there is a strong interaction of spin current and spin disorder yielding high spin Hall magnetoresistance change even at room temperature, which can be exploited in various spin-based applications and devices.

5.4 Experimental

5.4.1. Device fabrication

The experimental geometry for our Hall-bar magnetotransport measurements is shown in **Figure 5.6**, where the Hall-bar structure has been patterned onto the substrate denoted as the xy plane with one long segment (150 μm long and 10 μm wide) in the x direction and three shorter connected segments (10 μm long and 2 μm wide). To spin coat electron beam sensitive resist, the MMA:PMMA bilayer electron beam resist system was used to produce nanoscale structures with clean edges via lift-off. In a typical experiment, the substrate was placed upon the spin coater (Model WS-650MZ-23NPPB, Laurell Technologies corporation, Lansdale, PA, USA) and an aliquot (100 μL for each 0.5 in^2 of substrate area) of MMA was dispensed on top of it. The assembly was then spun at 300 rpm for 5 s and then at 4000 rpm for 60 s. After the spin coat, the MMA-coated substrates were annealed on a hot plate (Model C-MAG HS 7, IKA Works, Inc., Wilmington, NC, USA) at 130 $^\circ\text{C}$ for 3 min in air to remove the solvent. Same process for the second resist layer PMMA. Then, electron-beam lithography (EBL) (Model: Cabl-9510CC, CRESTEC Corporation, Tokyo, Japan) was used to define the device pattern, followed by development in a cold 3:1 v/v mixture of IPA:DI water at room temperature for 90 s. To clean the substrates and enhance the interaction between evaporated metal and substrate SiO_2/Si , the chips were O_2 plasma cleaned (Model: PK-12 RIE, Plasma-Therm, LLC, North Saint Petersburg, FL) with 40 sccm O_2 (with pressure 60 mTorr) at power 35 W for 15 s. Right after the plasma cleaning, the chips were loaded into electron beam evaporation (Electron Beam 10 kW 4-pocket Evaporator) chamber in 2 min, which was pumped down for 1 hr to 6×10^{-6} Torr. After reaching the target pressure, the chips were evaporated with metal layers based on different devices, followed by overnight liftoff in acetone. For the Hall bar, the 7 nm Pt was deposited on the substrate SiO_2/Si . Cr (5nm)/Au (100 nm) was deposited for the extended contacts.

CHAPTER 5. EFFECT OF MAGNETIC DISORDER FROM SPIN GLASS $\text{Fe}_{0.17}\text{ZrSe}_2$ ON SPIN CURRENT

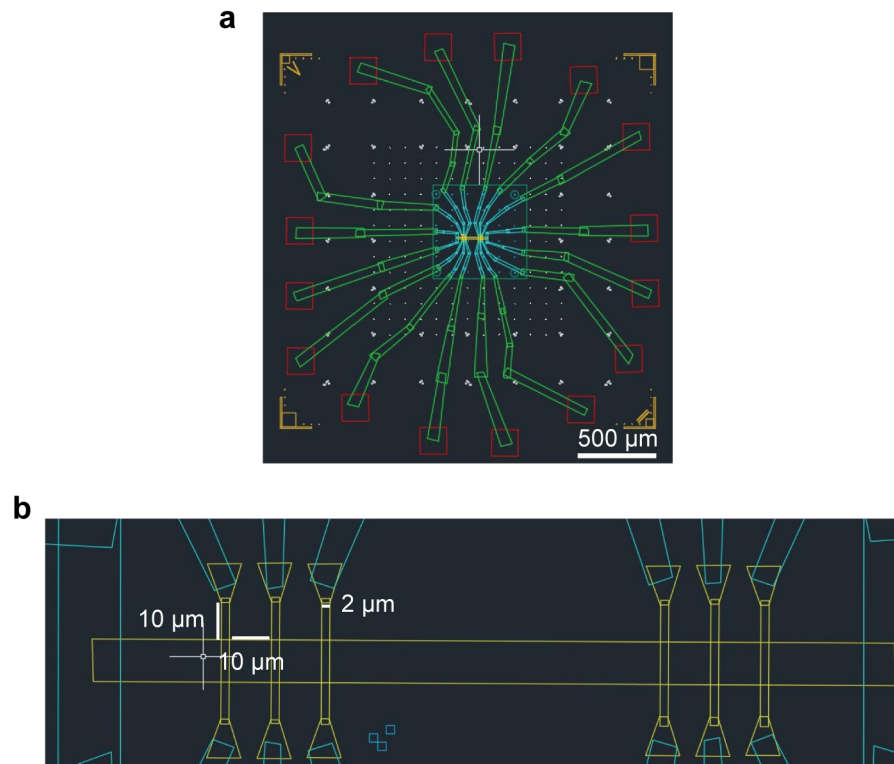


Figure 5.6. AutoCAD design of $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ device. (a) The design of the whole $\text{Fe}_{0.17}\text{ZrSe}_2/\text{Pt}$ device. (b) The enlarged image in the Hall bar area.

5.4.2. Oxygen plasma cleaning of the device

Figure 5.7 shows the deposited Pt thin film right after the lift off. Polymer residue can be seen on the substrate and the Pt thin film. No bunny ears were observed using MMA:PMMA bilayer electron beam resist system. After the oxygen plasma cleaning, the number of nanoparticles decreased a lot and the substrate, and the Pt thin film were much cleaner. The thickness of Pt thin film is approximately 7 nm.

