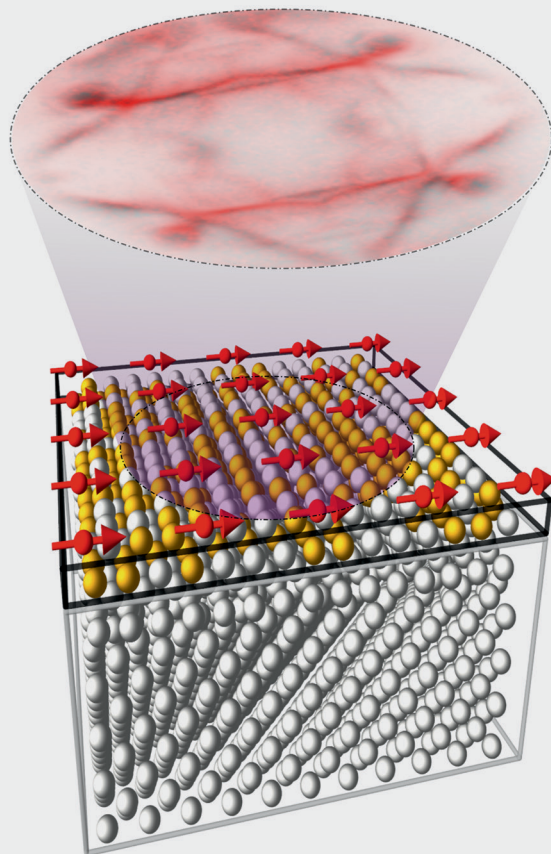




Competing spin-orbit coupling and exchange interaction in a two-dimensional ferromagnete

Xin Liang Tan

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Kurzzusammenfassung

Das Zusammenwirken von Austauschwechselwirkung und Spin-Bahn-Kopplung (SOC) in niedrigdimensionalen ferromagnetischen Materialien spielt eine wichtige Rolle für deren spinabhängige elektronische Eigenschaften und für mögliche Anwendungen in der Spintronik. Diese Dissertation untersucht die elektronische Struktur von atomar dünnen FePd-Legierungsfilme auf Pd(001) mittels spin- und impulsaufauflösender Photoemissionsspektroskopie. Ein besonderer Fokus liegt hierbei auf der durch die ferromagnetische Magnetisierung hervorgerufenen spontanen Symmetriebrechung, welche sich in einer Spinpolarisation der Valenzbandzustände und in SOC-induzierten Hybridisierungseffekten manifestiert.

Ein experimenteller Ansatz unter Verwendung eines synchrotronbasierten, spinauflösenden Impulsmikroskops wird eingesetzt, um diese Effekte zu untersuchen. Dabei wird zunächst der Einfluss der SOC auf die elektronische Struktur in Pd(001) charakterisiert, das in den folgenden Experimenten als Substrat dient. Eine systematische Tomographie der Fermi-Oberfläche von Pd belegt wesentliche Effekte der SOC, die zu energetischen Aufspaltungen und der Bildung von Loch-Taschen in der Bandstruktur sowie zu einer modifizierten Fermi-Oberflächen-Topologie führen. Anschließend wird der Einfluss der Austauschwechselwirkung auf die spinabhängige elektronische Struktur in ultradünnen, ferromagnetischen FePd-Legierungen untersucht. Es wird gezeigt, dass die Austauschwechselwirkung eine zweidimensionale halbmetallische Bandstruktur hervorruft, die durch die Legierungsstöchiometrie gezielt modifizierbar ist. Schließlich stehen kombinierte Effekte beider Mechanismen im Fokus. Das Zusammenwirken von Austauschwechselwirkung und SOC wird insbesondere durch Variation der Magnetisierungsrichtung untersucht, wobei magnetisierungsinduzierte Asymmetrien in der Bandstruktur und Hinweise auf nicht-kollineare Spin-Texturen über die gesamte Fermi-Oberfläche hinweg beobachtet werden.

Ein zentrales Ergebnis der Arbeit ist das Auftreten zweidimensionaler Halbmetallizität in zwei Monolagen FePd-Legierung auf Pd(001), was direkte Implikationen für die Entwicklung spinfilternder Heterostrukturen in elektronischen Bauelementen hat. Darüber hinaus wird das Auftreten von sogenannten Spin-Mixing-Hotspots an Kreuzungspunkten in der elektronischen Bandstruktur beobachtet, an denen SOC-induzierte Hybridisierung energetische Entartungen aufhebt und die Topologie der spinpolarisierten Bänder verändert. Diese Effekte werden experimentell aufgelöst und durch ab-initio Rechnungen bestätigt. Die Möglichkeit, diese Effekte durch gezielte Einstellung der Magnetisierung und Legierungsstöchiometrie zu kontrollieren, eröffnet Potenzial für spintronische Anwendungen, etwa für Spinfilter und Spin-Bahn-Drehmoment-Plattformen.

Diese Arbeit hebt die Vielseitigkeit der Impulsmikroskopie zur systematischen ex-

perimentellen Untersuchung der elektronischen Struktur hybrider ferromagnetischer Systeme hervor. Die Ergebnisse liefern grundlegende Einblicke in die Rolle des Zusammenwirkens von Austauschwechselwirkung und SOC in niedrigdimensionalen Materialien. Ebenso etablieren sie zwei Monolagen FePd-Legierung auf Pd(001) als Modellsystem zur Erforschung komplexer Spin-Textures, topologischer Transportphänomene und maßgeschneiderter spintronischer Funktionalitäten.

Abstract

The interplay between exchange interaction and spin-orbit coupling (SOC) in low-dimensional ferromagnetic systems plays a pivotal role in shaping their electronic and spin properties, with direct implications for spintronic applications. This thesis investigates the electronic structure of ultrathin epitaxial FePd alloy on Pd(001) using spin- and momentum-resolving photoemission spectroscopy, focusing on symmetry breaking and SOC-driven band hybridization.

A systematic approach using synchrotron-based spin-resolving photoelectron momentum microscopy is employed to explore these phenomena. The study begins with an analysis of SOC effects in bulk Pd, followed by exchange engineering in ultrathin FePd alloys, and culminates in the investigation of their combined effects. Fermi surface tomography reveals that SOC strongly influences the electronic band structure of Pd, leading to band splitting, hole pocket formation, and a modified Fermi surface topology. In the FePd alloy, exchange interaction induces a two-dimensional half-metallic band structure that is tunable via the alloy stoichiometry. The interplay between exchange interaction and SOC is further examined by varying the magnetization direction, demonstrating magnetization-induced asymmetries in the band structure and indications of non-collinear spin textures across the Fermi surface.

A key finding of this thesis is the emergence of two-dimensional half-metallicity in two monolayers of FePd alloy on Pd(001), which has direct implications for spin-filtering heterostructures in electronic devices. Additionally, spin-mixing hotspots appear near the band-crossing points where SOC lifts band degeneracies and alters the topology of spin-polarized bands. These features are experimentally resolved and corroborated by first-principles calculations. The ability to control these effects by tuning the magnetization and the alloy composition suggests potential applications in spintronic devices, including spin filters and spin-orbit torque platforms.

This work highlights the versatility of momentum microscopy in resolving spin-dependent electronic structures in hybrid ferromagnetic systems. The findings provide fundamental insights into the role of exchange interaction and SOC in low-dimensional materials, establishing two monolayers of FePd alloy on Pd(001) as a model system for exploring complex spin textures, topological transport phenomena, and engineered spintronic functionalities.

1 Introduction

The fascination with magnetism begins with its discovery, tracing back to ancient civilizations. The earliest recorded observation of magnetic phenomena originates from ancient China, where magnetite ore was utilized in navigational compasses [1]. This rudimentary understanding of magnetic properties revolutionized navigation, enabling maritime expeditions that expanded the boundaries of the known world. The compass illustrates the pivotal role of magnetism in human history, from aiding in the exploration of continents to its integral use in modern navigation systems [2]. The leap to more sophisticated technological applications marks the evolution of magnetism from a curiosity to a cornerstone of modern science and technology. Magnetic Resonance Imaging (MRI), for instance, epitomizes the advanced utilization of magnetic phenomena, enabling non-invasive medical imaging that has transformed diagnostic medicine [3, 4]. The versatility of magnetism, spanning from compasses to cutting-edge medical technology, underscores its significance across various scientific and technological domains.

Magnetism, in its various forms, arises from the collective behavior of electronic charges and spins in many-body systems. The intricate microscopic interactions between individual spins of electrons give rise to diverse types of macroscopic magnetically ordered states such as ferromagnetism, antiferromagnetism, ferrimagnetism, and non-collinear magnetic order [5, 6]. Recently, the discovery of altermagnetic order—a magnetic phase distinct from conventional ferromagnetic or antiferromagnetic orders—has highlighted the dynamic nature of research into magnetism and its ongoing evolution [7, 8]. The various forms of magnetic order reflect the delicate balance between spin-dependent interactions and their dependence on the microscopic details of the host material. Magnetism remains a vibrant field of study, where new phenomena continue to emerge, challenging and broadening our understanding of the electronic structure of complex materials.

Spin-dependent phenomena in solids are predominantly driven by two fundamental mechanisms: the exchange interaction and spin-orbit coupling (SOC) [9]. The exchange interaction arises from the antisymmetric nature of the electronic wave function for fermions, rooted in the Pauli exclusion principle, in combination with the Coulomb interaction. This interaction energetically favors the parallel alignment of spins within electronic states and may create spin splitting. On the other hand, SOC is a relativistic effect resulting from the interaction between an electron's spin and the electric field produced by the crystal lattice. This coupling modifies the electronic band structure, lifting degeneracies and introducing spin-dependent band splittings that are symmetry- and momentum-dependent [10, 11]. Understanding the interplay between exchange interaction and SOC is essential for various spin-

dependent phenomena, such as the anomalous Hall effect, the spin Hall effect, the quantum anomalous Hall effect, and topological magnetic systems, which are central to spintronic applications [12].

Ferromagnetism, driven by the exchange interaction, arises from the spin splitting of electronic bands, where one spin orientation is energetically favored over the other. This spin splitting results in distinct majority and minority spin bands, leading to spontaneous magnetization and a net magnetic moment in the absence of an external field. Concurrently, spin-orbit coupling (SOC) introduces momentum-dependent band splitting, which is highly sensitive to both crystal symmetry and spin direction. Unlike the exchange interaction, SOC-induced splitting is often anisotropic, giving rise to complex spin textures and band hybridization near degenerate points. Despite the well-established roles of exchange interaction and SOC individually, their coexistence and interplay remain less explored. Together, they shape the spin-dependent electronic band structure, modifying energy levels, and spin polarization, potentially giving rise to novel quantum phenomena. Experimentally resolving these effects with high precision remains a challenge but is crucial for linking microscopic electronic structures to macroscopic transport properties. Advanced experimental techniques such as spin-resolving momentum microscopy and magnetotransport measurements play a key role in overcoming these challenges and validating theoretical models [13, 14].

In this thesis, we investigate a model system to gain deeper insights into the interplay between exchange interaction and SOC in ultrathin $3d$ - $4d$ hybrid ferromagnetic systems. Specifically, the FePd alloy system grown on a Pd(001) substrate serves as a suitable platform for this exploration. Iron (Fe), a prototypical $3d$ itinerant ferromagnet, exhibits strong exchange interaction, while palladium (Pd), a $4d$ element, is a noble metal with significant SOC. The combination of Fe and Pd is particularly intriguing, as both exchange and spin-orbit interactions are expected to be sizable. This effect may be further intensified by the confinement of the ultrathin film and surface effects, which are known to enhance SOC contributions in low-dimensional systems. Recent theoretical predictions suggest that ultrathin FePd alloys may exhibit half-metallicity, characterized by a fully spin-polarized Fermi surface and the ability to host long-lived terahertz magnons [15]. These properties make FePd a promising candidate for spintronic applications and studies of spin dynamics, but the fundamental understanding of its electronic structure is lacking.

Resolving energy, spin, and momentum of the electronic states is indispensable to reveal the interplay between exchange interaction and SOC. Momentum microscopy, a state-of-the-art technique employed in this study, enables two-dimensional spin- and momentum-resolved imaging of the electronic structure, providing insights into the spin polarization and the momentum distribution of key aspects of the electronic structure [16, 17]. For instance, magnetization in ferromagnets breaks symmetries such as time-reversal symmetry, causing magnetization-dependent modifications to the band structure. The manifestation of non-collinear spin textures or the emergence of band asymmetries in momentum space can be resolved directly via momentum microscopy. This thesis attempts not only to deepen the understanding of FePd but

also serves as an experimental archetype for the other ferromagnetic and broader classes of magnetic systems.

This thesis is structured to provide a comprehensive analysis of the electronic structure of ultrathin FePd alloys on Pd(001) and the interplay between exchange and SOC. Chapter 2 lays the theoretical groundwork by introducing fundamental concepts of the electronic structure in solids and fundamental aspects of exchange interaction and SOC. The chapter also introduces the photoemission process and gives a brief account of theoretical methods such as Density Functional Theory (DFT) and the Korringa-Kohn-Rostoker method, which underpin the analysis in later chapters. Chapter 3 details the experimental methodologies employed in this study. The use of momentum microscopy for high-resolution mapping of the Fermi surface and spin textures is highlighted, alongside the techniques used to fabricate and characterize ultrathin FePd films on Pd(001). Attention is given to spin-resolved photoemission and dichroic measurements. Chapter 4 focuses on the Fermi surface tomography of palladium and rhodium, providing insights into their electronic structures and serving as a reference for subsequent studies of FePd alloys. Momentum-resolved photoemission data, combined with theoretical calculations, are used to estimate the orbital character in the electronic band structure of these systems. Chapter 5 explores the spin-polarized electronic structure of ultrathin FePd films on a single-crystalline Pd substrate, revealing the realization of two-dimensional half-metallicity. The chapter examines the spin-resolved electronic structure, symmetry-breaking effects, and the manifestation of exchange interaction in FePd thin films. Chapter 6 investigates the interplay between exchange interaction and SOC in two monolayers of FePd alloy on Pd(001). Specifically, it examines how broken mirror symmetry in the electronic structure emerges due to magnetization and the coexistence of exchange interaction and SOC. Experimental data from spin-resolved momentum microscopy and circular dichroism in photoemission complement the study of magnetization-induced broken symmetry in the electronic structure and its spin texture. Chapter 7 discusses the findings of the preceding chapters and points to their potential implications for spintronics and hybrid magnetic materials. It highlights the promise of FePd alloys as a platform for investigating the interplay between spin, orbital, and exchange interaction in low-dimensional systems. Chapter 8 provides a summary of our findings on the electronic band structures of Pd, Rh, and FePd alloy thin films on Pd(001) and outlines prospects for future research.

2 Background

This chapter presents the theoretical foundations necessary to understand the phenomena investigated experimentally in this thesis. These concepts encompass the electronic structure of solids, the mechanisms underlying spin-dependent phenomena, and the techniques used for their characterization. The basic aspects of exchange interaction and spin-orbit coupling (SOC), central to spintronic materials, are explored. Additionally, the theoretical methods employed by collaboration partners to supplement the experimental characterizations are briefly discussed.

Section 2.1 provides an overview of the electronic structure in solids, starting from Bloch's theorem, which describes the periodic nature of electronic wave functions in crystals. Then, spin-dependent interactions in a solid and their manifestations in the electronic structure are briefly introduced. The interplay between exchange interaction and SOC is discussed qualitatively.

The photoelectric effect, fundamental to photoemission spectroscopy, is addressed in Section 2.2. The discussion includes the photoemission process, the nature of final states, and techniques for resolving the out-of-plane momentum component ($k_{\perp}$) of electronic states, which are critical for accurate momentum-space mapping.

Finally, Section 2.3 introduces the theoretical methods used in this study. Density functional theory (DFT), a cornerstone of electronic structure calculations, is briefly described alongside the Korringa-Kohn-Rostoker (KKR) method, which is particularly well-suited for studying magnetic and spin-resolved phenomena in complex systems. These methods provide the computational framework for analyzing the electronic and magnetic properties of ultrathin FePd alloys.

2.1 Electronic structure in solids

2.1.1 Bloch's theorem

The wave function of a non-relativistic electron in a potential $V(\vec{r})$ can be expressed via the time-independent Schrödinger equation:

$$\mathcal{H}|\Phi(\vec{r})\rangle = [\mathcal{T} + V(\vec{r})]|\Phi(\vec{r})\rangle = \left[\frac{\hat{p}^2}{2m} + V(\vec{r}) \right]|\Phi(\vec{r})\rangle = E|\Phi(\vec{r})\rangle \quad (2.1)$$

The momentum operator $\hat{p}$ (through the kinetic energy operator $\mathcal{T}$) and the potential are contained in the Hamiltonian acting on the electron wave functions $\Phi(\vec{r})$. In a crystalline solid, the periodic arrangement of atoms gives rise to a periodic lattice potential. The electron wave function in such a periodic potential can be described

using Bloch's theorem [18]. According to this theorem, the wave function can be expressed as the product of a periodic function and a plane wave [19, 20]:

$$\Phi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{a}} u_{\vec{k}}(\vec{r}) \quad (2.2)$$

Here, $\vec{k}$ represents the electron wave vector in the crystal lattice, $\vec{r}$ is the electron's position vector, and $u_{\vec{k}}(\vec{r})$ is a periodic function sharing the periodicity of the crystal lattice. In a finite crystal, $\vec{k}$ assumes discrete values determined by the crystal's size and symmetry. However, in an infinite crystal, $\vec{k}$ forms a continuous spectrum. It is referred to as the crystal momentum. For any wave function satisfying the Schrödinger equation, there exists a wave vector $\vec{k}$ such that under a translation by a lattice vector $\vec{a}$, the wave function transforms as [21]:

$$\Phi_{\vec{k}}(\vec{r} + \vec{a}) = e^{i\vec{k}\cdot\vec{a}} \Phi_{\vec{k}}(\vec{r}). \quad (2.3)$$

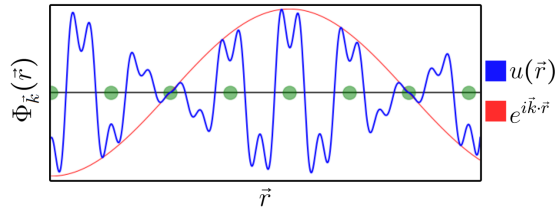
Figure 2.1a illustrates the schematic of a Bloch wave function in a one-dimensional lattice. The electronic states in a solid are described as Bloch states with a wave vector $\vec{k}$, while the periodic potential $V(\vec{r})$ reflects the symmetry of the crystal lattice. In momentum space, this periodicity gives rise to the formation of energy bands and band gaps in the electronic structure. Figure 2.1b presents the energy dispersion of a free electron in an empty lattice, along with the nearly free electron approximation, where a weak periodic potential induces band gaps in the electronic structure.

The band structure of a solid, $E_n(\vec{k})$, represents a complete set of energy eigenvalues labeled by the band index n (represented by different colors in Figure 2.1b) and the electron wavevector $\vec{k}$. The electronic wave functions depend on the spatial coordinates $\vec{r}$, the wave vector $\vec{k}$, and on the band index n . These wave functions can be further classified according to the irreducible representations Γ^δ of the crystal's symmetry group. Consequently, a Bloch state may be expressed as $|n, \Gamma^\delta, \vec{k}\rangle$ [22]. In a crystalline solid, the atomic angular momentum l ceases to be a good quantum number due to the breaking of spherical symmetry by the crystal field. As a result, states with different angular momentum values hybridize (e.g., sp or spd hybridization). The next subsection considers the additional effects introduced by the presence of the electron spin.

2.1.2 Spin-dependent interactions in a solid

Every electronic state in a solid can be identified by a complete set of quantum numbers $|n, \Gamma^\delta, \vec{k}, s\rangle$ formally with s being the spin quantum number. As long as the Hamiltonian only affects the wave function's spatial component, $|n, \Gamma^\delta, \vec{k}\rangle$ and $|s\rangle$ can be divided into separate spatial and spin components, as is the case in equation 2.1. Additional interactions in the Hamiltonian are necessary for the emergence of explicit spin effects in the electronic structure. Only in the context of relativistic quantum mechanics, the electron spin can be sufficiently addressed. In this case, the Dirac equation describes the problem of electrons moving in an electromagnetic field and replaces the Schrödinger equation. Solutions of the Dirac equations are rigorously

a Bloch wave functions in 1-D periodic lattice



b Nearly free-electron dispersion

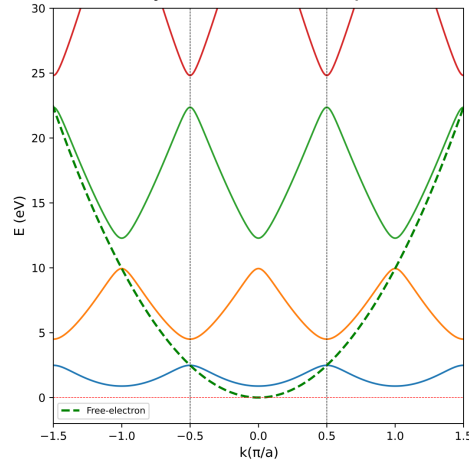


Figure 2.1: **a** Bloch wave functions in a one-dimensional lattice. The green solid circles represent the atom cores in a periodic one-dimensional chain. **b** Comparison between empty lattice free-electron dispersion and nearly free electron dispersion with a weak periodic lattice potential in the extended zone scheme.

used in modern electronic structure calculations. However, when it comes to the discussion of electronic wave functions, a Dirac spinor is not intuitive from a didactic standpoint. Therefore, one attempts to simplify the issue to a more manageable form whenever possible. The Dirac equation can be approximated in a non-relativistic limit as long as the particle's kinetic and potential energies are both small in relation to mc^2 . One obtains two-component spinors as specified in equation 2.5, while the other two components are infinitesimally small. The Pauli equation is the resultant description of a single-electron system [22, 23]:

$$\left[\underbrace{\frac{1}{2m} \left(\hat{\vec{p}} - \frac{e}{c} \vec{A} \right)^2 + eV(\vec{r})}_{\mathcal{H}_0} - \underbrace{\frac{e\hbar}{2mc} \hat{\vec{\sigma}} \cdot \vec{B}}_{\mathcal{H}_B} + i \underbrace{\frac{e\hbar}{4m^2c^2} \vec{E} \cdot \hat{\vec{p}}}_{\mathcal{H}_D} - \underbrace{\frac{e\hbar}{4m^2c^2} \hat{\vec{\sigma}} \cdot (\vec{E} \times \hat{\vec{p}})}_{\mathcal{H}_{SOC}} \right] \Phi = E\Phi, \quad (2.4)$$

in which

$$\Phi = \varphi_a(\vec{r}) |\uparrow\rangle + \varphi_b(\vec{r}) |\downarrow\rangle \quad (2.5)$$

The Hamiltonian in equation 2.1 is contained within the first term, $\mathcal{H}_0$, which governs the symmetry properties of the lattice and incorporates the vector potential A in the presence of an applied magnetic field. The Darwin term, $\mathcal{H}_D$, can be interpreted as a relativistic correction to the electron's energy. Importantly, the symmetry of the system described by $\mathcal{H}_0$ remains unchanged when $\mathcal{H}_D$ is included. The interaction between an external magnetic field, $\vec{B}$, and the electron spin, $\hat{\vec{\sigma}}$ (the vector of Pauli matrices), is described by $\mathcal{H}_B$. This term breaks time-reversal symmetry, as the magnetic field $\vec{B}$ does not satisfy the time-reversal symmetry condition. A consequence of this breaking is the field-induced splitting of degenerate energy levels, as observed in the Zeeman effect. Finally, $\mathcal{H}_{SOC}$ establishes a connection between the electron's spin and position.

Equation 2.4 was derived for a single-electron system, and $\mathcal{H}_B$ does not describe the situation in a ferromagnet where spin-dependent level splitting arises due to exchange and correlation in a many-electron system. The way to account for these effects is through a many-electron approach, such as density functional theory. An effective potential $V_{exc}^{\uparrow\downarrow}(\vec{r})$ contains exchange and correlation effects, and the density functional treatment of the many-electron problem results in a set of single-electron (Kohn–Sham) equations. For the single-electron Hamiltonian, this so-called exchange and correlation potential results in a spin-dependent contribution $\mathcal{H}_{ex}$. In the most basic instance of a Stoner–Wohlfarth-type model, this term may be described by:

$$\mathcal{H}_{ex} = \pm eV_{exc}^{\uparrow\downarrow}(\vec{r}). \quad (2.6)$$

The positive and negative signs correspond to the potentials for $|\uparrow\rangle$ and $|\downarrow\rangle$ electrons, respectively, resulting in degeneracy lifting in ferromagnetic systems. By incorporating the exchange term into equation 2.4, the Hamiltonian of a ferromagnetic system can be described by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_B + \mathcal{H}_D + \mathcal{H}_{SOC} + \mathcal{H}_{ex}. \quad (2.7)$$

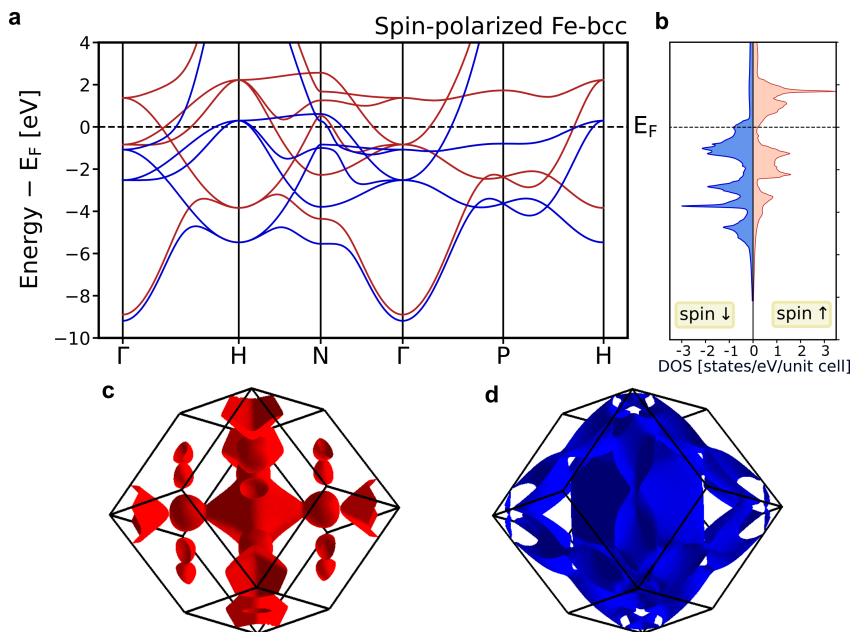


Figure 2.2: The spin-polarized non-relativistic band structure of Fe is computed using the FPLAPW method within the LDA+U framework implemented in `elk` code. (a) The band dispersion reveals the exchange-induced splitting between spin-up and spin-down bands. (b) The corresponding density of states (DOS) for spin-up and spin-down electrons is shown in red and blue, respectively. (c) and (d) illustrate the Fermi surface sheets composed of spin-up and spin-down electrons, respectively, highlighting the distinct electronic structure for each spin channel.

Since the spin aligns along the quantization axis set by the magnetic field vector $\vec{B}$, the term $\mathcal{H}_B$ establishes a direct connection between the spin component and real space. In contrast, the exchange interaction $\mathcal{H}_{ex}$ alone does not link spin to spatial coordinates. Instead, in ferromagnets, the spontaneous magnetization $\vec{M}$ arising from $\mathcal{H}_{ex}$ takes the role of an effective magnetic field. Consequently, $\mathcal{H}_B$ and $\mathcal{H}_{ex}$ are often treated together as a unified contribution, both responsible for breaking time-reversal symmetry [22].

2.1.3 Ferromagnetism and the Stoner criterion

Itinerant ferromagnetism or band magnetism is a form of magnetism that arises from the exchange interaction between delocalized electrons across the entire material, contrasting with magnetism which is based on localized interactions at individual atomic or ionic sites [24–26]. This phenomenon is fundamental to understanding the magnetic properties of metals, especially transition metals such as iron (Fe),

cobalt (Co), and nickel (Ni), which exhibit ferromagnetism due to their partially filled electron bands [27, 28].

The Stoner model provides a pivotal framework for explaining itinerant ferromagnetism through the exchange interaction among itinerant electrons [28, 29]. The model posits that a material exhibits ferromagnetic ordering when the exchange energy, characterized by the intra-atomic exchange interaction energy U , is sufficient to overcome thermal disturbances, leading to a magnetically ordered state. The condition for the onset of ferromagnetism, according to the Stoner criterion, is given by:

$$U\rho(E_F) > 1, \quad (2.8)$$

where U denotes the intra-atomic exchange interaction energy, and $\rho(E_F)$ is the density of states at the Fermi level, E_F . This criterion signifies that ferromagnetism arises when the product of U and $\rho(E_F)$ exceeds a critical threshold, indicating the system's propensity for spontaneous magnetic ordering.

In elemental crystals of Fe, Co, and Ni, the magnetic moments are attributed to electrons in partially filled bands (notably the $3d$ bands for these transition metals). When the Stoner criterion is satisfied, the ferromagnetic order becomes energetically favorable. The magnetic moments observed in these materials— $2.2 \mu_B/\text{atom}$ for Fe, $1.72 \mu_B/\text{atom}$ for Co, and $0.64 \mu_B/\text{atom}$ for Ni [30]—underscore the role of itinerant ferromagnetism in their magnetic behavior. The majority and minority spin bands are shifted in energy relative to each other.

While the Stoner model offers a simplified explanation for itinerant ferromagnetism, a more comprehensive understanding requires considering the contributions of exchange and SOC as described by the Dirac equation. The Stoner model, with its homogeneous mean-field assumption, may not fully capture the complexity of many-body effects and strong electron correlations present in these systems.

Figure 2.2 shows the spin-polarized band structure calculations of body-centered cubic Fe using full-potential linearized augmented-plane wave (FPLAPW) with local density approximation formalism (LDA+U). We can see that the spin degeneracy is lifted via exchange interaction along with the breaking of time-reversal symmetry, whereby $E_n(\vec{k}, \uparrow) \neq E_n(-\vec{k}, \downarrow)$ as shown in Figure 2.2a. In general, the localized d -like bands exhibit an exchange splitting of approximately 1.8 eV, as evident from the spin-resolved density of states in Figure 2.2b, where spin-up electrons of the majority band predominantly occupy the Fermi level. Due to the significant exchange splitting, the Fermi surfaces of the spin-up and spin-down electrons in Figure 2.2c and d are vastly distinct. Our theoretical calculations agree with existing literature on bcc Fe [31] while neglecting the effects of SOC [32].

2.1.4 Spin-orbit coupling in solids

Fundamentally an atomic property, SOC describes the interaction between an electron's spin $\vec{\sigma}$ and its orbital motion in an electric field, specifically its orbital angular

momentum $\vec{L}$ in a spherically symmetric potential. For the electrostatic potential $V(\vec{r})$ of a crystalline solid, the SOC Hamiltonian, $\mathcal{H}_{SOC}$, is expressed as [33]:

$$\mathcal{H}_{SOC} = \frac{e\hbar}{4m^2c^2} \hat{\sigma} \cdot [\vec{\nabla} V(\vec{r}) \times \hat{p}], \quad (2.9)$$

The wave function in a system with SOC is generally a linear combination of the two spin states, forming a two-component spinor. $\mathcal{H}_{SOC}$ is crucial in shaping a material's electronic structure, as it induces energy splittings in bands and lifts degeneracies at specific points in momentum space [22].

Spin-orbit coupling (SOC) lowers the symmetry of the electronic structure by modifying the allowed symmetry operations in a system. In the presence of SOC, the electronic states transform according to the relativistic double group, which is formed by combining the single-group symmetry operations with the SU(2) spin rotational group. Consequently, the number of irreducible representations decreases compared to the case without SOC, reflecting an overall reduction in symmetry. With SOC included, the single-group symmetry is no longer a valid quantum number, and each electronic band in momentum space (k -space) is expressed as a linear combination of distinct single-group representations at every k -point.

To gain deeper insights into the electronic structure of bulk single-crystalline Pd and Rh, we performed DFT calculations using the open-source **e1k** code [34]. The calculations were carried out using reference parameters available in the literature for Pd [35–37] and Rh [38, 39]. The impact of SOC is clearly observed in the computed electronic structures shown in Figures 2.3a and b. A direct comparison between calculations with and without SOC for paramagnetic Pd and Rh reveals pronounced band splitting due to symmetry lowering, particularly along the Γ –L direction.

In addition, when bands with identical double-group characters but different single-group (spatial) symmetries intersect, a band hybridization gap forms. This results in a change in the spatial symmetry of the bands across the hybridization region, fundamentally linking relativistic effects to the symmetry properties of the crystal lattice. SOC significantly affects the band structure at high symmetry points in the Brillouin zone, where band crossings frequently occur due to the underlying crystal symmetry. At these points, the inclusion of SOC lifts degeneracies by hybridizing spin and orbital states. Figures 2.3a and b show multiple band crossings between the W-point and the L-point, as well as the Γ –K direction, which are gapped due to band hybridizations.

The inclusion of SOC is predicted to influence the band dispersion and reshape the Fermi surface, as suggested by Figures 2.3c and d. In Pd, theoretical calculations indicate that the L-point hole pocket appears only when relativistic SOC effects are considered. This SOC-induced restructuring of the Fermi surface is crucial as it directly influences the material's transport properties, such as electrical conductivity, thermoelectric coefficients, and magnetoresistance.

In metallic systems such as Pd and Rh, the gaps opened by SOC at specific points in the Brillouin zone also influence the density of states near the Fermi level, impacting scattering processes and overall transport behavior. In ferromagnetic systems, where

SOC contributions are significant, these gaps can play a role in spin-dependent transport phenomena, such as the anomalous Hall effect. The redistribution of electronic states due to SOC-induced gaps is also crucial for understanding magnetic anisotropy, spin textures, and other spintronic properties [40–43].

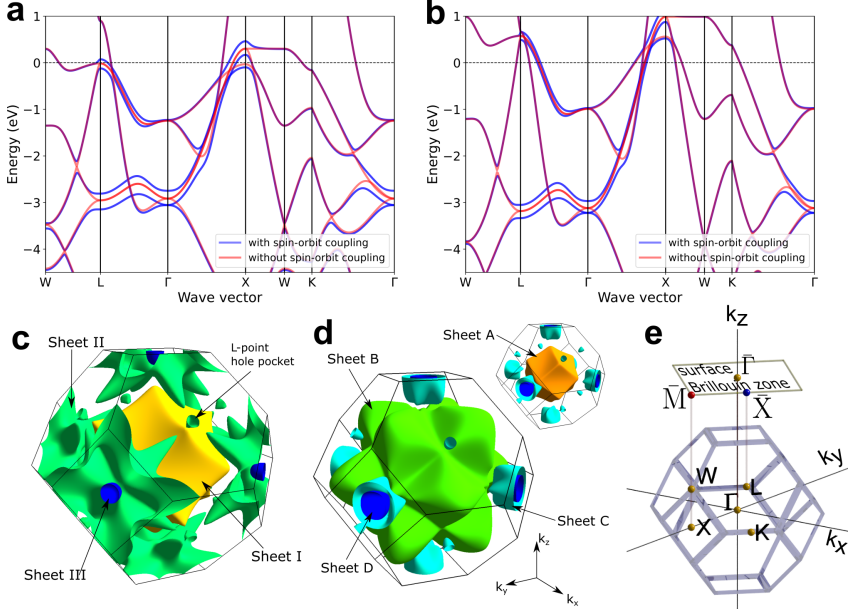


Figure 2.3: Band structure of Pd and Rh calculated using `elk` code with FPLAPW with LDA+U formalism. The band dispersions of **a** Pd and **b** Rh show the significant degeneracy lifting with the introduction of SOC in the theory. In addition, as Pd features an additional valence electron, the shift in the Fermi level of the otherwise similar dispersion can be visualized. **c** and **d** show the relativistic Fermi surface of Pd and Rh, respectively. **e** denotes the relevant high-symmetry points in the face-centered cubic Brillouin zone and its corresponding surface Brillouin zone.

On the other hand, degeneracy lifting of the Bloch states can also be induced by the breaking of inversion symmetry combined with SOC in a crystalline lattice. The time-reversal operation transforms time t to $-t$, momentum $\vec{k}$ to $-\vec{k}$, magnetic field $\vec{B}$ to $-\vec{B}$, and spin $\uparrow$ to $\downarrow$. According to Kramers' theorem, the time-reversal partner of the Bloch state $\varphi_{(\vec{k}, \uparrow)}$ with energy $E(\vec{k}, \uparrow)$ is $\varphi_{(-\vec{k}, \downarrow)}$ with the same energy $E(-\vec{k}, \downarrow)$. Furthermore, space inversion operation takes momentum $\vec{k}$ to $-\vec{k}$ and leaves the spin invariant. Therefore, any electronic state is at least two-fold degenerate when both time-reversal and inversion symmetries are present, since:

$$\left. \begin{array}{l} \text{time-reversal: } E(\vec{k}, \uparrow) = E(-\vec{k}, \downarrow) \\ \text{space inversion: } E(\vec{k}, \uparrow) = E(-\vec{k}, \uparrow) \end{array} \right\} \implies E(\vec{k}, \uparrow) = E(\vec{k}, \downarrow). \quad (2.10)$$

In the presence of SOC and broken inversion symmetry, equation 2.10 no longer holds, and the spin degeneracy is lifted, resulting in spin-polarized states. For example, an external electric field can generate a potential gradient that breaks inversion symmetry. Such an asymmetry may occur in noncentrosymmetric crystals [44, 45] and across surfaces and interfaces of crystalline lattices [10, 11, 46].

SOC may manifest through the Rashba-Bychkov effect, arising from quantum confinement in the film and the breaking of inversion symmetry induced by the surface potential barrier between the film and vacuum, as well as the interface barrier between the film and substrate. The Rashba-Bychkov effect was first predicted by Emanuel Rashba in 1959 and has since been observed in a wide range of materials [10, 11]. Within the model of Rashba and Bychkov, a two-dimensional free electron gas is confined by a one-dimensional asymmetric potential $V(\bar{z})$ perpendicular to it, forming the potential gradient $\vec{\nabla}V = \frac{\delta V}{\delta z}\bar{z}$. This reduces equation 2.9 to:

$$H_{SOC} = \alpha \vec{\sigma} \cdot \bar{z} \times \vec{k} \quad (2.11)$$

where α is the Rashba parameter which scales proportionally to $\vec{\nabla}V$. In this case, the free-electron parabolic bands undergo spin splitting, following the expression

$$E_{\pm}(\vec{k}_{\parallel}) = \frac{\hbar^2 \vec{k}_{\parallel}^2}{2m} \pm \alpha |\vec{k}_{\parallel}|, \quad (2.12)$$

where the splitting is proportional to $\vec{k}_{\parallel}$, as illustrated in Figure 2.4b [47].

The two Fermi contours are spin-momentum locked but exhibit opposite helicity with the expectation values for the spin aligned in-plane (k_x, k_y) and orthogonal to $\vec{k}_{\parallel}$.

Although the original model by Rashba-Bychkov qualitatively captures the principle behind the Rashba effect, experimental results showed that the effect's magnitude is several orders larger [16, 48–50]. The assumption where the potential gradient at an interface is dominated by the electric field normal to the interface, made in equation 2.11, turns out to be incomplete because the potential gradient $\vec{\nabla}V$ is governed by the potential drop near the nucleus and maintains spherical symmetry, $\vec{\nabla}V = \frac{\delta V}{\delta r} \frac{\vec{r}}{r}$, even in proximity to an interface [46, 51].

As a result, the SOC term is expected to follow the Russell–Saunders formula for atoms:

$$H_{SOC} = \frac{1}{2m^2c^2} \frac{\delta V}{\delta r} \frac{1}{r} (\vec{L} \cdot \vec{S}) \propto \vec{L} \cdot \vec{S}. \quad (2.13)$$

In other words, the interfacial potential gradient influences the Bloch wave function of the conduction electrons, causing them to acquire a momentum-dependent orbital moment, $\vec{L}_n(\vec{k})$, rather than directly modifying the SOC Hamiltonian itself. Such a scheme can be approximated in DFT where the SOC is significant only in a spatial region close to the nucleus [47, 52, 53]. Additionally, it is important to note that SOC does not break time-reversal symmetry, as shown in Figure 2.4b, and the spin-polarization vanishes in $\vec{k}$ -averaging at any given energy.

While both exchange interaction and SOC can contribute to the lifting of spin degeneracy in electronic structures, their underlying mechanisms differ fundamentally. Exchange interaction arises from the Pauli exclusion principle between electrons and results in an energy difference between parallel and antiparallel spin alignments. This leads to a homogeneous lifting of spin degeneracy across the electronic bands. In contrast, SOC is a relativistic effect that links the spin and orbital degrees of freedom, leading to spin splitting that is often momentum-dependent and more localized in certain regions of the Brillouin zone.

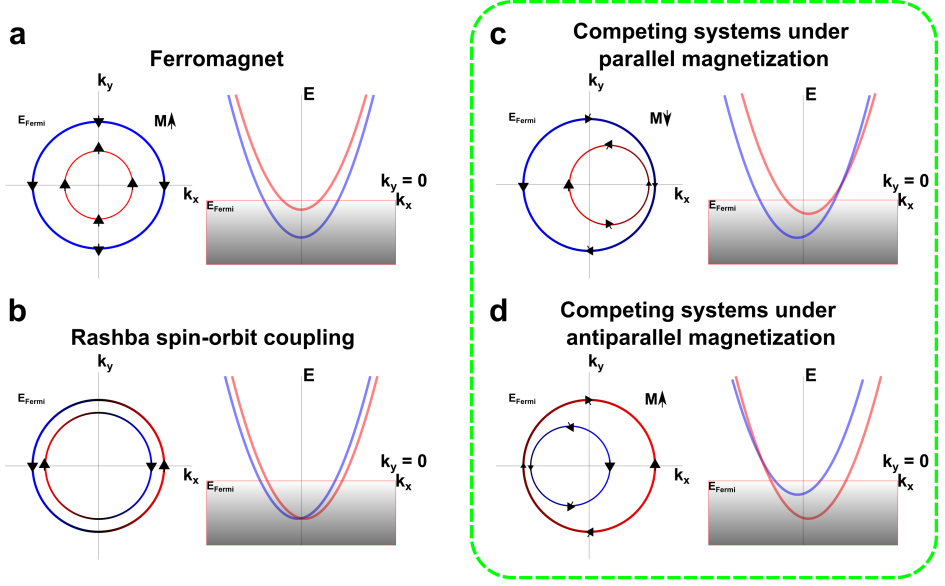


Figure 2.4: Simplified schematics depicting the interplay between SOC and exchange interaction in electronic structures [54]. The figure highlights the spin-degeneracy lifting of bands exclusively through **a** exchange and **b** SOC. In panels **c** and **d**, non-interacting bands are portrayed, demonstrating the competing effects of exchange and SOC under parallel and antiparallel magnetizations, respectively. The size of the arrows in the figure represents the magnitude of the local spin angular momentum. The spin quantization axis is along the $\vec{k}_y$ axis.

Figures 2.4a and b illustrate schematically contributions of the exchange interaction and SOC to spin degeneracy lifting by equations 2.6 and 2.12, respectively. Figure 2.4a sketches the spin-split bands of a ferromagnet with an in-plane magnetization in the y -direction M_y , yielding a majority spin-down band (blue) and a minority spin-up band (red). In contrast, the spin-split band resultant from Rashba-type SOC does not break time-reversal symmetry, and its splitting is proportional to $k_{\parallel}$.

In a system where both time-reversal symmetry and inversion symmetry are broken, the Fermi contour in the electronic structure can exhibit anisotropy. In the ferromag-

net model with in-plane magnetization depicted in Figure 2.4a, the introduction of SOC causes a reduction in symmetry. This combination leads to a two-fold symmetry in the Fermi contours, as seen in Figures 2.4c and d, which is different from the original isotropic system. Additionally, the anisotropy of the electronic states in momentum space is influenced by the magnetization direction in a ferromagnetic system [46], as shown in Figure 2.4c for magnetization in $-y$ direction ($\vec{M} \downarrow$) and Figure 2.4d for magnetization in $+y$ direction ($\vec{M} \uparrow$).

2.2 Photoelectric effect

Photoelectron spectroscopy (PES) is a technique for investigating the electronic properties of materials. In this technique, a material is exposed to light of a certain frequency, and the resulting photoemitted electrons are detected and spectroscopically analyzed. The information obtained from the photoemitted electrons provides valuable insights into the electronic structure of the material [55, 56].

The photoelectric effect, discovered by Hertz and Hallwachs in 1887 [57], forms the foundation of photoelectron spectroscopy. This phenomenon occurs when light of sufficient frequency strikes a material, leading to the emission of electrons from its surface. For this to happen, the energy of the incident photons must exceed the material's work function—the minimum energy required to liberate an electron from the surface.

To interpret the results of PES experiments, it is necessary to understand the underlying physics of the photoemission process, which is governed by the principles of energy and momentum conservation during the photoexcitation. When a photon is absorbed by a material, its energy is transferred to an electron, which is then ejected from the material's surface. The energy of the emitted electron follows the photoelectric equation:

$$h\nu = E_{\text{kinetic}} + E_{\text{binding}} + \phi \quad (2.14)$$

where $h\nu$ is the energy of the incident photons, E_{kinetic} is the kinetic energy of the emitted electron, and E_{binding} is the binding energy of the electron in the material, and ϕ is the material-dependent work function.

The kinetic energy of emitted photoelectrons is measured using a hemispherical analyzer, which employs an electrostatic field between two concentric hemispheres to disperse electrons based on their kinetic energy. After emission from the material, the electrons are guided by electrostatic lenses into the entrance of the analyzer, where they experience a radial electrostatic field that forces them onto curved trajectories. The degree of deflection depends on their kinetic energy, allowing energy filtering. Only electrons within a specific energy range pass through the exit slit and reach the detector, where their intensity is recorded. By scanning the electrostatic potential applied to the analyzer, the entire kinetic energy spectrum of the emitted electrons can be mapped, enabling a detailed reconstruction of the material's electronic structure.

In the simplest picture of PES, a beam of monochromatic photons of sufficiently high energy is directed at the material, and the emitted electrons are detected and

analyzed [58]. The interpretation of PES data requires accounting for various effects, including final state interactions of the photoemitted electron with other electrons, surface states, and many-body interactions. To address these complexities, models such as the three-step model and the one-step model have been developed [55, 59], each providing different perspectives on the photoemission process. Many-body effects, such as electron-electron interactions and electron-phonon coupling, further influence the spectral features, which may necessitate advanced theoretical approaches for accurate data interpretation [14, 60–62].

2.2.1 Photoemission process

Formally, the photoemission process can be described by the transition probability $w_{i \rightarrow f}$ from an N -electron initial state Ψ_i^N to an excited final state Ψ_f^N . This probability can be approximated using Fermi's Golden Rule [13, 14]:

$$w_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu) \quad (2.15)$$

where E_f^N and E_i^N are the final and initial state energies of an N -electron system. It is worthwhile to emphasize that this formalism is limited to weak perturbations, and higher-order perturbation terms must be included to describe nonlinear effects such as multi-photon absorption processes.

The interaction Hamiltonian H_{int} describing the coupling between the electromagnetic field and the electrons in the material can be expressed as [14]:

$$\begin{aligned} H_{int} &= \frac{1}{2m} \left(\vec{p} - \frac{e}{c} \vec{A} \right)^2 - e\Phi - \frac{\vec{p}^2}{2m} \\ &\approx \frac{e}{2mc} (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) \\ &\approx \frac{e}{mc} \vec{A} \cdot \vec{p} \end{aligned} \quad (2.16)$$

where e is the elementary charge, m is the electron mass, $\vec{A}$ is the electromagnetic vector potential, and $\vec{p}$ is the momentum operator of the electron. This form of H_{int} assumes that the interaction is dominated by the electric dipole term, which is valid when the photon wavelength is much larger than the characteristic length scale of the atomic orbitals. Within the dipole approximation, the spatial variation of the vector potential $\vec{A}$ is neglected on the atomic scale. The two-photon processes term $\vec{A}^2$ is dropped and $\vec{A}$ is taken to be bulk-like or constant over the atomic dimensions so that $[\vec{A}, \vec{p}] \sim \nabla \cdot \vec{A} = 0$ [14, 55].

The transition probability is governed by the matrix element $\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle$, which encodes the probability amplitude for an electron to absorb a photon and transition to a final state. The Delta function $\delta(E_f^N - E_i^N - h\nu)$ ensures energy conservation in the process. Since the final state $|\Psi_f^N\rangle$ contains an ejected photoelectron, the

measured photoemission intensity $I(E, \vec{k})$ is proportional to the modulus squared of the transition matrix element:

$$I(E, \vec{k}_f) \propto \sum_f \left| \langle \Psi_f^N | H_{int} | \Psi_i^N \rangle \right|^2 \delta(E_f^N - E_i^N - h\nu). \quad (2.17)$$

In the non-interacting electrons assumption, the one-electron dipole matrix element $M_{i \rightarrow f}^{\vec{k}}$ and the photoemission intensity $I_{i \rightarrow f}(\vec{k}_f, E) = \sum_{i,f} \Gamma_{i \rightarrow f}$ can be expressed as follows [14, 63]:

$$\mathcal{M}_{i \rightarrow f}^{\vec{k}} \equiv \langle \Phi_f^{\vec{k}} | H | \Phi_i^{\vec{k}} \rangle \quad (2.18)$$

$$I_{i \rightarrow f}(\vec{k}_f, E) \propto \left| M_{i \rightarrow f}^{\vec{k}} \right|^2 \delta(E_f - E_i - h\nu), \quad (2.19)$$

where $|\Phi_i^{\vec{k}}\rangle$ and $|\Phi_f^{\vec{k}}\rangle$ denote the wave functions of the electron before and after absorbing a photon with $\vec{k}$ under momentum conservation.