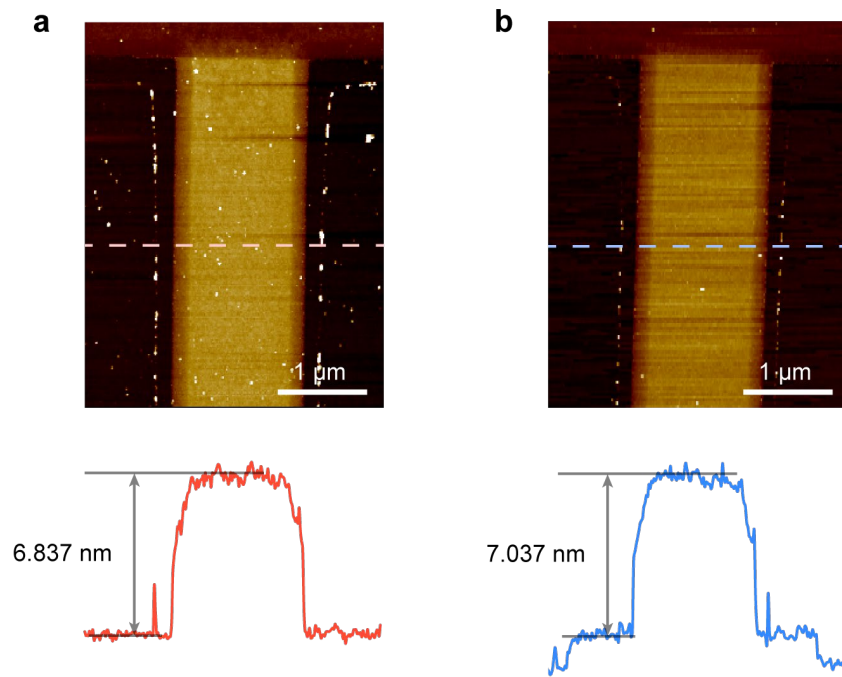


Figure 5.7. AFM images of the device contact legs before and after the oxygen plasma cleaning. (a) The AFM image and the line scan of the Pt thin film right after the lift off without O₂ plasma. (b) The AFM image of the same sample after O₂ plasma cleaning.

5.4.3. Mechanical exfoliation and transfer of the $\text{Fe}_{0.17}\text{ZrSe}_2$

$\text{Fe}_{0.17}\text{ZrSe}_2$ thin films were obtained following procedures reported in Chapter 4.

5.5 References

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Chapter 6

Conclusions

Magnetic ion intercalated MCh₂ (M = group 4 metal) systems have emerged as versatile platforms for investigating semiconducting spin glass materials. The incorporation of magnetic ions into MCh₂ introduces multiple tuning parameters, including intercalants and host lattices, enabling manipulation of optical, electrical, and magnetic properties, as well as exploring the interplay among composition, structure, and magnetism. This study focuses on the Fe-intercalated ZrSe₂ system due to its high spin-orbit coupling and semiconducting characteristics. Unlike the majority of Fe-intercalated transition metal dichalcogenides (TMDs), where intercalated Fe occupies only octahedral interstitial sites, in Fe intercalated ZrSe₂, Fe can occupy both tetrahedral and octahedral sites in a disordered manner, leading to the spin glass behavior of Fe_xZrSe₂. Chapters 2 and 3 confirm the random distribution of Fe ions between the host lattice van der Waals (vdW) layers in Fe_xZrSe₂ ($x = 0.17, 0.25, 0.33$), with its unique structure contributing to the spin glass behavior of Fe_xZrSe₂ crystals. All Fe_xZrSe₂ samples with varying x exhibit exchange bias, highlighting the correlation between spin disorder and exchange bias behavior. Fe_{0.33}ZrSe₂, in particular, demonstrates a giant exchange bias field of up to 3000 Oe at 100 K. The behavior observed in Fe_xZrSe₂ with different Fe concentrations underscores the intimate relationship between the spin glass phase and the exchange bias phenomenon, suggesting a potent strategy for designing highly tunable exchange bias systems with transition temperatures near room temperature. Such systems hold promise for future applications in spintronics devices. Chapter 4 shows high reversibility of Li ion electrochemical intercalation into semiconducting Fe_{0.17}ZrSe₂ and the Li intercalation has been demonstrated to be an effective strategy to manipulate the structural, optical, and electrical properties of Fe_{0.17}ZrSe₂. The enhancement of electron transport upon the Li intercalation in the materials lays down a robust groundwork for electrostatic control over spin polarization. Chapter 5 investigates the impact of the semiconductor spin glass Fe_xZrSe₂ on the generation and manipulation of spin-polarized current for spintronic devices, which highlights the potential application of the materials in spintronic technology.

Expanding beyond the materials investigated in preceding chapters, there is considerable intrigue in exploring a diverse array of tuning parameters in magnetic ion intercalated MCh₂ systems. This includes broadening the intercalant selection to encompass metals like Co, Ni, Cr, and Mn, while extending the host lattice to encompass materials such as HfSe₂ and TiSe₂. Thinning the materials down to a few layers allows for investigating the dimensional effect on their properties. Leveraging the remarkable attributes of building heterostructures, stacking 2D

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materials together and studying intercalated heterostructures, such as intercalated $\text{ZrSe}_2/\text{ZrS}_2$ and $\text{ZrSe}_2/\text{HfSe}_2$ due to their similar lattice parameters, presents a promising avenue for exploration.

Furthermore, employing electrostatic (including ionic liquid) gating offers direct control over carrier density and the ability to externally tune RKKY exchange interactions, thereby probing their impact on magnetic state and ordering temperature. Utilizing van der Waals (vdW) heteroepitaxy enables the assembly of two identical 2D layers with a predetermined interlayer screw/twist along the out-of-plane axis, facilitating the formation of moiré patterns. Leveraging expertise in vdW heteroepitaxy and intercalation (electro)chemistry, new 2D structures with controlled intercalant superlattices can be created, allowing for the study of the spatial periodicity of intercalated transition metal ions and its influence on magnetic ordering.