An intuitive picture of the photoemission process in solids can be described using the *three-step model*, as shown in Figure 2.5 [64]. It involves three distinct steps: photoabsorption, electron transport, and emission of the photoelectron. In this model, the photoemission process can be described as follows:

1. A photon is absorbed by an electron in the bulk solid, creating an excited state. This process is described by Fermi's Golden Rule, which relates the transition rate between two quantum states to the matrix element of the perturbation that drives the transition.
2. The excited electron scatters on its way from within the solid to the surface as depicted by the dashed blue line in Figure 2.5. This process is usually described by the inelastic mean-free path of electrons in the solid [65, 66].
3. The excited electron at the surface of the solid is emitted into the vacuum, crossing the surface barrier. The electron ultimately occupies a free-electron plane wave state (red line) in the vacuum with phase-matching conditions at the surface.

The one-electron picture and *three-step model* provide a qualitative framework for understanding the photoemission process in solids, and it has been successful in explaining experimental observations [55, 56]. However, it is a simplified picture of the complex photoemission process, and it often does not appropriately account for the effects of many-body interactions, SOC, and other interactions that can strongly influence the photoemission spectrum, such as lattice vibration [67] and the photoemission recoil effect [68, 69].

2.2.2 Photoemission final state and $\vec{k}_\perp$

Momentum conservation dictates that the momentum of the initial electronic state in the solid must be transferred to that of its photoexcited final state, thereby enabling

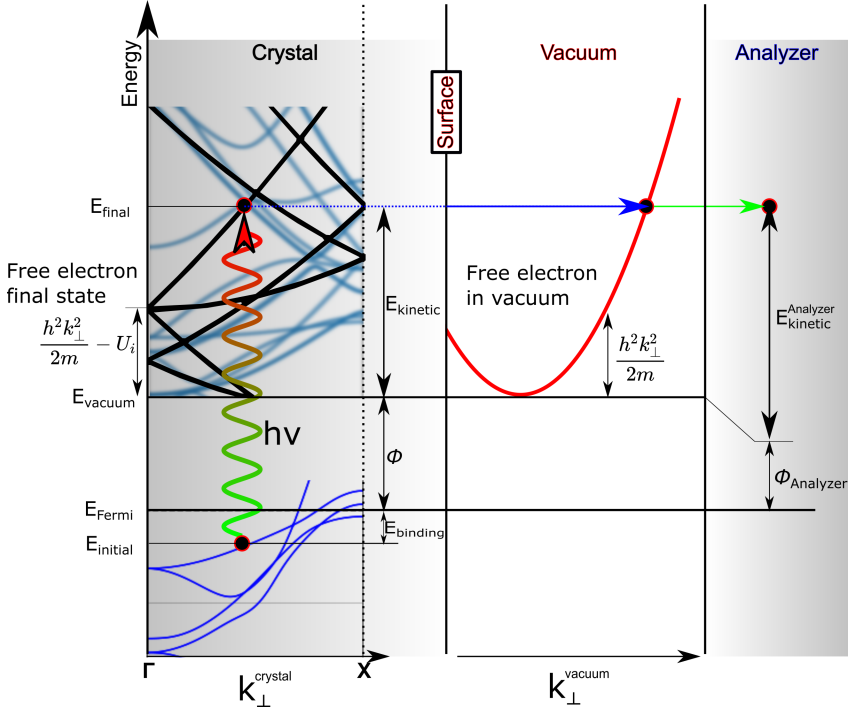


Figure 2.5: Kinematics of one-electron photoemission in the *three-step model*. The process is modeled using photoexcitation with photons of $h\nu = 75$ eV for a palladium single crystal. The thin blue lines represent the theoretical ground state electronic structure of Pd along the Γ -X direction, while the blurred blue lines indicate the broadening of states at higher energies. The black lines correspond to the free-electron-like dispersions in the empty lattice approximation.

the band structure of the system to be probed. Since the photon momentum is negligible in the ultraviolet spectrum, it can be disregarded at this point. However, in the soft- and hard X-ray regimes, its contribution may become significant and should be considered [70]. The magnitude of the measured momentum $\vec{p}$ of a free electron in vacuum with kinetic energy E_{kinetic} can be defined as

$$|\vec{p}| = \hbar |\vec{k}| = \sqrt{2m_e E_{\text{kinetic}}}. \quad (2.20)$$

The in-plane momentum component, $\vec{k}_{\parallel}$, is conserved parallel to the surface of the sample, owing to the periodicity of the crystal lattice. In the plane of the surface, momentum conservation is described by:

$$\vec{k}_{\parallel}^i + \vec{G}_{\parallel} = \vec{k}_{\parallel}^f, \quad (2.21)$$

where $\vec{k}_{\parallel}^f$ and $\vec{k}_{\parallel}^i$ are the final and initial electron wave vectors, respectively, and $\vec{G}_{\parallel}$ is the in-plane reciprocal lattice vector [13].

Due to the abrupt transition between the crystal surface and vacuum, only the in-plane component of the wave vector, $\vec{k}_{\parallel}^i$, is conserved. To reconstruct the out-of-plane component, $k_{\perp}^i$, which corresponds to bulk electronic states, the free-electron final state model [71] may be employed. For photoemission involving transitions from bulk electronic states, a common approximation for determining the perpendicular wave vector component $k_{\perp}$ is to approximate the final state band dispersion using a free electron final state model, leading to:

$$E_f(\vec{k}) = E_f(k) = \frac{\hbar^2 k^2}{2m} + (E_{\text{vacuum}} - U_i), \quad (2.22)$$

This describes a sphere in momentum space and a parabolic energy dispersion relation for the absolute value of the wave vector k . The photoelectron may undergo scattering by the crystal, modifying the wave vector $\vec{k}$ by a reciprocal lattice vector $\vec{G}$ [72]:

$$E_f(\vec{k} + \vec{G}) = \frac{\hbar^2}{2m} \left((k_{\parallel,x} + G_{\parallel,x})^2 + (k_{\parallel,y} + G_{\parallel,y})^2 + (k_{\perp} + G_{\perp})^2 \right) + (E_{\text{vacuum}} - U_i). \quad (2.23)$$

Within this model, the discontinuity at the surface is approximated by a free-electron-like dispersion, shown as a red curve in Figure 2.5, with its minimum at $E_f(0)$ offset by an inner potential U_i , which represents the average effective potential experienced by electrons inside the crystal.

The center of the free-electron sphere in momentum space is located at $-\vec{G}$. In the reciprocal lattice, a given E_f defines a $\vec{k}$ -spherical shell, which intersects the Brillouin zone. The radius of this free-electron final state sphere is given by:

$$|\vec{r}_k| = \frac{\sqrt{2m}}{\hbar} \sqrt{E_{\text{kinetic}} + U_i}. \quad (2.24)$$

In this study, the momentum distribution of constant initial-state electronic band structures at various E_f values is investigated by scanning across photon energies using a tunable synchrotron light source [73].

In addition, two-dimensional electronic states do not disperse with $\vec{k}_{\perp}^{\text{initial}}$, and therefore, such an approximation is only applied when probing bulk states, where the $\vec{k}_{\perp}^{\text{initial}}$ of the initial state must match that of the final state. It is crucial to note that the free electron final state approximation does not hold in general, particularly for low E_{kinetic} measurements or photoemission using low- $h\nu$ photons.

As shown in Figure 2.6, this can be understood intuitively with an evanescent or decaying wave function when the initial state is excited into a gap in the final state band structure, as in the simple case of a nearly free electron model. This topic will be discussed further in section 4.1.1, where the study demonstrates the limitations of the model in the low energy limit.

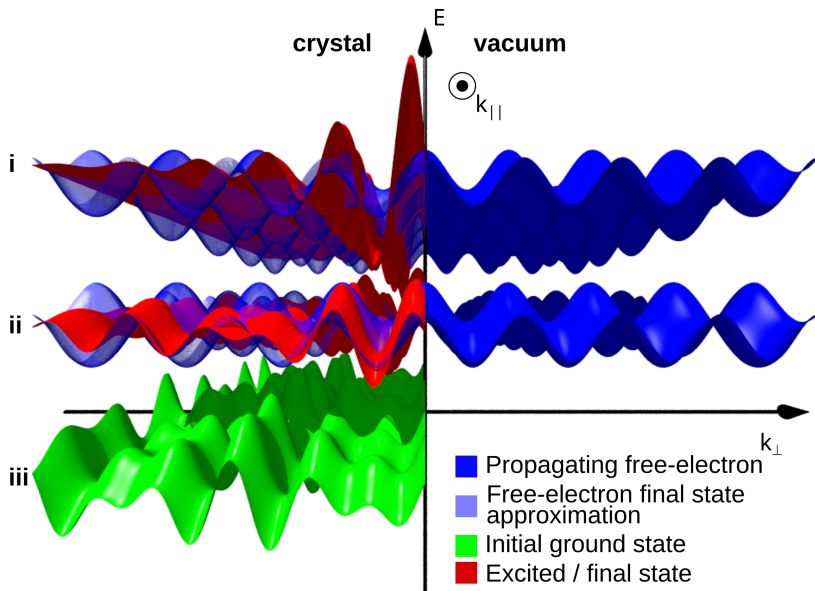


Figure 2.6: Illustration of the wave function matching condition between the solid and vacuum along the sample surface in photoemission. **i** Final state where the evanescent state dominates and the free-electron approximation fails. See section 4.1.1 for further investigations. **ii** Free-electron final states match reasonably well with the final state in the unoccupied bands. **iii** Ground state of the wave function in a crystal.

2.3 Theoretical methods

While the focus of this thesis lies in experimental work, it is crucial to underscore the essential role that theoretical calculations play in interpreting experimental results. DFT [74, 75] is a quantum mechanical framework widely used in condensed matter physics, materials science, and quantum chemistry to calculate electronic properties [76, 77]. It is based on the Hohenberg-Kohn theorems [74], which establish a one-to-one correspondence between the electron density and the external potential, simplifying the many-body problem. In DFT, the electronic system is described by non-interacting particles moving in an effective potential. The Kohn-Sham equations are solved, and the electron density is used to compute various electronic properties [75]. DFT has been instrumental in the discovery of novel materials, the study of electronic structures, and the rational design of materials.

The `elk` code is an all-electron FPLAPW DFT code [78], which can provide electronic structure calculations for materials. FPLAPW is characterized by linearization of the Schrödinger equation, resulting in improved convergence properties and augmentation of the interstitial electron density using localized basis functions. It ensures a full potential treatment, allowing the consideration of all electron-nucleus interac-

tions without pseudopotentials. The LAPW basis is created by dividing space into spherical regions around atoms, referred to as muffin-tins, as well as the unoccupied interstitial space. The basis functions inside the muffin-tins are formed through linear combinations of atomic-like orbitals, while plane waves occupy the interstitial region.

Atomic-like local orbitals are a set of basis functions that are spatially localized around specific atomic sites or regions within a crystal, in which the expectation values of projected orbital characters of the electronic states can be resolved. At the interface between these regions, the functions and, when necessary, their derivatives are adjusted to ensure the continuity or differentiability of the basis functions [34]. LAPW calculations typically employ exchange-correlation functionals, such as LDA and generalized gradient approximation (GGA), to account for electron-electron interactions. This method is well-suited for a wide range of materials, including metals, semiconductors, insulators, and magnetic compounds.

In this thesis, we primarily employed the FPLAPW method for electronic properties determination of bulk metallic systems of Pd(001) and Rh(001), in which the corresponding spin and local orbital characters of the electronic bands are resolved. The theoretical band calculations in Figures 2.2 and 2.3 are obtained using the open-source `elk` code. The calculations are consistent with those reported in the literature [35–39].

Additionally, the Korringa-Kohn-Rostoker formalism employed with DFT by Dr. Ján Minár’s and Dr. Arthur Ernst’s collaborating groups is aptly utilized for the one-step photoemission calculations and the electronic states of the alloy ultrathin films, respectively. The KKR method [79–81] provides direct access to the Green’s function of a given system.

The surface Green’s function [82] is used to formulate observed physical values in almost all surface spectroscopic methods [83, 84]. In addition to the fact that the perturbation can be managed methodically, the Green-function formalism has the advantage of providing access to the spectral weight function or density of states of the ground-state electrons or quasiparticles using the diagonal terms of the constructed Green’s function.

Our collaboration with Dr. Ján Minár primarily focuses on theoretically evaluating the photoemission results of the bulk electronic structure in a single crystalline system. [59, 85]. In this case, the photoemission intensity or the photocurrent was evaluated via the time-reversed low-energy electron diffraction (LEED) state [86]. Local spin density approximation (LSDA) and atomic-spheres approximation (ASA) were used in the one-step model of photoemission calculations implemented in the `SPR-KKR` band structure software package [87]. The one-step photoemission calculations are presented in detail in Chapter 4.

Meanwhile, our collaboration with Dr. Arthur Ernst primarily focuses on the treatment of chemical disorders in the ground-state electronic structure with coherent potential approximation (CPA) [88, 89]. The effective medium whose scattering properties correspond to the averaged scattering properties of the disordered alloy being approximated is then described by the Green’s function that was produced using the CPA. The method is employed extensively in Chapters 5 and 6 for the evaluation of

ultrathin FePd alloy on a Pd(001) substrate.

3 Methodology

This chapter introduces the details of momentum microscopy, the main technique used in this study, and associated experimental techniques for sample fabrication and characterization. Section 3.1 provides a general description of the working principle of a momentum microscope. Section 3.1.4 explains electron spin detection principles using an imaging spin filter. Finally, the sample preparation and fabrication process of Pd(001), Rh(001), and FePd alloy monolayers on Pd(001) is described in section 3.2.

3.1 Momentum microscopy

Building on our discussion of the photoemission process and photoelectron spectroscopy in Section 2.2, having a large acceptance angle in photoemission experiments is crucial, as it allows for probing an extended region of momentum space. The advent of momentum microscopy has significantly enhanced this capability by enabling direct access to momentum-space information without being constrained by the physical limitations of the acceptance angle or the angular-to-momentum resolution conversion. A schematic of the momentum microscope utilized in this thesis is presented in Figure 3.1a. Furthermore, the imaging characteristics of momentum microscopy contribute to high data acquisition efficiency, which is particularly beneficial for experiments involving time- and surface-sensitive systems, as well as for two-dimensional spin detection. These advantages will be revisited in Section 3.1.4 [16, 90, 91].

The invention of the immersion lens was a major breakthrough in optical microscopy, as it significantly improved the resolving power of microscopes beyond what was possible with conventional air-based lenses. Traditionally, the resolution of an optical system is limited by diffraction, which depends on the wavelength of light and the numerical aperture of the lens [92]. By introducing a medium with a higher refractive index—such as water or oil—between the objective lens and the specimen, immersion lenses reduce diffraction effects and increase numerical aperture, thereby enhancing image resolution. Since its introduction at the 1855 Paris Exposition [93], immersion lens technology has been instrumental in advancing high-resolution optical microscopy.

A similar principle can be applied to charged particles, where an "immersion lens" is realized through a strong electrostatic field instead of an optical medium [94]. In electron microscopy, electrostatic immersion lenses are used to manipulate electron trajectories and improve imaging precision. Unlike photons, which travel freely in air,

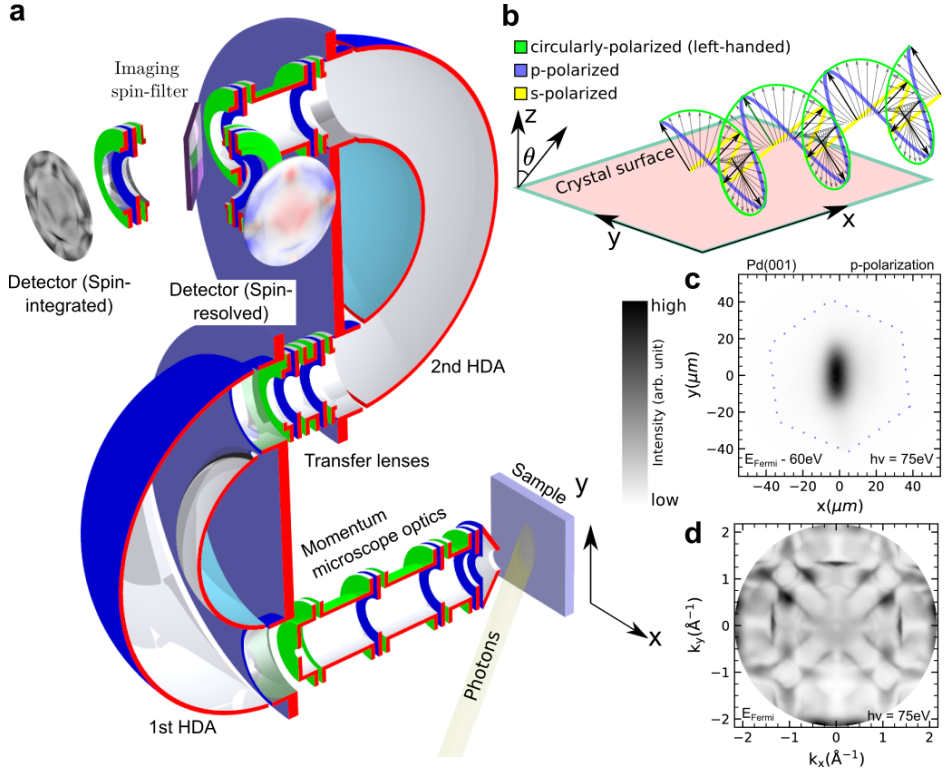


Figure 3.1: **a** Schematic of the momentum microscope system with imaging spin filter at the NanoESCA beamline, consisting of a cryogenic six-axis sample stage, imaging electrostatic lenses, a double-hemispherical analyzer, and spin-filter crystal with branches for spin-integrated and spin-resolved imaging. The W(001) spin-filter crystal is mounted on a goniometer, which can be inserted or retracted. **b** The electric field vectors $\vec{E}$ for p-, s-, and left-handed circularly-polarized photons for the experimental geometry. θ denotes the emission angle with respect to the sample normal. **c** Real space microscopy of Pd(001) photoexcited with the focused synchrotron beam. **d** Momentum map obtained via switching to momentum microscopy mode while preserving all conditions in **c**.

electrons have a limited mean free path in ambient conditions, necessitating their use in vacuum.

In this study, an electrostatic immersion lens (objective lens) is employed to extract photoelectrons from the sample surface. From the perspective of angular acceptance in photoemission experiments, this setup provides a key advantage: the increased "index of refraction" effectively expands the emission angle with respect to the sample normal θ , as denoted in Figure 3.1 b, forming a virtual image with a larger angular spread of θ' . This enhancement allows for collecting photoelectrons over an entire half-sphere, corresponding to a solid angle of 2π sr above the crystal surface. The relationship governing this behavior can be expressed as:

$$\frac{\sin \theta}{\sin \theta'} = \frac{\frac{|\vec{p}_{||}|}{|\vec{p}|}}{\frac{|\vec{p}'_{||}|}{|\vec{p}'|}} = \frac{|\vec{p}'|}{|\vec{p}|} = \sqrt{\frac{eU_{ext}}{E_{kinetic}} + 1} \quad (3.1)$$

Here, U_{ext} represents the accelerating potential of the objective lens, while $\vec{p}'$ and $\vec{p}'_{||}$ denote the total and in-plane momenta of the accelerated photoelectron, respectively. Similarly, $\vec{p}$ and $\vec{p}_{||}$ correspond to their field-free counterparts. The immersion lens strongly accelerates the photoelectron in the direction normal to the sample surface, while its in-plane momentum remains unchanged, leading to the condition $\vec{p}'_{||} = \vec{p}_{||}$.

In this study, all measurements are conducted with an accelerating potential of $eU_{ext} = 15$ keV. Under this condition, the kinetic energy of the photoelectron is negligible in comparison to U_{ext} ($U_{ext} \gg E_{kinetic}$), allowing us to simplify equation 3.1 by approximating the constant term as negligible. Substituting equation 2.20 into this relation, we obtain:

$$\sin \theta' = \frac{|\vec{p}_{||}|}{\sqrt{2meU_{ext}}} \quad (3.2)$$

This equation is fundamental to the concept of momentum microscopy. As $\sin \theta'$ decreases with large U_{ext} , according to the small-angle approximation, the photoelectron cone becomes infinitesimally narrow. Consequently, the lateral position in the focal plane becomes directly proportional to $\sin \theta'$. This allows the microscope to inherently quantify the parallel momenta of the photoelectrons, providing precise information about the momentum distribution of the photoelectrons.

The combination of projective and transfer lenses in a momentum microscope enables switching between real-space and momentum-space imaging. Figure 3.1 c illustrates the real-space imaging mode, which is used to select a small sampling area. The hexagonal shadow, outlined by a dotted line, represents the edges of the field aperture within the microscope. This aperture plays a crucial role in filtering out higher-order diffraction fringes from the beamline mirrors and precisely defining the sampling region. By switching the electrostatic lens to momentum-space imaging mode, a direct momentum map of the selected sampling region is obtained [95]. Further refinement of the image and regional selection in both real and momentum space can be precisely controlled using the field aperture and contrast aperture in the momentum microscope optics section, respectively.

High-resolution band mapping, as shown in Figure 3.1d, would not be possible without the use of an energy filter. The momentum microscope employs an aberration-compensated double-hemispherical analyzer scheme. The first hemispherical deflection analyzer (HDA) acts as the workhorse of energy filtering, while the second HDA compensates for the spherical aberration introduced by the first. Coupling the two hemispheres in an S-shaped setup effectively completes a full 360° trajectory. The closed trajectories of the photoelectrons can be interpreted using the classical Kepler’s three laws of planetary motion. As a result, the photoelectrons are refocused at the endpoint of the double-hemispherical analyzer with respect to the entrance plane, therefore compensating the 180° aberration introduced by the first HDA [91].

NanoESCA beamline endstation at Elettra

The momentum microscopy experiments were carried out at the NanoESCA beamline of the Elettra synchrotron in Trieste, Italy. The beamline is capable of providing both linearly polarized and circularly polarized photons in the energy range between 35 eV and 660 eV. The X-ray angle of incidence, as measured from the sample surface, was fixed at 25° as shown in Figure 3.1b together with the $\vec{E}$ field vector of the photons in different polarizations. s-polarization is defined as the geometry in which the electric field vector $\vec{E}$ is aligned parallel to the sample surface along the x-axis. In contrast, p-polarization refers to its orthogonal counterpart in the yz -plane, where the electric field impinges the sample surface at an angle of 25°. The illuminated region or the X-ray beam spot on the sample is about 40 μm by 20 μm in size in real space, as shown in Figure 3.1c, along with the edges of the field aperture.

Photoelectrons emitted into a complete half-sphere of 2π sr solid angle above the crystal surface were collected by an electrostatic immersion lens and mapped onto a valence band spectral intensity distribution of lateral momenta (k_x, k_y) of the crystal such as the momentum map shown in Figures 3.1d. Here, the photoelectron momentum map is obtained from the illuminated spot in Figures 3.1c. Meanwhile, the perpendicular momentum k_z is not conserved due to the breaking of translational symmetry at the sample surface, as discussed in section 2.2.2. The sample remained stationary throughout the experiments. Hence, the three primary variables are photon energy, photon polarization, and the selected photoelectron energy. All measurements were performed with the sample temperature kept at 100 K.

In all measurements, the lateral momentum resolution of the momentum microscope is better than 0.02 $\text{\AA}^{-1}$. The overall energy resolutions are better than 50 meV for photon energies below 200 eV and 100 meV for photon energies above 200 eV. All experimental results, unless otherwise specified, are raw photoelectron intensity maps with no additional image processing or symmetrization, except for the mandatory flat field correction of the multichannel plate detector. The work function of the analyzer, ϕ_{Analyzer} , in Figure 2.5 is 4.55 eV.

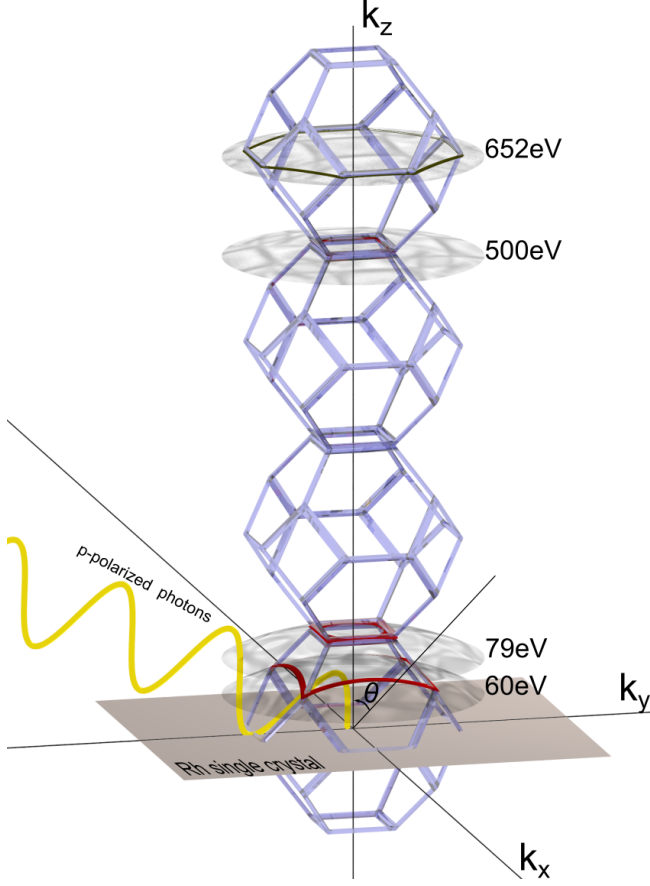


Figure 3.2: Constant initial state (Fermi level) experiment on Rh(001). The conservation of momentum holds for in-plane x and y dimensions, while the out-of-plane z dimension is approximated by a free-electron final state model where the final state is modulated by excitation energy.

3.1.1 Fermi surface tomography

Photoemission processes in the low-energy regime pose a complex challenge, as the final state of the photoelectron significantly influences the measured intensity distributions, $I(E, \vec{k})$, as discussed in previous studies [96, 97]. In our study, we categorize these processes into two distinct energy regimes: the low-energy regime (34–200 eV) and the high-energy regime (>200 eV). In the high-energy limit, we adopt the free-electron final state model, which assumes that the photoelectron's final state approximates a free-electron-like dispersion. Under this model, the initial state—described by the ground-state wave function within the crystal—is excited into a free-electron-like

final state, as depicted by the red solid line in Figure 2.5. A step-potential analogy, illustrated in Figure 2.6, provides insight into the wave-matching condition between the wave functions inside the crystal (blue) and in vacuum (red) at the surface barrier. The simplicity of the free-electron model allows for the extraction of the out-of-plane wave vector, k_1 , under the assumption of a constant crystal inner potential. Experimental data, analyzed within the free-electron final state framework, are presented in Figure 3.2, demonstrating the application of the model at different photon energies.

The kinetic energy of the measured photoelectrons is selected in combination with the photon energy, keeping the probed initial state constant. The final states are approximated as plane waves, representing a free electron-like iso-energy sphere in momentum space that cuts across the Brillouin zone. The radius of this iso-energy sphere is given by equation 2.24, with the inner potential, U_i , generalized as a material-dependent quantity. For the single crystals in our study, we determined values of $U_i = 19.25$ eV and 18.50 eV for Pd(001) and Rh(001), respectively, by comparing a series of constant initial state measurements with the calculated ground states [71].

In our microscopy results, the lateral wave vectors (k_x, k_y) are kept constant, along with the momentum resolution. As a result, the sample size of photoelectrons decreases with the reduced solid angle of emission in real space while simultaneously cutting across the iso-energy spherical surface of constant solid angle in momentum space at higher energies. This leads to lower photoelectron transmission. For example, in the case of Pd, the acquisition time for the Fermi surface at a photon energy of 55 eV was 30 seconds, whereas a similar experiment at a photon energy of 620 eV required 1200 seconds, or 20 minutes. This effect is further amplified by the reduced cross-section for photoemission at higher energies [98]. Additionally, the beamline photon flux follows a downward trend as the photon energy increases [99], contributing to the overall reduction in photoelectron statistics in the high-energy regime.

3.1.2 Matrix elements in the photoemission response

The spectral signature in a photoemission process can be described by the transition matrix element introduced in equation 2.18. Assuming the dipole approximation, the vector potential $\vec{A}$ determines the $\vec{E}$ field vector of the photons, which can be decomposed into its three components of (E_x, E_y, E_z) . In this thesis, p-polarized photons and s-polarized photons have polarization vectors of $\vec{E}_p = (0, E_y, E_z)$ and $\vec{E}_s = (E_x, 0, 0)$, respectively, as seen in Figure 3.1b. Meanwhile, circularly-polarized photons can be described by introducing a $\pm 90^\circ$ phase difference between E_x and E_y , resulting in $\vec{E}_{\odot, \ominus} = (\pm i E_x, E_y, E_z)$ for left- and right-handed circular polarizations. In general, the matrix element in photoemission depends on both the experimental geometry and the initial ground state and final states. Therefore, with known constant variables of experimental geometry, it can be employed to extract information from the initial states.

Linear polarization serves as a valuable tool not only for determining the symmetry of the observed states but also for simplifying the observable electronic bands by

sorting the orbital symmetry of the initial states according to the dipole selection rule [55]. Under the dipole approximation, the initial state can be categorized as either even or odd with respect to reflection in the mirror plane defined by the Poynting vector of the incident photon and the direction of photoemission. The observable final state of photoemission must exhibit even parity, as an odd parity results in a node in the electron wave function. In this thesis, the yz -plane is aligned with a crystal mirror plane in all experiments. The matrix elements for p- and s-polarizations can be expressed as:

$$\mathcal{M}_{i \rightarrow f}^{\vec{k}} = \langle \Phi_f^{\vec{k}} | \vec{E} \cdot \vec{r} | \Phi_i^{\vec{k}} \rangle \quad (3.3)$$

$$\begin{pmatrix} \mathcal{M}_{p-pol}^{\vec{k}} \\ \mathcal{M}_{s-pol}^{\vec{k}} \end{pmatrix} = \begin{pmatrix} \langle \Phi_f^{\vec{k}} | E_y \cdot \hat{y} | \Phi_i^{\vec{k}} \rangle + \langle \Phi_f^{\vec{k}} | E_z \cdot \hat{z} | \Phi_i^{\vec{k}} \rangle \\ \langle \Phi_f^{\vec{k}} | E_x \cdot \hat{x} | \Phi_i^{\vec{k}} \rangle \end{pmatrix}. \quad (3.4)$$

As a result, even symmetry initial states with respect to the yz -plane are observed in p-polarization, while odd symmetry initial states are observable in s-polarization [100].

3.1.3 Dichroisms in the angular distribution of photoelectrons

Dichroism in photoemission intensities is represented as the asymmetry between two experimental spectral weights I_A and I_B :

$$I_{A-B}(k_x, k_y) = \frac{I_A(k_x, k_y) - I_B(k_x, k_y)}{I_A(k_x, k_y) + I_B(k_x, k_y)}, \quad (3.5)$$

where the variables A and B are the experimental quantity of interest, such as photoemission intensities from right and left circularly polarized photons.

Linear dichroism (LD) in the angular distribution is inherently present in photoemission experiments conducted with p-polarized photons [101, 102]. The experimental geometry, as depicted in Figure 3.1b, involves p-polarized photons incident in the yz -plane at an angle of incidence $\delta = 25^\circ$. The photoelectron intensities for photons incident along the positive (I_+) and negative (I_-) y -directions are measured, and their difference is referred to as LD.

The electric field vector $\vec{E}$ of the p-polarized photons can be expressed as $\vec{E}_\pm = \begin{pmatrix} E_x \\ \pm E_y \sin \delta \\ E_z \cos \delta \end{pmatrix}$, where the $\pm$ sign indicates the direction of incidence along the y -axis.

In the experimental setup, where both the xz -plane and yz -plane are crystalline mirror planes, the photoemission intensity from p-polarization along the positive y -direction, I_+ , can be referred to as the single experimental quantity I_{p-pol} . Then, the LD is the difference between the photoemission intensities measured for opposite directions along the y -axis and can be expressed as:

$$LD(k_x, k_y) = \frac{I_{p-pol}(k_x, k_y) - I_{p-pol}(k_x, -k_y)}{I_{p-pol}(k_x, k_y) + I_{p-pol}(k_x, -k_y)}. \quad (3.6)$$

In this equation, the LD is the asymmetry in the photoemission intensities observed for the positive and negative k_y -directions. The momentum distribution of the LD thus reflects this asymmetry in the photoelectron intensities. Note that for all experimental data presented in this thesis, both the xz -plane and yz -plane are crystalline mirror planes.

On the other hand, the $\vec{E}$ of the left and right circularly polarized photons can be written as $\vec{E}_{\odot, \ominus} = \begin{pmatrix} \pm iE_x \\ E_y \sin \delta \\ E_z \cos \delta \end{pmatrix}$. Circular dichroism (CD), the asymmetry between the photoemission intensities from left and right circularly polarized photons, $I_{\odot}$ and $I_{\ominus}$ respectively [101, 102], can be written as:

$$CD(k_x, k_y) = \frac{I_{\odot}(k_x, k_y) - I_{\ominus}(k_x, k_y)}{I_{\odot}(k_x, k_y) + I_{\ominus}(k_x, k_y)}. \quad (3.7)$$

CD is not only a consequence of the experimental geometry but can also arise from an intrinsic chiral system [103–105] or a magnetic system [106]. Unlike its linear counterpart, CD requires independent measurements with right- and left-handed circularly polarized photons, which are then inserted into equation 3.7. To minimize the effects of photon flux drifting and changes in the photon Poynting vector over time, measurements were carried out by switching between the two polarizations routinely within a single dataset.

Both LD and CD can be formulated in terms of photoemission intensities arising from the matrix elements, as defined in Equation 2.19. Based on Equation 3.3, the photoemission matrix element in Cartesian coordinates is expressed as:

$$\mathcal{M} = \langle \Phi_f | \vec{E} \cdot \vec{r} | \Phi_i \rangle = E_x \mathcal{M}_x + E_y \mathcal{M}_y + E_z \mathcal{M}_z. \quad (3.8)$$

Each component $\mathcal{M}_j = \langle \Phi_f | E_j j | \Phi_i \rangle$, where $j = x, y, z$, corresponds to the matrix element along the respective Cartesian axis.

The LD in the yz -mirror plane can be derived to yield:

$$LD(0, k_y) \propto \sin \delta \cos \delta \Re(\mathcal{M}_y^* \mathcal{M}_z). \quad (3.9)$$

while the CD in the xz -plane is given by:

$$CD(k_x, 0) \propto \cos \delta \Im(\mathcal{M}_x^* \mathcal{M}_z). \quad (3.10)$$

In Equations 3.9 and 3.10, $\Im$ and $\Re$ refer to the imaginary and real parts, respectively, whereas $*$ denotes complex conjugate.

Figure 3.3 illustrates the momentum-resolved photoemission LD and CD of FePd alloy on Pd(001) at a photon energy of $h\nu = 35$ eV. Figures 3.3a and b show the Fermi surface maps obtained using left- and right-handed circularly polarized photons, respectively, revealing distinct variations in photoemission intensity due to the helicity-dependent interaction of light with the electronic states. The resulting CD,

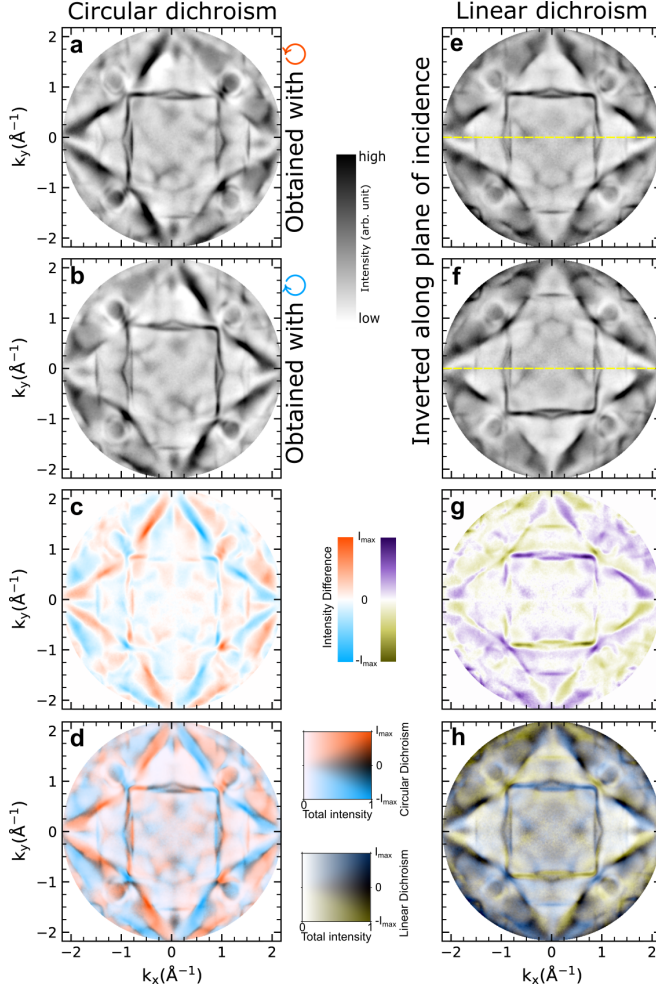


Figure 3.3: Momentum-resolved photoemission LD and CD of FePd alloy on Pd(001) at $h\nu = 35$ eV. (a) Fermi surface map acquired with left-handed circularly polarized photons. (b) Same as (a) but with right-handed circularly polarized photons. (c) Circular dichroism $CD(k_x, k_y)$ and (d) its composite color representation incorporating photoemission intensities. (e) Fermi surface map obtained with p-polarized photons. (f) Mirror image of (e) across the xz -plane, corresponding to the crystalline mirror plane. (g) Linear dichroism $LD(k_x, k_y)$ and (h) its composite color representation with photoemission intensities.

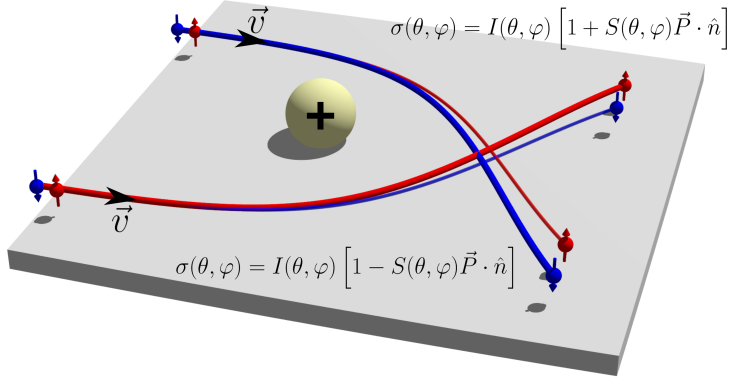


Figure 3.4: Depiction of the spin-dependent scattering of unpolarized electrons from two different sides of a charged scattering center (+). The solid colored lines qualitatively show the equipotential curves for spin-up (red) and spin-down (blue) electrons in the presence of SOC. The thickness of the line represents the cross-section of scattering for the polarized electrons.

$CD(k_x, k_y)$, is presented in Figure 3.3c. Figure 3.3d provides a composite color representation of the CD signal, incorporating the overall photoemission intensity to enhance visualization. Notably, along the yz -crystalline mirror plane, the CD diminishes.

For comparison, Figures 3.3e and f show Fermi surface maps obtained with p-polarized photons and their mirror image across the xz -plane, which corresponds to the crystalline mirror plane. The $LD(k_x, k_y)$ is calculated as the asymmetry between the two mirror-ed sets, and is presented in Figure 3.3g. Figure 3.3h combines the LD signal with the photoemission intensity for better visualization. In this case, the xz -crystalline mirror plane in which the p-polarization experimental map is mirrored has diminished LD.

Pronounced dichroisms in photoemission arise from both extrinsic and intrinsic factors. Extrinsic factors include the experimental geometry, while intrinsic factors are tied to the symmetries of Bloch wave functions [63, 107]. Both LD and CD exhibit strong sensitivity to orbital symmetry variations [36, 102] and may serve as experimental signatures of orbital angular momentum textures [101, 108].

3.1.4 Imaging spin-filter

One of the key advantages of momentum microscopy is its ability to perform two-dimensional imaging of the iso-energy momentum distribution of photoelectrons. This technique can be extended to a spin-polarized low-energy electron diffraction

(SPLEED) experiment for spin-resolved measurements. The spin-orbit coupling (SOC) term, as described by equation 2.9, introduces spin dependence in electron scattering [9]. An intuitive depiction of this mechanism is shown in Figure 3.4, where the interaction between spin and the motion of charged particles in an electromagnetic field is illustrated. In the rest frame of the electrons, the charged scattering center (+) moves, and the current produced by this moving charge generates a magnetic field, which then interacts with the magnetic moments of the electrons. Notably, the spin-orbit potential scales with the atomic number, making relativistic effects more pronounced as the nuclear charge increases.

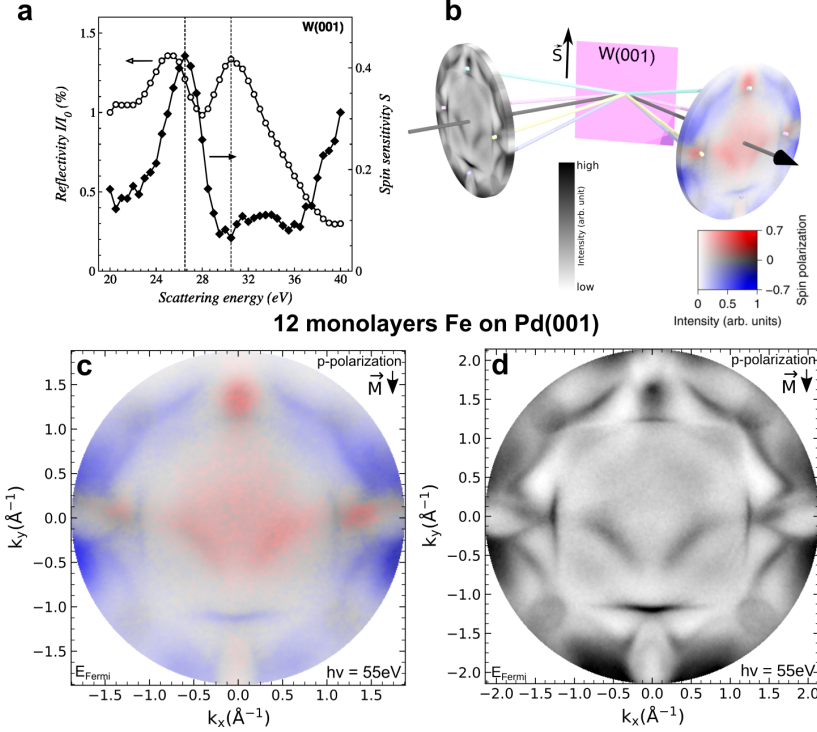


Figure 3.5: **a** shows the contrast between the specular reflection of (00) SPLEED spots and the corresponding spin sensitivity. Adapted from [56]. **b** shows the setup for the spin-dependent scattering experiment using a clean W(001) surface. The decelerating and accelerating electrostatic lenses pre- and post-scattering are not shown. **c** shows the resultant spin-resolved Fermi surface measurement of Fe(001) with **d** the measurement from the spin-integral experiment as reference. The spin-resolved Fermi surface agrees with the theoretical results in Figure 2.2.

The differential scattering cross-section σ for spin-dependent scattering [9] can be

expressed as:

$$\sigma(\theta, \varphi) = I(\theta) [1 \pm S(\theta) \vec{P} \cdot \hat{n}], \quad (3.11)$$

where θ and φ are the polar and azimuthal angles, respectively, and $\hat{n}$ denotes the normal to the scattering plane. The term $I(\theta)$ represents the spin-integrated scattering amplitude, while $S(\theta)$ is the spin sensitivity, describing the probability of a polarized electron being scattered (+ for spin-up, - for spin-down). The vector $\vec{P}$ denotes the spin polarization of the electron.

A key characteristic of Equation 3.11, specifically the term $\vec{P} \cdot \hat{n}$, is that only the polarization vector component perpendicular to the scattering plane contributes to the scattering asymmetry, as illustrated in Figure 3.4. In contrast, the components parallel to the scattering plane have no effect. While the derivation of Equation 3.11 relies on associated Legendre functions for spherical harmonics, the potential within a solid is not truly spherically symmetric. As a result, multiple scattering contributions become significant in low-energy scattering events [9, 109]. Consequently, in addition of pronounced energy dependence as shown in Figure 3.5a, $I(\theta)$ and $S(\theta)$ exhibit azimuthal dependence, necessitating their generalization to $I(\theta, \varphi)$ and $S(\theta, \varphi)$ [109, 110]. Building upon these principles, polarized Bragg reflections can be obtained by diffracting low-energy electrons from crystals with strong SOC. The spin-dependent scattering cross-section in tungsten is particularly large for electrons with energies below 100 eV [90, 109]. Similarly, spin-resolved detection can be integrated into momentum microscopy, enabling a two-dimensional spin detection scheme or imaging spin-filtering [16, 90, 110].

It is noted that the Cartesian coordinates x and y , along with k_x and k_y in both real and momentum space imaging of the microscope, are interchangeable in the scattering geometry shown in Figure 3.5b, which takes place as the final steps in the momentum microscopy experiment, as depicted in Figure 3.1. The contrast between specular reflection of electrons with different spins in the (00) LEED beam at various scattering energies is exploited for spin resolution. Figure 3.5a illustrates the modulation of spin sensitivity, S , and spin-averaged reflectivity, $R = \frac{I}{I_0}$, as functions of scattering energy. Two scattering energies, 26.5 eV and 30.5 eV, which exhibit significant reflectivity, are selected, with spin sensitivities $S_l(x, y)$ of 42% and $S_h(x, y)$ of 5%, respectively. These values are used to solve the simultaneous equations of the measured photocurrents $I_{l,h}(x, y)$:

$$I_l(x, y) = I_0(x, y) (1 + S_l(x, y) P(x, y)) R_l(x, y) \quad (3.12)$$

$$I_h(x, y) = I_0(x, y) (1 + S_h(x, y) P(x, y)) R_h(x, y), \quad (3.13)$$

where $I_0(x, y)$ is the incoming photocurrent, and $R_l(x, y)$ and $R_h(x, y)$ represent the spatial distribution of reflectivity at the low and high scattering energies of 26.5 eV and 30.5 eV, respectively. The spin sensitivities for the two energies, $S_{l,h}(x, y)$, are considered isotropic and are taken as constant. Meanwhile, $R_{l,h}(x, y)$ is determined experimentally by measuring the spatial distribution of unpolarized electrons from a known spatially homogeneous source. In this study, secondary electrons photoexcited

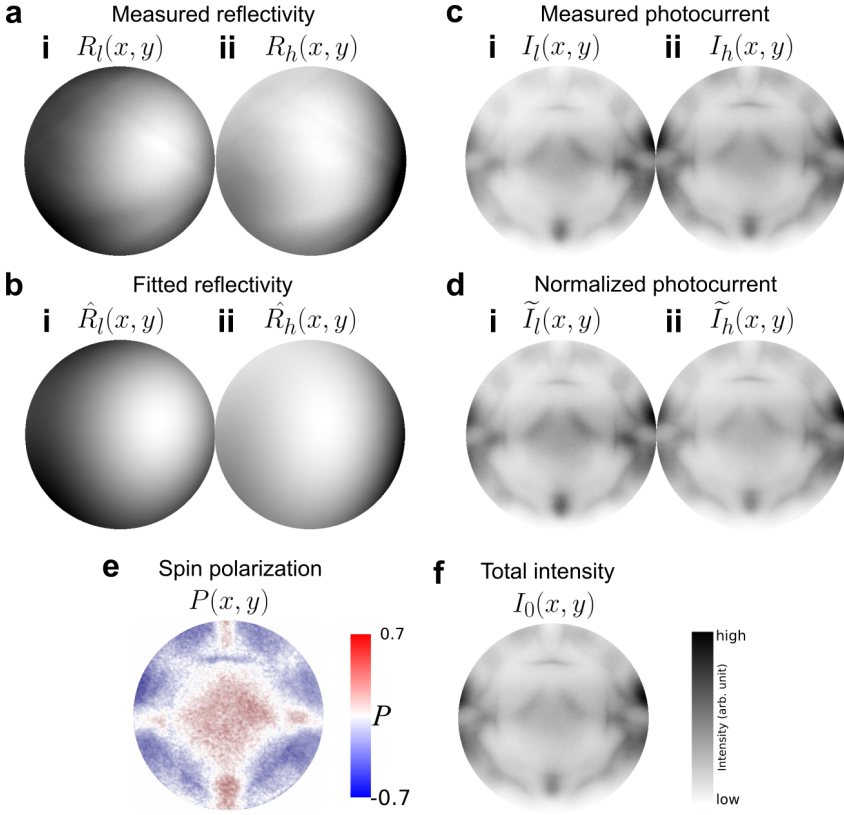


Figure 3.6: Spin-resolved measurements on body-centered cubic Fe(001) were performed using a W(001) spin-filter crystal, ultimately yielding the spin-resolved momentum map shown in Figure 3.5c. **a** shows the spatial distributions of reflectivity maps, measured using featureless flat-field PEEM images of the Cu(001) surface, while **b** presents their cubic polynomial fit. **c** depicts the momentum distribution of photoemission intensities measured at the Fermi level of Fe(001). **d** shows the momentum maps in **c** normalized with the fitted reflectivity maps from **b**. Panels **i** and **ii** in **a-d** correspond to measurements taken with 26.5 eV and 30.5 eV scattering energies, respectively. **e** shows the momentum distribution of the spin polarization, and **f** presents the total intensity of the spin-integrated momentum maps for the Fermi surface of Fe(001).

from a clean Cu(100) surface with unpolarized photons from a mercury discharge lamp were employed, with the microscope set to defocus the image for further image homogeneity. For a more consistent analysis, an additional step of curve fitting to a two-dimensional cubic function was applied to the measured $R_{l,h}(x, y)$, yielding a fitted normalization factor $\hat{R}_{l,h}(x, y)$. Finally, the proper quantities of $P(x, y)$ and $I_0(x, y)$ for the photoelectron are obtained:

$$P(x, y) = \frac{\tilde{I}_l(x, y) - \tilde{I}_h(x, y)}{S_l(x, y)\tilde{I}_h(x, y) - S_h(x, y)\tilde{I}_l(x, y)} \quad (3.14)$$

$$I_0(x, y) = \frac{S_l\tilde{I}_h(x, y) - S_h\tilde{I}_l(x, y)}{S_l(x, y) - S_h(x, y)}. \quad (3.15)$$

where $\tilde{I}_{l,h}(x, y)$ represents the photocurrent $\frac{I_{l,h}(x, y)}{\hat{R}_{l,h}(x, y)}$, normalized to the fitted distribution of reflectivity reference $\hat{R}_{l,h}(x, y)$. Figure 3.6 illustrates the step-wise procedure for obtaining the spin-resolved Fermi surface of the prototypical ferromagnet of body-centered cubic Fe(001). The final result, as shown in Figure 3.5c, is reconstructed by multiplying the spin polarization with the recovered total intensity of the incoming photocurrent. In this case, a two-dimensional color scaling is applied to the two components. It is also important to note that the measurements in Figure 3.6 are flipped with respect to the scattering plane of the spin filter, as shown in Figure 3.5b.

All spin-resolved measurements presented in this thesis were performed using a W(001) spin-filter crystal. Unlike the electron-atom scattering exploited in a Mott detector, spin-dependent scattering in the SPLEED setup is effective only with a pristine W(001) crystal surface. A routine of well-established procedures is followed to prepare a clean, carbon-free W(001) crystal surface. An oxide layer is fabricated on W(001) through cycles of flash-annealing at 1700 K in 5×10^{-8} mbar of O_2 partial pressure. Right before measurements, a final single high-temperature flash-annealing at 2500 K in ultra-high vacuum is performed to remove the oxide, revealing a pristine W(001) surface that is stable for at least two hours. After two hours, a routine flash-annealing at 1700 K in ultra-high vacuum may desorb the adsorbates and partially recover a clean W(100) surface for another two-hour cycle.

3.2 Ultrathin FePd alloy on Pd(001)

The preparation of clean Pd(001) and Rh(001) single-crystal surfaces in this study follows a well-established routine, involving repeated cycles of Ar^+ ion sputtering followed by annealing via electron bombardment at 900 K for 10 minutes [15, 111]. The surface quality is assessed using LEED and Auger electron spectroscopy to verify the crystallinity and confirm the absence of contaminants. Both Pd(001) and Rh(001) adopt a face-centered cubic (fcc) structure.

The fabrication procedure for two monolayers of the ultrathin FePd alloy on clean Pd(001) [15, 111], as shown in Figure 3.7a, is as follows: First, the Pd(001) surface is

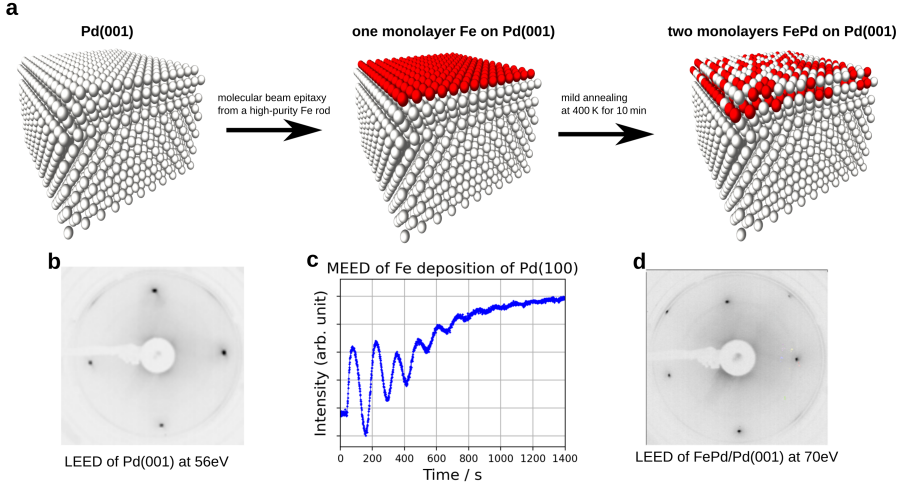


Figure 3.7: **a** shows the step-wise fabrication of the FePd alloy on a Pd(001) substrate. **b** presents the LEED pattern of a clean Pd(001) surface after repeated cycles of Ar^+ ion sputtering and annealing. **c** depicts the MEED oscillations observed during the epitaxial growth of Fe on Pd(001) for optimizing the deposition rate. Finally, **d** shows the LEED pattern of a two-monolayer FePd alloy on Pd(001).

prepared, and the crystal temperature is quenched to room temperature (300 K) by transferring it to a sample stage with a large heat capacity. Epitaxial growth of one complete monolayer of Fe on Pd(001) is achieved via molecular beam epitaxy from a high-purity Fe rod, which is heated by electron bombardment. The deposition rate is determined via medium energy electron diffraction (MEED) oscillations, shown in Figure 3.7c. The oscillation pattern agrees with prior findings [111, 112] of a layer-by-layer growth mode up to 4.2 monolayers, as the oscillation diminishes significantly after the fourth peak.

Next, the monolayer Fe on Pd(001) is heated to 400 K and held at this temperature for 10 minutes to facilitate the formation of a two-atomic-layer thick FePd alloy. The overall Fe-to-Pd ratio in the alloy is determined by the nominal Fe monolayer precursor. LEED of the alloy film shows defined diffraction spots similar to those of Pd(001), supporting previous studies that suggest the formation of a disordered pseudomorphic alloy with a face-centered tetragonal (fct) structure [15, 111].

In this study, the composition of the Fe-to-Pd ratio in the alloy film is further fine-tuned to achieve the desired electronic properties. The content is quantified using the nomenclature of monolayers (atomic-thick layers). For instance, $Fe_{0.9}Pd_{1.1}/Pd(001)$ corresponds to a two-atomic-layer thick FePd alloy with a composition of $Fe_{0.9}Pd_{1.1}$ on Pd(001).

Additionally, a 12-monolayer thick Fe film is fabricated on Pd(001), which resembles a bulk Fe crystal with a body-centered cubic (bcc) structure. The fabrication

procedure follows the same process as the epitaxial film growth up to 12 monolayers, followed by mild annealing at 400 K for 10 minutes, similar to the alloying process.

4 Fermi Surface Tomography of Palladium and Rhodium

In Chapters 2 and 3, the fundamental principles of constant-initial-state photoemission as a tool for probing the bulk electronic structure of solids are introduced. Building on these principles, Chapter 4 focuses on the application of constant-initial-state photoemission to study the Fermi surfaces of Pd(001) and Rh(001). Section 4.1 presents a detailed analysis of the three-dimensional Fermi surface of Pd(001), reconstructed using constant-initial-state momentum microscopy. The limitations of the free-electron final state model in photoemission, along with the role of evanescent states, are explored in Section 4.1.1 through a complex band structure approach. Section 4.1.2 investigates the orbital symmetry of electronic states via dichroism in photoemission. Finally, Section 4.2 provides a comparative study of the bulk band structures of Pd(001) and Rh(001), highlighting key similarities and distinctions between these transition metals.

4.1 Fermi surface of palladium

To establish a fundamental framework, the theoretical ground state of face-centered cubic Pd, as shown in Figure 2.3, was calculated using `elk` code [34] with LDA+U exchange-correlation [34] ($U = 1.0\text{eV}$, $J = 0.3\text{eV}$) [35], including spin-orbit coupling (SOC) in the second variation. A K-point mesh size of $15 \times 15 \times 15$ was employed, and the Fermi surface was plotted onto a $100 \times 100 \times 100$ grid. To ensure convergence for the unoccupied bands, a total of 70 empty states were considered.

The Fermi surface of Pd, shown in Figure 2.3c, can be classified into three separate Fermi sheets or bands. Sheet I (yellow) predominantly exhibits a free electron-like character, appearing as a deformed sphere in the zone center at the Γ -point, with spikes pointing towards the high-symmetry points L and X at the zone boundary. Sheet II (green) contributes significantly to the density of states near the Fermi energy and is visualized as interconnected hollow tubes between the X-points of the Brillouin zone, often referred to as a "jungle gym". It features horn-like features pointing away from the X-point towards the L-point. Upon the inclusion of SOC in the calculations, as depicted in Figure 2.3c, a small hole pocket at the L-point is observed. Sheet III (blue) manifests as elliptical hole pockets around the X-points, with the radius of the hole pocket being notably affected by the inclusion of SOC.

The Fermi level is determined by directly comparing the radii of the Sheet II contours between theoretical and experimental data in subsequent sections. Although

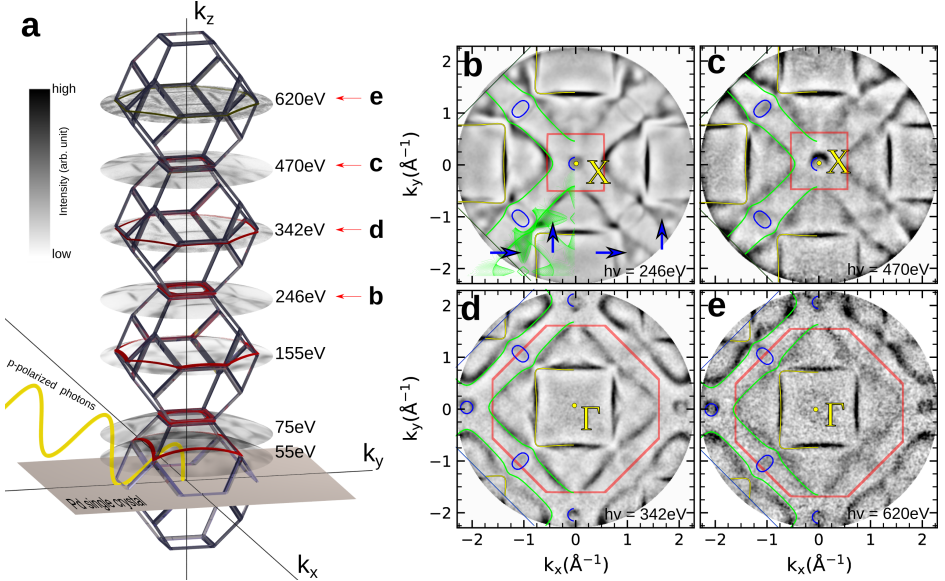


Figure 4.1: **a** Experimental geometry and isoenergy spherical cuts of the free electron final state in 3D momentum space, corresponding to the experimental momentum maps. **b, c, d, e** Experimental momentum maps at the Fermi energy, obtained at soft X-ray photon energies of 246 eV, 470 eV, 342 eV, and 620 eV, respectively. The red overlay indicates the intersections between the corresponding momentum disc and the first Brillouin zone boundary in a nearly-free electron final state model. The theoretical Fermi contours of Pd, based on the local density approximation (LDA), are shown in the left half of **b, c, d, e**. The green overlay represents the k_z -projection of Fermi Sheet II, and the blue arrows highlight the horn-like features.

the results are consistent with previous literature [35, 37], the Fermi energy of both the X and L hole pockets is overestimated in the full-potential linearized augmented plane wave (FPLAPW) calculations when compared to experimental data. As a result, when compared to the theoretical calculations, the radii of the hole pockets of Sheet III probed in the experiments are relatively larger. For Pd(001), a value of $U_i = 19.25$ eV is used, determined by comparing a series of constant initial state momentum maps, shown in Figures 4.1, with those of the calculated ground states, as shown in Figure 2.3.

Figures 4.1b and c show the spherical cuts with the X-point of the Brillouin zone at the origin, while Figures 4.1d and e feature those cutting across the Γ -high symmetry point. Notably, there is a remarkable overall consistency in the Fermi surface topology between the third ($h\nu = 246$ eV, 342 eV) and fourth zones ($h\nu = 470$ eV, 620 eV). The theoretical predictions closely align with the experimental results, consistent with a minor deviation in energy for Sheet III.

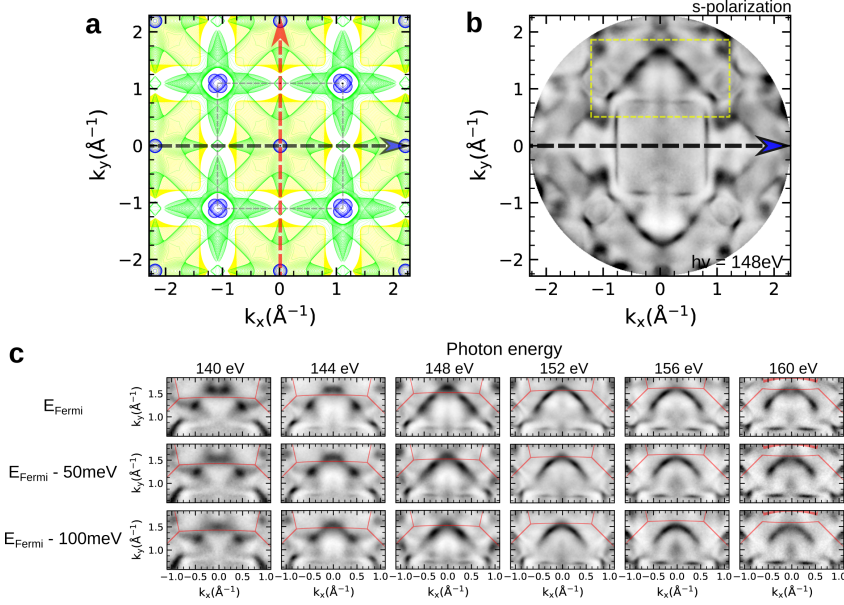


Figure 4.2: **a** Projection of the Fermi surface contours of the LDA+U ground state in k_z dimension. **b** Momentum map taken with s-polarized photons of 148 eV. **c** Magnified constant momentum maps at the Fermi energy, 50 meV and 100 meV below the Fermi energy, respectively, in the region enclosed by a dashed yellow rectangle in **a** across photon energies in between 140 eV and 160 eV.

However, the limitations of the free-electron final state model become evident when examining the momentum map obtained at a photon energy of 246 eV in Figure 4.1b. Specifically, as indicated by the two blue arrows, the green overlay highlights a horn-like feature of Sheet II near the projected X-point, appearing around $(k_x, k_y) = (0, \pm 1.15) \text{\AA}^{-1}$ and $(\pm 1.15, 0) \text{\AA}^{-1}$. This observation is unexpected, as the horn-like feature of Sheet II should not appear in the ΓKX plane but should instead be located in the vicinity of the L-point of the Brillouin zone. A comprehensive analysis was conducted to further investigate this anomaly in the photoemission spectral response at lower photon energies. Constant initial state momentum microscopy was employed, systematically scanning across fine intervals of photon energies to access a broader energy-momentum phase space [71].

For further visualization, a projection of the calculated Pd Fermi surface in Figure 2.3 along the surface normal $k_{\perp}$ axis is shown in Figure 4.2a. These contours are composed of 100 equally divided cross-sections of a complete Brillouin zone of Pd.

By leveraging the capabilities of the momentum microscope, particularly its ability to sample large regions of momentum space in the low-energy regime via an electrostatic immersion lens, constant-initial-state momentum maps are acquired with

2 eV photon energy steps. This approach facilitates the reconstruction of detailed three-dimensional spectral responses in momentum space, mapping electronic states as a function of photon energy along the k_x and k_y directions. Figure 4.2b highlights an intriguing case of spectral intensity modulations along the "jungle-gym" bands at an excitation energy of 148 eV. These features, if not carefully analyzed, could be mistakenly attributed to the ground-state electronic structure of Pd. To clarify their origin, Figure 4.2c follows a similar convention as Figure 4.1, overlaying the Brillouin zone boundaries corresponding to different final states. Here, the momentum distribution of intensity modulation over a series of photon energies and binding energies reveals that its low-intensity regions coincide with the zone boundary overlay across a broad energy range, consistent with the free-electron final state model.

To visualize the trend across the tomography, an extracted cut of the spectra along the k_x -axis is presented in Figure 4.3a as a function of photon energy. The bulk zone boundary (red) is overlaid across the photon energy cuts of the measurements at the Fermi energy in Figure 4.3a. This observation can be attributed to the forbidden band gaps in nearly free electronic bands, which arise due to the periodic lattice potential, as shown in Figure 2.2a. The lack of spectral intensity in the results can be associated with the band gap in the photoelectron final state.

At around $h\nu = 155$ eV, the final state sphere cuts close to the Γ KX plane of the Brillouin zone. Across different photon energies, the apparent reduction in spectral intensity of the "jungle-gym" Fermi sheet II can be directly correlated with the band gap at the zone boundary in the final state. Although the zone boundary of the free electron final state model is mapped by a singular constant $U_i = 19.25$ eV, additional intensity suppression is observed, following a similar structure at the zone boundary. This effect will be further explored as a function of photon energy in subsection 4.1.1.

The breakdown of the free electron final state model near the zone boundary can be understood as the unavailability of a final state, resulting in strong damping of the final state. In the low-energy regime, this breakdown becomes apparent in the measurements. While the Sheet III hole pocket is expected around the X-point of the bulk zone boundary between photon energies of 70 eV and 90 eV, no significant contribution from Sheet III was observed. Interestingly, strong photoemission spectral intensity with Sheet III signatures was observed away from the X high symmetry point. This observation is attributed to final state damping due to surface barrier potential, with the convention of the complex band structure in photoemission adopted to capture these anomalies.

4.1.1 Photoemission Complex Band Structure

Thus far, the electronic structure of Pd has been explored based on an infinite crystalline solid, where stationary Bloch waves are composed of an ensemble of real energy eigenvalues. However, in the presence of a surface barrier potential, a complex-valued wave vector must be adopted, causing the amplitude of the corresponding wave functions to expand or decay exponentially along the out-of-plane ($\perp$) direction. This phenomenon leads to the formation of evanescent states [113], as illustrated in Fig-

ure 2.2c. Consequently, the $k_{\perp}$ component of the photoelectron momentum becomes ill-defined within the free-electron-like dispersion framework or even with respect to bulk real states.

Such states can be interpreted as final state self-energy effects or as the result of inelastic scattering of the photoelectron, both of which are known to limit the probing depth in photoemission. Consequently, the momentum-resolved photoelectron spectral function must satisfy the wave-matching condition for both the Bloch wave extending across the lattice and the evanescent states, in addition to the incoming plane wave in vacuum, as illustrated in Figure 2.6c [114].

Building upon prior studies on self-energy effects in itinerant magnets [17], detailed evidence of final state self-energy has been demonstrated using constant-initial-state momentum microscopy. In this study, lifetime broadening due to initial-state correlations or valence bands is strongly suppressed, as the initial state is constrained to the Fermi level. Therefore, the modulation observed in the tomographic spectra can be attributed primarily to the photoemission final state.

As shown in Figure 4.3a, the free-electron final state model exhibits significant deviations, especially near the Brillouin zone boundaries. These discrepancies become particularly pronounced when the photoelectron final states approach high-symmetry points such as X and the back-folded Γ -points. To better interpret the experimental observations in Figure 4.3a, the complex band structure of the system is calculated using an optical potential model by collaborator Dr. Ján Minár, as illustrated in Figure 4.3b. This approach incorporates both the real and imaginary components of the photoelectron wave vector in the out-of-plane direction ($k_{\perp}$), and plots the corresponding transmission probability in normal emission geometry.

The results reveal a distinct departure of the observable real part of the complex band structure (depicted in blue) from the bulk states (in red), particularly at lower photon energies. As the excitation energy increases, the final state band structure gradually converges toward the free-electron-like behavior. Crucially, near the zone boundaries at X and the back-folded Γ -point, dispersionless, waterfall-like features emerge, indicated by orange arrows in Figure 4.3b. These features are characteristic signatures of strong damping in the photoelectron's final state.

This damping is a consequence of the imaginary component of the wave vector in the complex band structure framework. In regions of the Brillouin zone where there are band gaps or forbidden states, such as near the zone boundaries, the crystal potential prevents the formation of propagating (real k) Bloch states. Instead, the solution to the Schrödinger equation yields complex wave vectors, where the imaginary component leads to an exponential attenuation of the wave function into the bulk. These evanescent states correspond to final states with short inelastic mean free paths, suppressing their contribution to the photoemission intensity.

Physically, this means that while such states can still contribute to the overall signal via tunneling or decay into the vacuum, they are strongly localized near the surface and decay rapidly into the bulk. As a result, their presence manifests in the measured band structure as non-dispersive, vertically extended waterfall-like features, highlighting the non-propagating character of the final states in these regions.

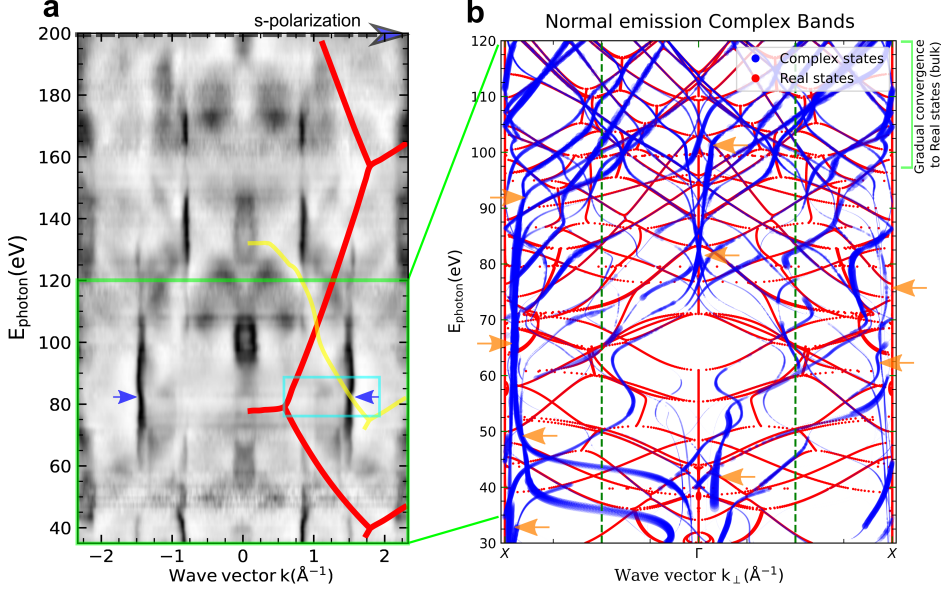


Figure 4.3: **a** Cross-sections along the k_x axis (arrow in Figure 4.2b) of the constant-initial-state momentum maps at the Fermi energy, measured with s-polarized photons. The zone boundary of the free-electron final state model is plotted as a solid red line on the right half. The semi-transparent green box highlights the energy range covered in **b**. Blue arrows indicate "kink" features in the spectra, while the yellow line marks the ghost duplicate of the zone boundary. **b** The real part of the out-of-plane wave vector component of the complex photoemission band structure (blue) and the ground-state band structure (red) for normal $((k_x, k_y) = (0, 0))$ photoemission geometry as a function of photon energy. The transmission probability (photocurrent) of the complex states is plotted as a function of line thickness on a logarithmic scale. Orange arrows highlight the waterfall-like features in the complex band structure.

This phenomenon reflects the interplay between the complex self-energy of the final state and the crystal periodicity and underscores the limitations of the free-electron approximation when modeling final states near symmetry-imposed band gaps.

A key reference point for validating our discussion is the well-characterized feature of the Sheet III hole pocket, which is clearly visible in both the calculated Fermi surface and experimental measurements at higher photon energies, as shown in Figure 4.1. Owing to its well-defined topology and alignment along the normal emission direction (i.e., Γ to X), this feature serves as a reliable benchmark for validating the interpretation of the experimental band structure. As previously noted, the momentum location of the Sheet III hole pocket is expected to occur near the X-point of the bulk Brillouin zone boundary around a photon energy of 75 eV. However, in the experimental data, the feature manifests near 105 eV, as seen in Figure 4.3a, aligning well with the predicted crossing at the X-point from the complex band structure calculations in Figure 4.3b.

Moreover, the phenomenon of ghosting, the appearance of replicas or shifted band features, is observed at multiple photon energies. These correspond to energies where the real part of the complex final state dispersion grazes or intersects the X-point. Such ghost features are direct manifestations of the complex-valued wave vectors in the final state, particularly the imaginary component, which governs spatial damping and modifies the momentum-resolved intensity distribution.

Notably, the momentum dependence of this damping can also be inferred by tracking regions of suppressed photoemission intensity near the bulk zone boundaries. These ghost zone boundaries exhibit distorted dispersions, mimicking the waterfall-like features previously discussed. One such trajectory is highlighted by the yellow solid line overlaid in Figure 4.3a. These features are crucial for understanding how spectral kinks indicate deviations from the free-electron final state approximation in photon energy-dependent measurements.

One striking example of this phenomenon is the observation of kink-like anomalies in the constant-initial-state energy spectra. The region marked by blue arrows in Figure 4.3a is selected for further investigation due to its strong intensity and sharp spectral signature. Figure 4.4 offers a detailed view of the momentum-resolved intensity near these kink-like features, corresponding to the teal rectangle highlighted in Figure 4.2a. Experimentally, a distinct ghost replica of the zone boundary appears to cross the bands near 84 eV photon energy, coinciding with the location of the kinks.

This is further evidenced by the sudden momentum displacement of the Fermi Sheet I feature orthogonal to the ghost replica of the zone boundary, as observed in the spectra between Figures 4.4c and d. The lack of intensity along the plotted ghost zone boundary in Figure 4.3a provides additional support for the presence of a local gap-induced damping effect. Importantly, while these ghost features may resemble intrinsic kinks or quasiparticle interactions in the ground-state band structure, they originate from evanescent states and are governed by damping effects and momentum conservation constraints inherent to the photoemission process. As such, they should not be misinterpreted as signatures of many-body interactions or ground-state band renormalization.

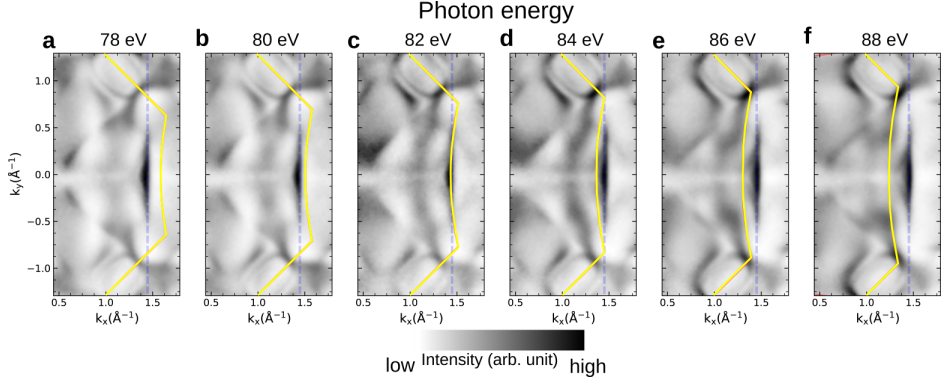


Figure 4.4: Magnified constant-initial-state momentum maps in the vicinity of the kink-like structure highlighted by a teal rectangle in Figure 4.3a. Yellow and blue overlays serve as visual guides for the ghost replica of the zone boundary and the anchor of k_x , respectively, illustrating the kink-like feature across the gap in the final state.

4.1.2 Orbital-resolved band structure

From a symmetry perspective, classifying atomic orbitals into even and odd categories provides a foundational framework for understanding the behavior of electronic states in crystalline systems. This classification is based on the transformation properties of orbitals under mirror symmetry operations. Figure 4.5a presents the atomic orbitals with angular momentum quantum number $\ell = 2$, constructed from spherical harmonics and visualized along the z -axis. These orbitals are categorized as either even or odd with respect to the yz crystalline mirror plane: even orbitals remain invariant under mirror reflection, while odd orbitals exhibit a change in sign.

This distinction plays a critical role in analyzing symmetry-dependent phenomena in photoemission experiments. Specifically, dipole selection rules dictate that, along the yz mirror plane, only odd orbitals contribute to the photoemission signal when using s -polarized photons, whereas even orbitals are selectively excited with p -polarized photons. This polarization sensitivity enables the experimental separation of orbital contributions.

However, unlike isolated atomic systems, the valence electronic states in solids are delocalized and subject to significant orbital hybridization, especially away from high-symmetry points in the Brillouin zone. This hybridization results in orbital mixing, which complicates the direct identification of orbital symmetry but can still be disentangled through careful analysis.

To explore this, orbital-projected FPLAPW calculations are shown in Figures 4.5b and c, separately highlighting the contributions from even and odd orbitals. These projections not only reveal the symmetry characteristics of the bands but also serve as a powerful tool for identifying the effects of relativistic SOC. As previously discussed

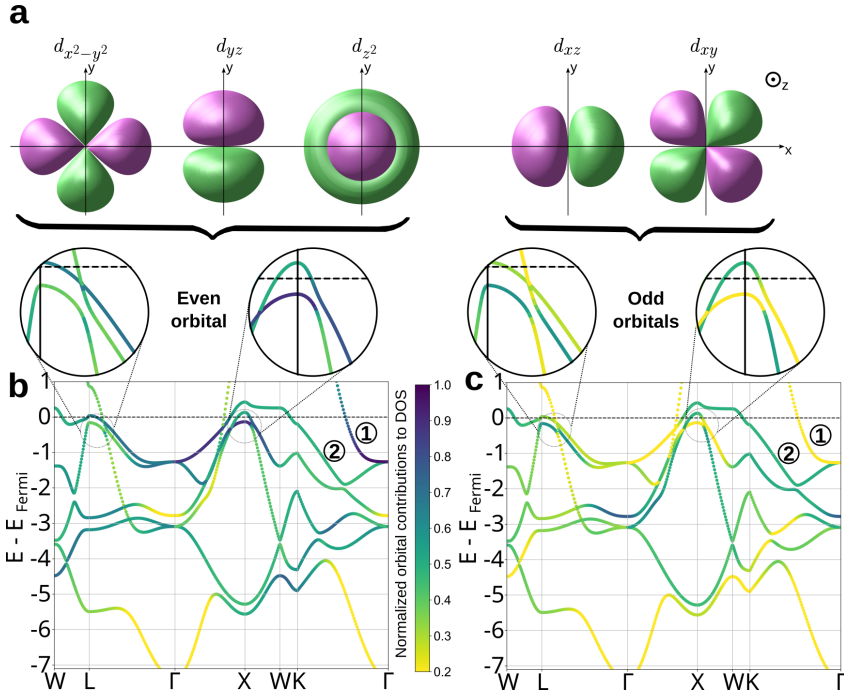


Figure 4.5: **a** Illustration of the five d -orbitals, which are atomic orbitals with an angular momentum quantum number $l = 2$. The orbital projections of the valence bands of Pd(001) are classified into **b** even and **c** odd characters.

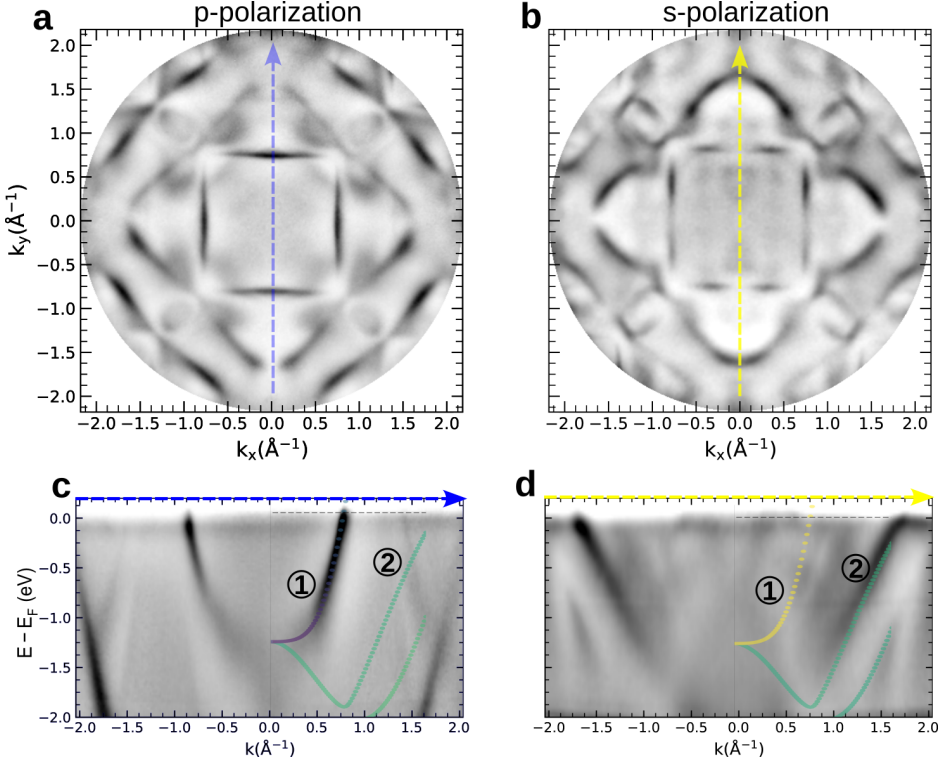


Figure 4.6: The momentum maps at Fermi energy obtained using (a) p-polarized and (b) s-polarized photons at a photon energy of 155 eV. (c) and (d) represent the respective energy-momentum cuts indicated by the colored dashed arrows in (a) and (b). The experimental results are overlaid with the theoretical calculations presented in Figure 4.5, where the circled numbers denote the corresponding bands of interest.

in Figure 2.3a, SOC-induced avoided crossings manifest as changes in orbital character along the bands. These crossings are clearly resolved in the orbital projections, as illustrated in the inset of Figure 4.5, underscoring the utility of orbital-resolved calculations in unraveling complex band interactions governed by SOC.

The momentum disc closest to the Γ KX high-symmetry plane, probed using a photon energy of 155 eV, is selected to evaluate the orbital-resolved photoemission response. Figures 4.6a and b present the Fermi surface maps obtained using p- and s-polarized photons, respectively, while Figures 4.6c, d, e, and f show the corresponding energy-momentum cuts, as indicated by the colored dashed arrows.

Significant differences in the photoemission intensity of band ① (Sheet I) and band ② (Sheet II) along the Γ -K direction, when comparing p- and s-polarized photons, are observed in Figures 4.6c (blue dashed arrow in a) and d (yellow dashed arrow in

b). These differences can be understood through their respective gerade (even) and ungerade (odd) symmetries. Band ① exhibits a strong d_{z^2} character (even), which is forbidden in s-polarization, leading to a discontinuity along the Γ -K direction. In contrast, band ②, primarily characterized by d_{xz} (odd), exhibits strong intensity under s-polarized excitation and weaker intensity under p-polarized excitation. Neglecting final state contributions, this symmetry analysis remains strictly qualitative, and the orbital projections are evaluated only along the yz mirror plane. A more comprehensive theoretical interpretation will be provided in Section 4.1.3.

4.1.3 One-step photoemission calculations

A more comprehensive understanding of the photoemission spectra of Pd is achieved through the theoretical evaluation of the momentum-resolved photoelectron spectral response of Pd using the one-step photoemission formalism. These calculations, performed by collaborator Dr. Ján Minár, employ the one-step model of photoemission within the framework of the local spin density approximation (LSDA) and the atomic-spheres approximation (ASA), as implemented in the SPR-KKR band structure software package [87]. A lattice constant of 7.3507 a.u. is used in the simulations. This formalism enables direct comparison with experimental spectra.

Figure 4.7 displays direct comparisons of the momentum distribution of photoemission spectral intensities at selected photon energies. These measurements are taken with respect to the nearly-free electron final state sphere, intersecting the L-, X-, and Γ - high symmetry points of the Pd crystal at photon energies of 55 eV, 75 eV, and 155 eV, respectively. Each set of momentum maps at the specified photon energies, acquired using both p- and s-polarized photons, is compared with its corresponding one-step photoemission calculation.

Using photons of 55 eV, Figure 4.7a distinctly resolves the L-point hole pocket, which notably disappears in Figure 4.7b. This observation provides direct evidence for the existence of a small, previously unconfirmed hole pocket at the L-point associated with Sheet II [35, 37], as highlighted by green arrows in Figure 4.7a. The polarization-dependent visibility of this feature is attributed to the orbital character of the underlying electronic states, which exhibit even symmetry near the L-point, as illustrated in Figure 4.5. This symmetry consideration accounts for the enhanced visibility of the hole pocket under p -polarized illumination and its suppression under s -polarization, in accordance with dipole selection rules.

The pronounced suppression of photoelectron intensity near the zone boundary around the X-point, particularly within the region $(k_x, k_y) = (\pm 0.5, \pm 0.5)$, as seen in Figures 4.7c and d measured at a photon energy of 75 eV, is attributed to significant final state damping effects. This suppression reflects the reduced transmission probability of photoelectrons due to the strong spatial attenuation of the final state near the Brillouin zone boundary. In contrast, the hole pocket of Sheet III remains observable at other photon energies away from the X-point, as evidenced in Figures 4.3a and in the momentum maps recorded at 55 eV shown in Figures 4.7a and b, where it is indicated by blue arrows. These observations are consistent with both experimental and

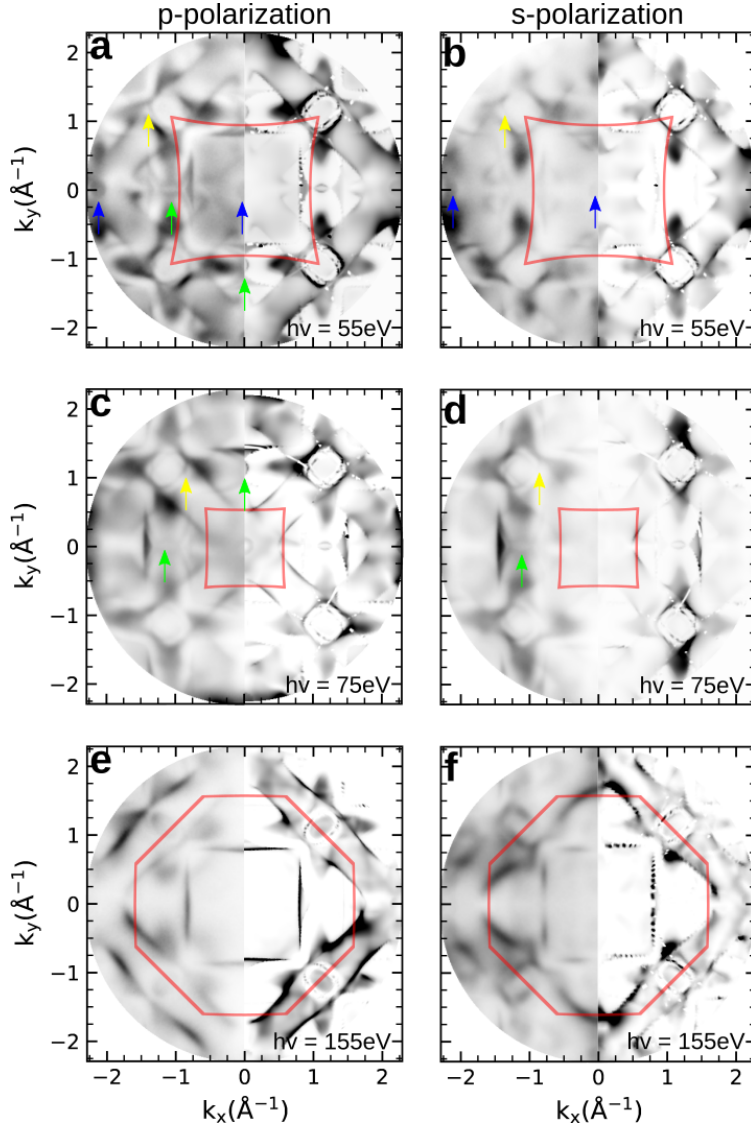


Figure 4.7: Experimental photoelectron momentum maps of the Fermi surface (left half) and their fully relativistic one-step model counterparts (right half) for photon energies of $h\nu = 55$ eV (a-b), 75 eV (c-d), and 155 eV (e-f), respectively. Momentum maps (a, c, e) correspond to photoexcitation by p -polarization, whereas momentum maps (b, d, f) correspond to s -polarization. The blue and yellow arrows indicate the Sheet III hole pocket, while the green arrows highlight the L-point hole pocket in Sheet II.

theoretical results in Figure 4.3, underscoring the role of the complex band structure and the emergence of evanescent final states in shaping the photoemission response in these regions.

Furthermore, Figures 4.7e and f provide compelling evidence of orbital-selective photoemission from Sheet I along the Γ -K high-symmetry direction, as discussed in Section 4.5. In both s - and p -polarized measurements, Sheet I manifests as a square-like feature with discontinuities at the corners. However, a distinct difference arises in the continuity of its sides: under p -polarization, the square exhibits continuous edges, whereas under s -polarization, the side along the Γ -K direction appears broken. This behavior reflects the dominance of even symmetry orbitals along this direction and their enhanced coupling to p -polarized light, consistent with the symmetry analysis of the underlying electronic states.

This disparity arises from the underlying orbital character of Sheet I. Along the Γ -K direction, the dominant contribution to Sheet I originates from orbitals with even symmetry relative to the yz crystalline mirror plane. As a result, p -polarized photons efficiently probe these even symmetry orbitals, while s -polarization suppresses them, leading to the observed discontinuity in the s -polarized spectra. Notably, this symmetry-driven selection rule no longer holds away from the yz mirror plane, as discussed in Section 3.1.3, where orbital mixing becomes more pronounced due to reduced symmetry constraints.

In Figures 4.7a-d, two concentric, orthogonal ellipses, indicated by the yellow arrows, are observed, corresponding to the Sheet III hole pocket centered at X-points in the Brillouin zone. Figure 4.3b provides additional evidence of the nearly dispersionless nature of these ellipses at photon energies below 150 eV, emphasizing their proximity to the zone boundary. This observation is associated with the bulk zone boundary at $(k_x, k_y) = (\pm 1.15, \pm 1.15)$ or the $\bar{M}$ -point of the surface Brillouin zone. It should be noted that the final state self-energy dominates at this specific momentum, resulting in $k_\perp$ broadening of the states. However, this effect is a consequence of photoemission final state self-energy and should not be directly interpreted as information from the bulk band structure or a surface state.

Next, the manifestation of linear dichroism (LD) in the bulk electronic structure, probed by constant initial-state momentum microscopy carried out from photon energies of 35 eV to 200 eV, is examined. Figure 4.8a shows an extracted plot along the k_y -axis (red arrow in Figure 4.2a) of constant initial-state momentum maps obtained using polarized photons, while Figure 4.8b presents the one-step photoemission calculations based on the same configuration. As described in Section 3.1.1, LD is evaluated along the k_y -axis, which lies in a crystalline mirror plane.

In Figure 4.8a, three significant asymmetrical points are primarily observed, marked as (A) and (B) pairs, near the L-point of the Brillouin zone. (A) is characterized by a strong intensity, while (B) shows a diminished intensity. Around these points of interest, a strong LD signal is observed from a band of Sheet I with even orbital character, as shown in Figure 4.5b near the L-point at Fermi energy. The LD signals alternate with a period of half a Brillouin zone over the range of photon energies

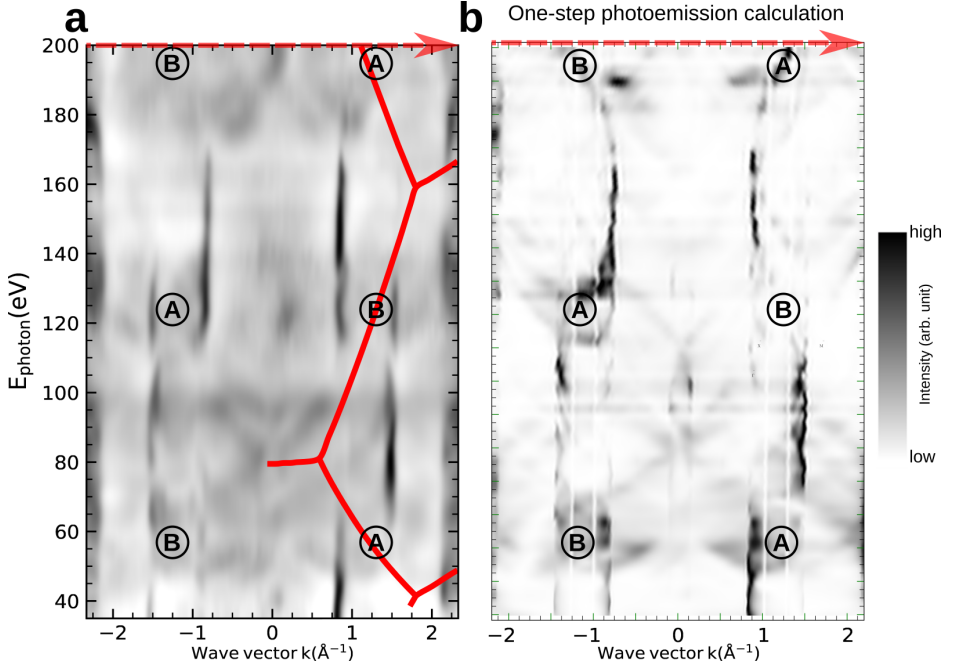


Figure 4.8: **a** Cross-sections along the k_y axis (red arrow in Figure 4.2b) of the constant initial-state momentum maps at Fermi energy, taken with p-polarized photon. The zone boundary of the free electron final state model is plotted in a solid red line on the right half. **b** One-step photoemission calculation using the same parameters.

probed. This alternation is interpreted as the inversion of orbital character across high-symmetry points in the Brillouin zone. Referring to the free electron final state zone boundary, it is observed that (A) and (B) are not equivalent but alternate with a period of half a Brillouin zone. The orbital character of the bulk electronic states is expected to adhere to the crystalline symmetry of the face-centered cubic Brillouin zone, which is inverted between (A) and (B) in the 3D Brillouin zone.

In stark contrast, the asymmetry observed with p-polarized photons completely diminishes when s-polarized photons are utilized, as shown in Figure 4.3a. This distinct behavior arises from the orientation of the electric field vector along the plane of the sample surface, highlighting the nuanced influence of polarization on the observed LD effects.

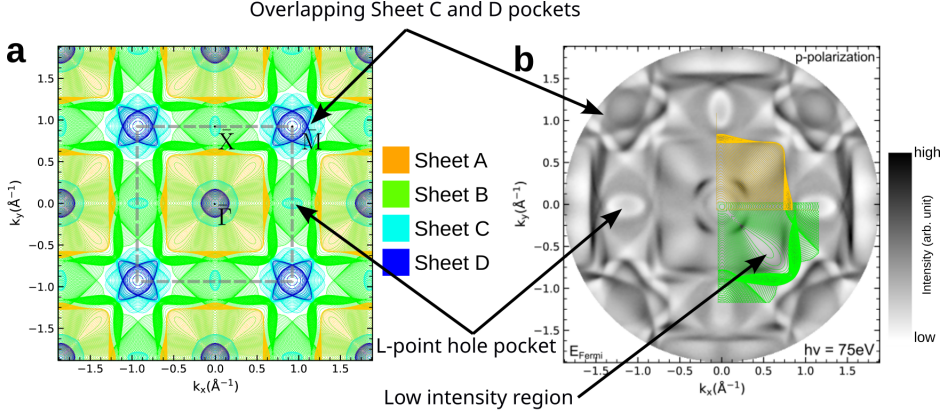


Figure 4.9: **a** Projection of the Rh(001) Fermi surface contours of the LDA+U ground state in the k_z dimension. **b** Photoelectron momentum map of Rh(001) measured with p-polarized photons at 75 eV. The orange and green overlays on the two quadrants represent the k_z -projected Sheet A and Sheet B Fermi surfaces of Rh, respectively.

4.2 Fermi surface of rhodium

Neighboring Pd in the periodic table, the electronic structure of Rh is complementary to that of Pd, as it has one less valence electron while featuring a face-centered cubic lattice with a slightly smaller lattice constant. The Fermi surface of Rh, as shown in Figure 2.3d, lacks the "jungle gym" Fermi surface topology of Pd. By comparing the respective band diagrams of Pd and Rh in Figures 2.3a and b, we can see the similarity of the two electronic structures with a shift in the Fermi level due to the valence number difference. For the same reason, Rh has an extra Fermi sheet compared to Pd as an additional band crosses the Fermi energy. Such a difference can be seen with the band extrema of Pd situated below the Fermi energy at L and X high symmetry points in Figure 2.3a.

The Fermi surface of Rh can be categorized into four distinct Fermi sheets, as shown in Figure 2.3d, along with its k_z -projection in Figure 4.9a. Sheet A (orange) primarily exhibits a free-electron-like character, appearing as a deformed sphere centered at the Γ -point. It features spikes extending toward the L- and X-high-symmetry points at the zone boundary and is entirely enclosed by Sheet B. Sheet B (green) manifests as a large Fermi sheet that is slightly electron-deficient, forming the characteristic "jungle gym" structure. It also extends toward the K-high-symmetry point while closely interlocking with both Sheet A and Sheet C. Sheet C (teal) consists of large, deformed elliptical hole pockets located around the X-points, with petal-like protrusions extending toward the K-point. The radius of these hole pockets is significantly modified upon the inclusion of SOC in theoretical calculations. Similar to Pd, the inclusion of SOC introduces an additional small hole pocket at the L-point. Sheet D (blue)

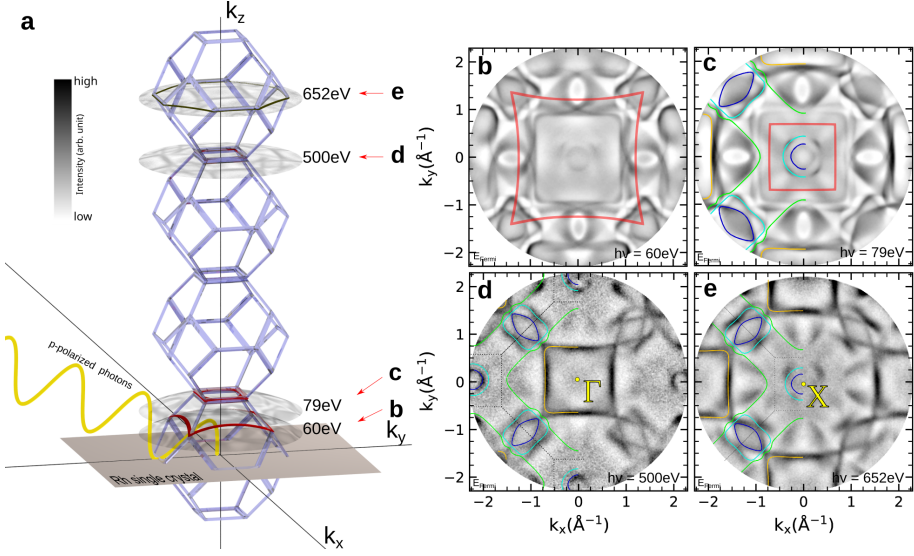


Figure 4.10: **a** Experimental geometry and equi-energy free electron final state spherical cuts in 3D momentum space corresponding to the experimental momentum maps. **b**, **c**, **d**, **e** show the experimental momentum maps obtained with p-polarized photons of 60 eV, 79 eV, 500 eV and 652 eV, respectively. The red overlay illustrates the intersections between the corresponding momentum disc and the first Brillouin zone boundary in a nearly-free electron final state model, whereas the theoretical Fermi contour of rhodium from local density approximation is overlaid on the left half of **c**, **d**, **e**.

appears as elliptical hole pockets around the X-points and is fully enclosed by Sheet C. Consistent with the case of Pd, the Fermi energy in the theoretical calculations was adjusted to align with the experimentally observed d-like Sheet B.

Based on the study of Pd, a similar experimental pipeline was carried out to investigate the Fermi surface of Rh [71]. A series of measurements was performed between photon energies of 34 eV and 100 eV in 2 eV intervals, and another set between photon energies of 500 eV and 652 eV in the soft X-ray regime. The free-electron final state model used for Rh assumed an inner potential, U_i of 20.25 eV.

Figure 4.9b shows a momentum map measured at 75 eV, cutting close to the X-point, where the data strongly deviate from the free-electron final state approximation. Remarkably, the momentum map appears very similar to the k_z projection of the Rh Fermi surface shown in Figure 4.9a. First, we observe the overlap of the Sheet C and Sheet D hole pockets, which resemble a projection of the k_z component. These pockets appear filled due to $k_\perp$ broadening by the imaginary wave vector. The comparable intensities of these overlapping pockets are quite surprising, as they are positioned half a Brillouin zone away from one another. Similarly, the L-point hole

pocket is observed, despite being nearly a quarter of a Brillouin zone away from the L-point in the free-electron final state approximation. The pocket also appears filled rather than hollow, due to the k_z broadening.

While the k_z projection of Sheets A and B can be difficult to distinguish due to their coverage of most of the Brillouin zone, Figure 4.9b shows overlays of the two sheets on the quadrants of the experimental data. The edge of Sheet B forms the outer edge of a square-like feature, while Sheet A forms the inner square-like feature. Additionally, the projected Sheet B also covers the $\bar{\Gamma}$ -point of the surface Brillouin zone. Around the $\bar{\Gamma}$ -point, the projection features a four-fold-like symmetry, with a lack of intensity resembling petals. These features are clearly evident in the experimental data, suggesting that at this particular energy, the evanescent wave functions from multiple $k_{\perp}$ components manifest at the same energy.

Figure 4.10a shows the free electron final state cuts across the Brillouin zones for the selected momentum maps in Figure 4.10b-e. Our interpretation of the free electron final state model in the lower photon energy regime allows us to explain the lack of spectral weight for the Sheet C and Sheet D hole pockets in Figure 4.10c, where the free electron final state sphere cuts across the X-point of Rh, which corresponds to a zone boundary.

As observed in the data measured at 75 eV, the deviation from the free electron final state model is significant in both Figures 4.10b and c at photon energies of 60 eV and 79 eV, respectively. Similarly to Figure 4.9b, the spectral weight in Figure 4.10c from Fermi Sheet B manifests as a four-fold petal-like background projection around the origin. Although the L-point hole pocket of Fermi Sheet C in Rh is slightly larger than predicted by theory, our experimental results are generally in agreement with the FPLAPW calculations. By ensuring convergence to the free electron final state model at higher photon energies, Figures 4.10d and e present experimental results obtained at the Γ and X-points at photon energies of 508 eV and 652 eV, respectively.

In conclusion, low photon energy measurements offer high-resolution mapping of the projected Fermi surface and yield detailed insights into the electronic states. However, due to the limited photoelectron escape depth and the associated uncertainty in perpendicular momentum ($k_{\perp}$), such measurements do not provide precise access to the full three-dimensional band structure. While the free-electron final state approximation is often employed to estimate $k_{\perp}$ values, it becomes increasingly unreliable near the Brillouin zone boundaries, where final-state damping effects dominate. In all cases, particularly near high-symmetry points and zone boundaries, caution must be exercised when interpreting the data based on this approximation.

To achieve a comprehensive understanding of the bulk electronic structure, these low-energy experiments must be complemented by measurements in the soft X-ray regime, where the increased photoelectron kinetic energy enhances $k_{\perp}$ resolution and enables more accurate three-dimensional momentum mapping. When combined with detailed theoretical modeling of both initial and final states, including one-step photoemission calculations, this approach allows us to resolve the full band dispersion and extract the orbital character of the electronic states. This ultimately enables a reconstruction of the three-dimensional electronic structure across the entire Brillouin

zone.

5 Exchange Interaction in Ultrathin Half-metallic FePd alloy

This chapter investigates the emergence of spin polarization in the electronic structure of ultrathin FePd alloy layers on Pd(001). Section 5.1 briefly introduces the characteristics of a half-metal and its spin-polarized electronic structure. Section 5.2 outlines the spin-resolved momentum microscopy on FePd alloy thin film on Pd(001). The results highlight the spin-polarized electronic states and the fully spin-polarized Fermi surface. Next, Section 5.3 covers the tuning of exchange splitting in the spin-polarized bands of FePd films and optimizes the FePd film to become a half-metal. Section 5.4 presents additional calculations performed by collaborator Dr. Arthur Ernst to supplement the experimental results, demonstrating the two-dimensional half-metallicity in FePd alloy.

5.1 A brief introduction of ferromagnetic films and half-metals

The Mermin-Wagner theorem forbids the emergence of magnetic ordering in isotropic low-dimensional systems, such as two-dimensional thin films [115, 116]. According to the theorem, the finite correlation length of the order parameter prevents the appearance of magnetic ordering through time-reversal symmetry breaking, as no true Goldstone mode exists outside the zero temperature limit or in the presence of an external field. It is shown that in two-dimensional systems, the fluctuations of the order parameter are always massive. However, this restriction can be circumvented through the introduction of anisotropy in the system [115]. In simple terms, the emergence of ferromagnetic order in a two-dimensional itinerant system requires the breaking of time-reversal symmetry along an anisotropy in the system, such as via spin-orbit coupling (SOC). As we will see in this chapter, in FePd alloy thin film, SOC allows the Mermin-Wagner limit for two-dimensional ferromagnetism to be overcome.

Half-metals, a unique subclass of ferromagnets, are characterized by their ability to conduct electrons in only one spin channel—typically the majority (spin-up) channel—while the other, minority (spin-down) channel is insulating. This spin-selective conductivity is illustrated in Figure 5.1a, where the density of states (DOS) for the minority band shows a gap at the Fermi level. In such systems, a spin channel gap exists for one spin polarization but not the other, resulting in a fully spin-polarized Fermi surface. This distinctive property makes half-metals highly attractive for spin-

tronic applications, as they can function as ideal spin filters and efficient spin injectors, key components in devices based on spin-transfer torque and spin-orbit torque [117, 118]. Despite significant theoretical advancements and the prediction of numerous half-metallic candidates, experimental validation remains limited and, in many cases, inconclusive.

So far, all known half-metals exist at cryogenic temperatures, which makes them impractical for technological applications [118]. Historically, Heusler alloys and complex oxides have been among the most well-known examples of half-metals. However, structural imperfections [119, 120], surface and interface effects [121, 122] often lead to the breakdown of half-metallicity. For instance, experiments on the prototypical half-metallic Heusler alloy NiMnSb [123, 124] and magnetite Fe₃O₄ [125, 126] demonstrated significant discrepancies in net spin polarization due to the structural differences between the surface and the bulk.

As a result, typical ferromagnets lose their high spin polarization and half-metallicity at their surface or when reduced to sub-nm thickness. Aside from recent theoretical predictions [127, 128], no experimental evidence of a two-dimensional half-metal exists. In addition to structural factors, the ubiquitous relativistic effect of SOC [129] and thermal depolarization mechanisms, such as magnon and phonon excitations [130, 131], are detrimental to half-metallicity at finite temperatures. On the experimental side, the verification of half-metallicity is often limited due to challenges in resolving the spin characteristics of the electronic states [9, 132].

This chapter presents a bottom-up optimization pathway for the realization of a two-dimensional half-metallic film via direct band structure engineering. Figure 5.1b illustrates the fundamental concept of a half-metallic FePd surface monolayer, which consists of two atomic layers of a disordered alloy on a non-magnetic Pd substrate. The electronic structure of the Pd(001) substrate has been investigated in detail in Chapter 4. The epitaxial monolayers (ML) of the disordered FePd alloy on Pd(001) single crystals were fabricated [15, 111] using molecular beam epitaxy from a high-purity Fe rod, followed by mild annealing as described in Section 3.2.

At the core of this endeavor lies the goal of achieving a fully polarized Fermi surface, which is unattainable through exchange interaction alone [116]. To overcome this challenge, SOC is leveraged to lift the band degeneracy at local k -points, thereby creating a spin channel gap at the Fermi energy. In this approach, two elemental ingredients are utilized: iron (Fe) and palladium (Pd). Fe, known for its large exchange interaction, lays the foundation for robust magnetic interaction within the system. On the other hand, Pd, characterized by its susceptibility to polarization via the proximity effect, also possesses significant SOC. Through systematic alloying and manipulation of stoichiometry, band hybridization points near the Fermi energy are engineered, opening a gap in one of the spin channels. This results in the realization of a two-dimensional half-metallic film.

As discussed in the previous section, the confined dimensionality of the thin film makes the surface and interfacial electronic states the primary focus. The two-dimensional confinement in space also implies that the out-of-plane momentum is no longer a good quantum number. In other words, the electronic states of a two-

dimensional film do not disperse along the out-of-plane wave vector, $k_{\perp}$. Therefore, the momentum-resolved electronic structure of the thin film is described using the

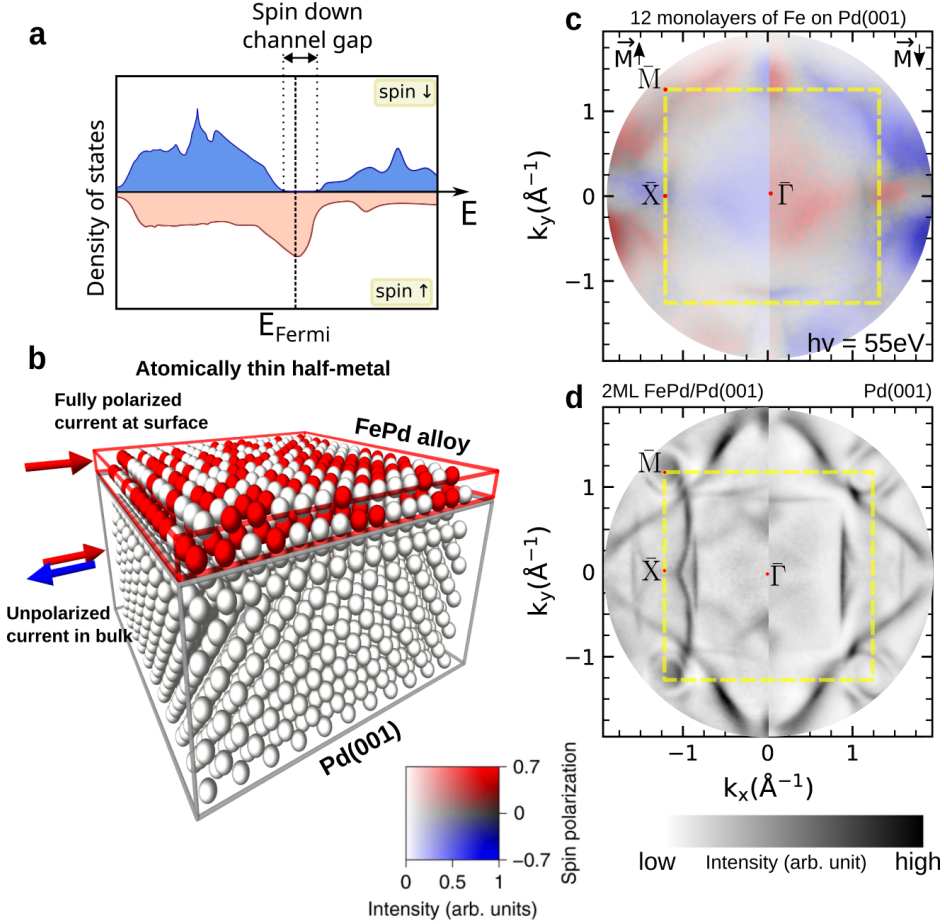


Figure 5.1: **a** Schematic density of states for a half-metal. A gap opens at the Fermi level in the spin-down channel, rendering it insulating, while the spin-up channel remains metallic. **b** Illustration of a dimensionally confined half-metallic film: a two-monolayer-thick FePd alloy grown on Pd(001). **c** Spin-resolved Fermi surface of body-centered-cubic Fe, represented by a 12 ML Fe film on Pd(001), measured p-polarized photons at 55 eV, under antiparallel remanent magnetization directions, $+y$ (left half) and $-y$ (right half), along the spin-quantization axis. **d** Fermi surface of a two-monolayer FePd film on Pd(001) (left half) alongside that of the Pd(001) substrate (right half), measured using s-polarized photons at 35 eV. Dashed yellow lines indicate the surface Brillouin zone corresponding to a cubic lattice.

corresponding surface Brillouin zone convention, as shown in Figure 2.3e.

5.2 Spin-resolved electronic structure of FePd/Pd(001)

As a reference, the Fermi surface of a prototypical body-centered-cubic (bcc) Fe system, consisting of 12 ML of Fe on Pd(001), was measured using spin-resolved momentum microscopy, as shown in Figure 5.1c. The left and right halves of Figure 5.1d depict the antiparallel pairs of remanent magnetization vectors along the $+y$ and $-y$ directions, respectively. The magnetization along the y -axis aligns with the spin quantization axis of our experimental setup. In the left half, the majority band of Fe is populated by spin-up (red) electrons, whereas the minority states are populated by spin-down (blue) electrons. This observation is consistent with the textbook example of bulk bcc Fe states, as illustrated in Figure 2.2. Upon reversing the magnetization direction from $+y$ to $-y$, the spin character of the bands switches: the majority band transitions from spin-up to spin-down, while the minority band undergoes the opposite transformation. This underscores the hallmark of a ferromagnetic band structure, where time-reversal symmetry is broken, and the spin polarization is switchable via magnetization.

Figure 5.1d shows the spin-integrated Fermi surface of two ML FePd/Pd(001) and bulk Pd(001). A strong hybridization of states is evident in the stark contrast between the Fermi surface of the disordered alloy MLs and that of bulk Pd(001), particularly near the Brillouin zone boundary.

Spin-resolved momentum microscopy measurements on two ML FePd/Pd(001), shown in Figures 5.2a and c, reveal a defining characteristic of half-metallic systems: a nearly fully spin-polarized Fermi surface. The absence of spin-down states at the Fermi level provides strong evidence for the half-metallic nature of this system.

At an energy of 0.2eV below the Fermi level, the onset of the minority spin-down band becomes apparent in the momentum maps presented in Figures 5.2b and d. Notably, the spin polarization of the two ML FePd/Pd(001) system exhibits a negative sign compared to Fe(001), indicating an inverted spin character. The majority spin-up bands, which dominate the spectral intensity at the Fermi surface, are aligned antiparallel to the magnetization direction along the $-y$ -axis. In addition to its half-metallic nature, the two ML FePd/Pd(001) system exhibits a negative spin polarization, distinguishing it from the bcc Fe(001) shown in Figure 5.1c.

To comprehensively investigate the electronic states, both s - and p -polarized photons were employed in the photoemission experiments. The resulting measurements reveal a strong polarization-dependent sensitivity to the electronic states, attributed to matrix element effects in the photoemission process. As shown in Figure 5.2b, the minority spin-down band is prominently observed under s -polarized excitation, whereas the corresponding spectral weight is significantly suppressed in the p -polarized data (Figure 5.2d). This difference originates from the optical selec-

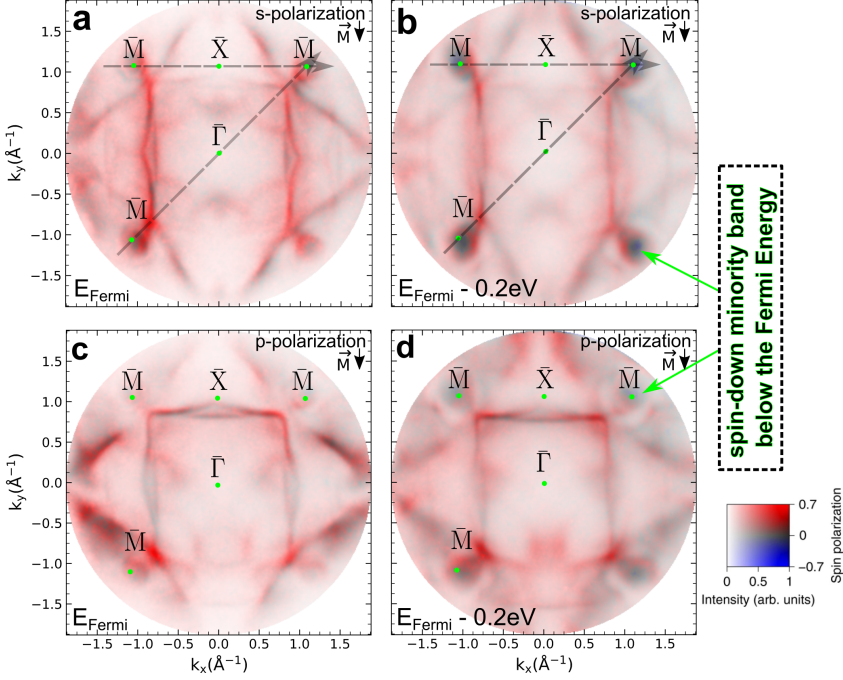


Figure 5.2: Experimental spin-resolved (a,c) Fermi surface and (b,d) momentum maps at 0.2 eV below the Fermi level of two ML FePd/Pd(001), obtained using (a,b) s-polarized and (c,d) p-polarized photons at 35 eV, respectively. Green arrows indicate the maximum of the spin-down minority band centered at $\bar{M}$. The sample is magnetized in the $-y$ -direction.

tion rules, which modulate the transition probabilities based on the symmetry of the electronic orbitals and the polarization of the incident photons.

In addition, spin-resolved measurements reveal the absence of detectable spin-down states above the maximum of the minority band up to the Fermi level. This absence serves as direct spectroscopic evidence of a highly spin-polarized Fermi surface, supporting the classification of two ML FePd/Pd(001) as a candidate half-metallic system. The onset of the minority spin channel in the valence band, defined by the maximum of the spin-down states, establishes the lower bound of the spin channel gap, while the spin-up states remain metallic. Consequently, the Fermi surface is fully spin-polarized, a key criterion for half-metallicity.

To investigate the energy dispersion of the majority and minority spin states, energy-momentum cuts along the surface high-symmetry directions were extracted from a series of spin-integrated momentum maps, as shown in Figures 5.3a and b for s-polarized and p-polarized light, respectively. These measurements complement the spin-resolved momentum maps in Figure 5.2 by capturing the dispersion of the bands

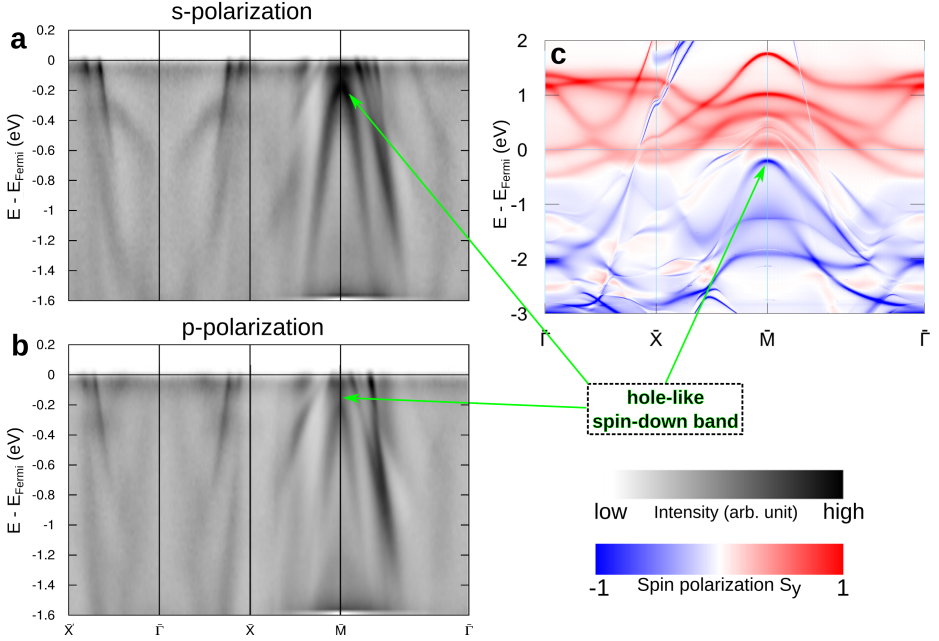


Figure 5.3: Energy-momentum cross-sections obtained from the spin-integrated momentum maps using **a** s- and **b** p-polarized photons at 35 eV, respectively. **c** Theoretical electronic structure of the topmost two surface layers of two ML FePd/Pd(001). Green arrows denote the maximum of the hole-like spin-down band centered at $\bar{M}$.

observed at the Fermi energy and 0.2 eV below it.

In particular, the experimental data reveal a hole-like band at the $\bar{M}$ -point, with its maximum located approximately 175 meV below the Fermi energy. This observation coincides with the onset of the spin-down minority band in the spin-resolved momentum maps in Figures 5.2b and d. Moreover, Figures 5.3a and b further confirm the intensity differences between s- and p-polarizations, demonstrating that the band dispersion is captured in both measurements, albeit with varying photoemission intensities due to matrix element effects.

To support the experimental findings, layer- and spin-resolved Korringa-Kohn-Rostoker (KKR) calculations with the Coherent Potential Approximation (CPA) were performed to provide theoretical insight into the underlying physics. Figure 5.3c presents the theoretical spin-resolved Bloch spectral function for the first two surface layers of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$, assuming a nominal Fe content of 0.9 ML. The calculations predict a near-ideal half-metallic state localized at the surface, consistent with the experimental results.

Interestingly, along the $\bar{\Gamma}$ - $\bar{X}$ direction, a spin channel gap emerges for the spin-down free-electron-like states, reinforcing the realization of a half-metallic Fermi surface.

This confirms that the minority spin states are absent at the Fermi energy, a defining characteristic of half-metallicity. Overall, the theoretical calculations corroborate the surface-sensitive experimental measurements, demonstrating that the half-metallic electronic wave function is predominantly confined to the top two layers of the system. The implications of this two-dimensional confinement will be further explored in Section 5.4.

5.2.1 Role of spin-orbit coupling

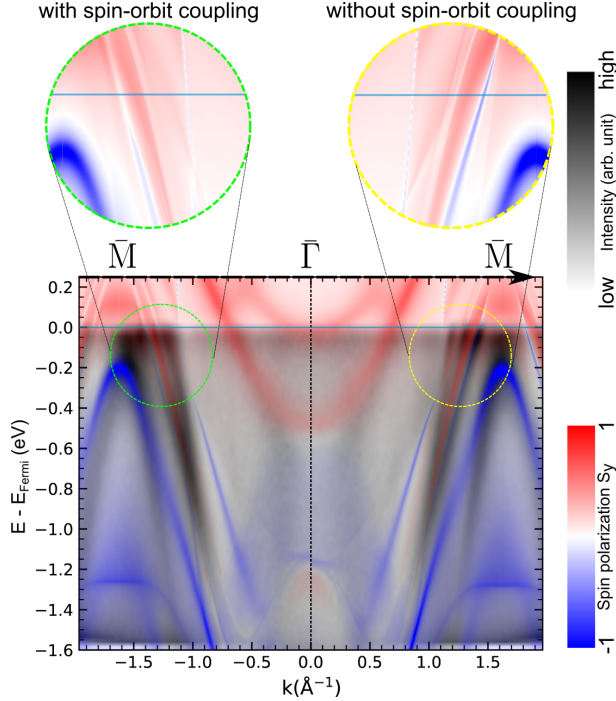


Figure 5.4: **a** Experimental spin-integrated energy-momentum dispersion along $\bar{M}-\bar{\Gamma}-\bar{M}$ of two ML FePd/Pd(001), overlaid with calculated spin-resolved band structures with (left half) and without (right half) SOC.

Figure 5.4 shows the experimental spin-integrated energy-momentum dispersion along the $\bar{M}-\bar{\Gamma}-\bar{M}$ direction for two ML FePd/Pd(001), with overlaid theoretical band structures calculated both with and without the inclusion of SOC. These results highlight the significant role SOC plays in shaping the electronic structure and the emergence of a half-metallic Fermi surface.

In the absence of SOC (left half of Figure 5.4), the spin-up and spin-down bands are largely decoupled, allowing the spin-down minority band to cross the Fermi level

near the $\bar{M}$ -point, contributing to a non-half-metallic state. This is because, without SOC, there is no interaction between the majority and minority spin bands, resulting in a gapless spin-down state at the Fermi level.

However, upon inclusion of SOC in the calculations (right half of Figure 5.4), the electronic structure is significantly modified. SOC induces band hybridization at specific $\vec{k}$ -points near the spin-down Fermi level crossing, which leads to the opening of the spin-down channel gap. As a result, a fully polarized Fermi level emerges, characterized by the absence of spin-down states at the Fermi energy. The maximum of the minority band now defines the highest occupied spin-down electronic states in the vicinity of $\bar{M}$ -point. This manifests a half-metallic state, where the spin-down gap opens up at the Fermi energy, and only spin-up states remain at the Fermi surface. Notably, the minority hole-like band, while still present in the system, is largely unaffected by SOC. This highlights that SOC's primary influence is on the spin-down band near the Fermi level, where it prevents the band from crossing the Fermi level, thereby ensuring the half-metallic character of the system.

Figure 5.5 presents the calculated spin-resolved band structure along $\bar{\Gamma}$ - $\bar{M}$ and $\bar{\Gamma}$ - $\bar{X}$ for $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$. The electronic structure exhibits a key characteristic of broken time-reversal symmetry, in which $E_n(\vec{k}, \uparrow) \neq E_n(-\vec{k}, \downarrow)$. However, unlike a conventional ferromagnetic system shown in Figure 2.2, where the spin-up and spin-down bands can be approximately related by an energy displacement, the exchange-split electronic states of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ exhibit significant deviations in dispersion due to hybridization.

Figures 5.5c,d and e,f illustrate the formation of a gap for the spin-down bands along $\bar{\Gamma}$ - $\bar{M}$ and $\bar{\Gamma}$ - $\bar{X}$, respectively. In the absence of SOC, the free electron-like spin-down band would be expected to cross the Fermi level, thereby destroying the half-metallic property of the system. Notably, as demonstrated in Section 5.3, the spin channel gap centered around the Fermi energy can be precisely tuned by optimizing the composition of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$, thereby achieving half-metallicity in the thin film. Thus far, the contribution of SOC has been discussed primarily in the context of spin channel gap formation at the Fermi energy. Additional roles of SOC in the interplay between exchange and SOC will be explored in Chapter 6.

5.3 Exchange engineering of FePd thin-film

At the core of ferromagnetism lies the breaking of time-reversal symmetry due to magnetic ordering. This symmetry breaking lifts the spin degeneracy of electrons, leading to exchange splitting, as illustrated in Figure 2.2. A direct approach to investigating exchange splitting arising from exchange interaction involves adjusting the nominal Fe content in the thin film. This variation modulates both intralayer and interlayer exchange interaction, providing an effective means to control the degree of spin polarization [15].

As discussed in Sections 5.2 and 5.2.1, the energy gap of the spin-down bands is primarily dictated by the position of the spin-down minority band maximum. By

systematically studying the relationship between exchange splitting and the nominal Fe content in the FePd alloy film, the exchange interaction can be finely tuned. This tunability provides a pathway for engineering half-metallicity in FePd thin films with tailored spin-polarized electronic states.

Here, two different two ML FePd films of different nominal Fe content of 0.9 ML and 0.7 ML are fabricated on Pd(001). The dispersions along $\bar{M}$ - $\bar{X}$ are shown in spin-integrated band dispersions in Figure 5.6a. The band dispersion along $\bar{M}$ - $\bar{X}$ experiences a significant shift. The hole-like spin-down band can be observed in both cases. In the FePd film with 0.7 nominal Fe content, the hole-like spin-down band appears to shift towards the Fermi level, and its maximum touches it. To supplement our experimental observation, Figure 5.6b shows the spin-resolved theoretical calculation of the respective alloy with 0.9 ML and 0.7 ML nominal Fe content. The theoretical calculations agree well with the band dispersions observed in our experimental data. It shows that at 0.7 nominal Fe content, the FePd film is not half-metallic, and the half-metallicity is destroyed when the spin-down minority band touches the Fermi level.

Theoretical models of FePd/Pd(001) with varied nominal Fe contents are used to evaluate the general relationships between the exchange splitting and nominal Fe content in the bilayer alloy. Figure 5.7 shows the theoretical electronic structures

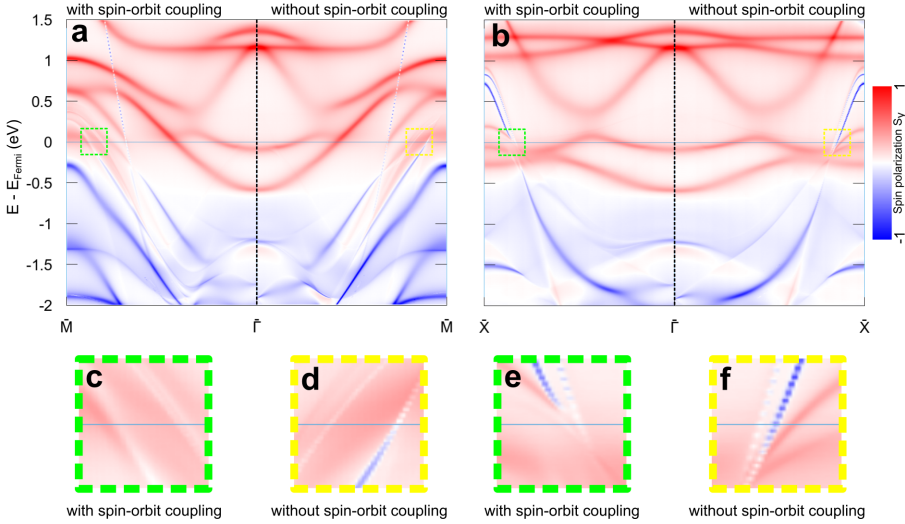


Figure 5.5: **a** Calculated energy-momentum dispersions along **a** $\bar{\Gamma}$ - $\bar{M}$ and **b** $\bar{\Gamma}$ - $\bar{X}$ of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ with (left-half) and without (right-half) SOC. The magnified regions in the vicinity of Fermi energy highlight the gap formation along **c,d** $\bar{\Gamma}$ - $\bar{M}$ and **e,f** $\bar{\Gamma}$ - $\bar{X}$ with and without SOC, respectively.

along $\bar{M}-\bar{\Gamma}$ of the bilayer alloy in 1.5 ML, 0.9 ML, and 0.7 ML nominal Fe contents, respectively. Although feasible in a theoretical model, the 1.5 ML of Fe confined within the top two FePd alloy bilayers is not demonstrated in experiments. However, our study uses it to verify the relationship between the total exchange splitting and the nominal Fe content.

As shown in the theoretical calculations, a reduction in nominal Fe content from 0.9 ML to 0.7 ML, as shown in Figures 5.7b,c and Figures 5.6b, decreases the exchange splitting at the $\bar{M}$ -point by approximately 0.2 eV. Conversely, increasing the Fe content from 0.9 ML to 1.5 ML enhances the exchange splitting at $\bar{M}$ by about 0.6 eV. Beyond exchange splitting control, the theoretical calculations predict the loss of half-metallicity in the two ML FePd alloy with nominal 0.7 ML Fe ($\text{Fe}_{0.7}\text{Pd}_{1.3}/\text{Pd}(001)$), as shown in Figures 5.6b, highlights the crucial role of nominal Fe content in achieving optimal half-metallic conditions. In this case, the Fermi surface is no longer exclusively spin-up polarized. Along the $\bar{M}-\bar{X}-\bar{M}$ high-symmetry line of the surface Brillouin zone, the spin-down hole-like band at $\bar{M}$ for $\text{Fe}_{0.7}\text{Pd}_{1.3}/\text{Pd}(001)$ reaches its maximum at the Fermi level. In contrast, in $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$, this maximum lies

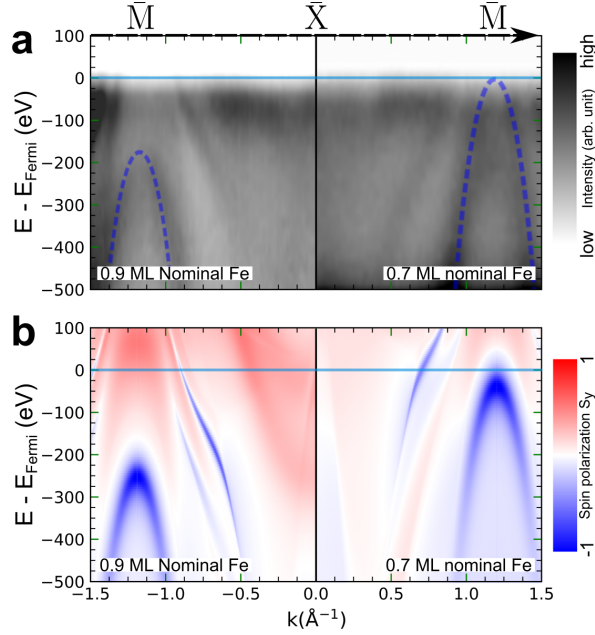


Figure 5.6: **a** Experimental spin-integrated energy-momentum dispersions along $\bar{M}-\bar{X}-\bar{M}$ of two MLFePd/Pd(001) with of 0.9 ML (left-half) and 0.7 ML (right-half) nominal Fe contents respectively. Blue dashed lines indicate the hole-like spin-down bands. **b** Spin-resolved calculations along $\bar{M}-\bar{X}-\bar{M}$ for the dispersions shown in **a**.

approximately 175 meV below the Fermi level. Additionally, a spin-down band near the midpoint of $\bar{M}-\bar{X}$ crosses the Fermi level, leading to the breakdown of a fully spin-polarized Fermi surface.

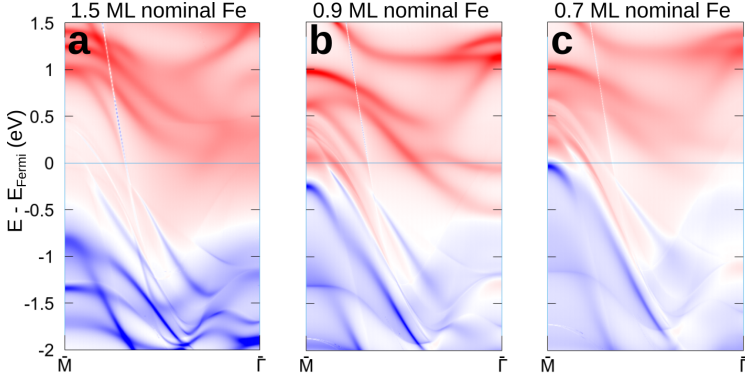


Figure 5.7: Theoretical electronic structures along $\bar{M}-\bar{\Gamma}$ of FePd alloy thin-film in **a** 1.5 ML, **b** 0.9 ML, and **c** 0.7 ML nominal Fe contents respectively.

As the theoretical calculations demonstrate, the spin-polarized electronic structure can be effectively engineered by balancing the exchange interaction and SOC. It is, however, important to note that due to the alloying nature of the ML fabrication, a lower Fe content will inevitably induce further inhomogeneity within the thin film; meanwhile, a higher Fe content is expected to induce structural phase transition and further disorder into the bulk [111, 112].

5.4 Two-dimensional half-metallicity and proximity spin polarization

A central result of our investigation is the identification of two-dimensional half-metallicity in a binary alloy thin film. Our study employed inherently surface-sensitive photoemission experiments, limiting the probing depth to the surface MLs. To substantiate these findings, we complemented our approach with additional layer-dependent KKR calculations, providing additional validation of the confinement of half-metallic electronic states within the thin film.

Figures 5.8a-d present the spin-resolved Bloch spectral functions from the surface layers, integrated over thicknesses ranging from one ML to five ML, along $\bar{M}-\bar{\Gamma}$. A key observation emerges: beyond three layers, the two-dimensional half-metallicity is lost, as evidenced by the crossing of hole-like spin-down states crossing the Fermi level in Figures 5.8c and d.

A layer-resolved comparison of the Fermi surfaces for $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ is shown in Figure 5.8e, where the quadrants correspond to integrations of the Bloch spectral

functions from the topmost, top two, top three, and top five layers. As evident in Figures 5.8c and d, the presence of spin-down states at the Fermi level becomes prominent with increasing integration beyond two layers. In particular, at the $\bar{M}$ -point, the spin-down band crosses the Fermi level when contributions from more than the top two layers are included, inherently showing that the half-metallicity is confined to the two ML of FePd alloys.

To further analyze the origin of these contributions, we examine the layer-resolved Bloch spectral function of the third layer, which corresponds to the topmost layer of the substrate, as shown in Figure 5.8f. The calculations reveal that this layer

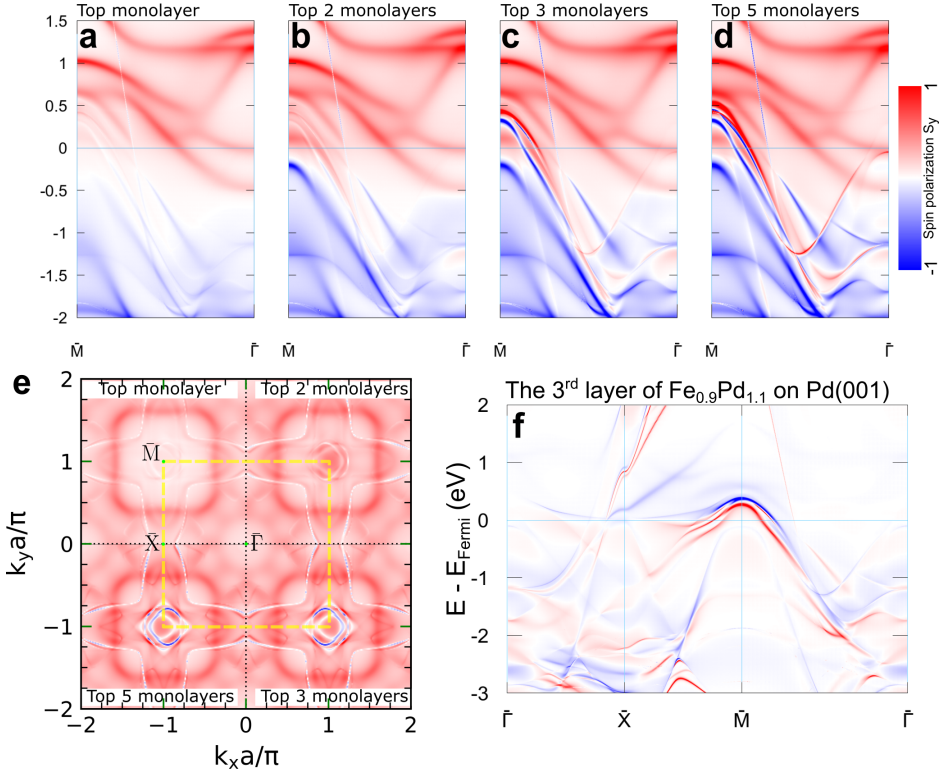


Figure 5.8: The calculated spin-resolved spectral weight of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ along the $\bar{M}-\bar{\Gamma}$ direction is presented for different layer integrations: **a** the uppermost layer, **b** the topmost two layers, **c** the topmost three layers, and **d** the topmost five layers of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$. The four quadrants in panel **e** illustrate the spin-resolved Fermi surface obtained from the surface-layer integrations of **a-d**. Meanwhile, **f** depicts the spin-resolved spectral weight originating from the third layer of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$, which corresponds to the uppermost layer of the Pd substrate.

is ferromagnetic and spin-polarized due to significant hybridization with the half-metallic thin film. The proximity to the FePd alloy induces spin polarization in neighboring Pd atoms, causing the spin-up majority electronic states of polarized Pd to shift to lower energies [15].

A highly anisotropic exchange splitting is observed within this layer, primarily due to band hybridization with the thin film. The strongest effects occur near the $\bar{M}$ -point, which is also heavily populated by electronic states of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$. Furthermore, the interfacial Pd layer, as shown in Figure 5.8f, exhibits opposite spin polarization relative to the ferromagnetic film. This inversion is evident in the exchange splitting: the spin-down and spin-up states of the Pd layer are shifted in the opposite direction compared to the neighboring FePd film, resulting in positive polarization at the Fermi level, in contrast to FePd.

6 Interplay between Exchange Interaction and Spin-orbit Coupling in two ML FePd alloy

This chapter provides a detailed investigation of the interplay between spin-orbit coupling (SOC) and exchange interaction in two monolayers (ML) of FePd/Pd(001) and its impact on the electronic structure. In Chapter 5, we examined the emergence of half-metallicity and time-reversal symmetry in the band structure of two ML FePd/Pd(001), as well as the tunability of the exchange interaction through stoichiometric variation in this two-dimensional system, thereby realizing a half-metallic state. Building upon that foundation, the present chapter focuses on the competing effects of SOC and exchange interaction as manifested in the experimentally observed band structure, supported by fully relativistic theoretical calculations.

Section 6.1 addresses the influence of the magnetization vector orientation on the symmetry properties of the electronic structure. Specifically, we analyze the momentum-resolved distribution of electronic states in the FePd alloy and its dependence on the magnetization direction, revealing a symmetry lowering of the Fermi surface. Section 6.2 examines the signatures of circular dichroism (CD) across the band structure to elucidate asymmetries induced by the interplay between SOC and exchange interaction. Finally, Section 6.3 investigates the non-collinear spin texture of the electronic structure using spin-resolved momentum microscopy, highlighting the complex modifications of spin texture induced by SOC in the presence of exchange interaction.

All theoretical calculations discussed herein were performed by our collaborator, Dr. Arthur Ernst, and are used to complement and support the experimental findings presented in this chapter.

6.1 Manifestation of broken mirror symmetry in the electronic structure by magnetization

The interplay between exchange interaction and SOC plays a fundamental role in shaping the electronic structure of magnetic materials, particularly near the Fermi level. Among the control parameters available, magnetization serves as a primary variable for switching and manipulating the spin-resolved band structure through symmetry breaking, spin reorientation, and SOC-induced mixing of electronic states.

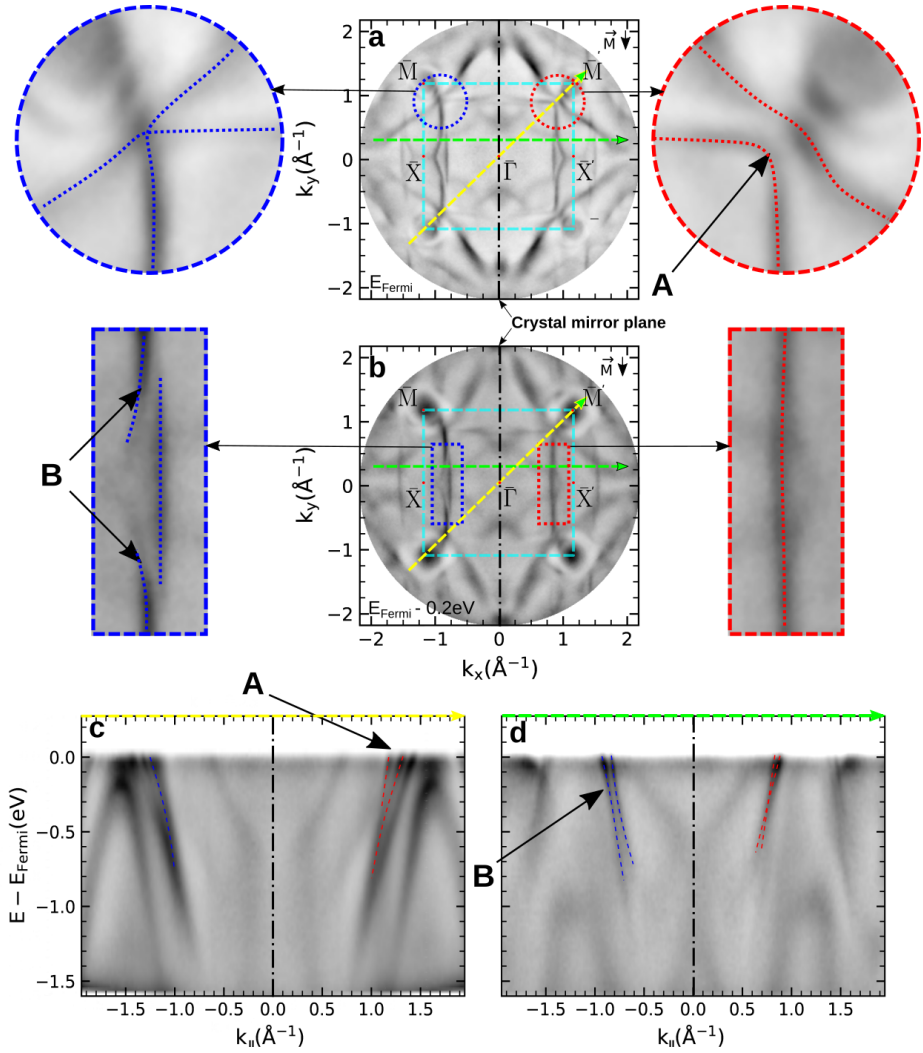


Figure 6.1: Experimental photoelectron momentum maps: **(a)** Fermi surface contour of two ML FePd/Pd(001) and **(b)** momentum map at 0.2 eV below the Fermi level, measured using s-polarized photons at 35 eV under in-plane remanent magnetization in the $-y$ direction. The teal dashed line denotes the surface Brillouin zone boundary, with red dots marking high-symmetry points. **(c)** and **(d)** show extracted band dispersions along the yellow and green dashed lines in **(a)** and **(b)**, respectively. The insets highlight key features. Points A and B mark the pronounced band asymmetries. The black dash-dotted line indicates the crystal mirror plane and the photon incidence plane (see Section 3.1). Dotted lines serve as guides to visualize the asymmetries.

For instance, Figure 5.1c illustrates the reversal of spin polarization of electronic states at the Fermi level in Fe(001) upon switching the magnetization to the antiparallel direction. This operation is a time-reversal transformation in the context of the symmetry relations expressed in Equation 2.10. Under the same motivation, we investigate the two-monolayer FePd/Pd(001) system under systematically controlled in-plane magnetization along the crystalline mirror planes, enabling direct observations of additional magnetization-induced effects in the electronic structure.

As a reference for the FePd alloy, Figure 3.5d displays the spin-integrated two-dimensional Fermi surface contour of prototypical ferromagnetic Fe(001), magnetized *in situ* along the $-y$ direction. The Fermi surface exhibits mirror symmetry with respect to both the yz and xz crystallographic planes, with only minor intensity modulations attributed to linear dichroism effects. The use of momentum microscopy, with its inherent capability for full two-dimensional k -space imaging, makes it particularly well-suited for resolving such symmetry features.

In contrast, the Fermi surface of two ML FePd/Pd(001), shown in Figure 6.1a, exhibits pronounced asymmetries with respect to the yz mirror plane, violating the condition $E(k_x, k_y) = E(-k_x, k_y)$, as highlighted in the insets. The measurements were performed with the photon incidence direction ($-k_y$) aligned along the Γ -X mirror plane and the magnetization vector (also along $-y$). s-polarization is employed in the measurements in Figure 6.1 to simplify the observation, as linear dichroism induced by p-polarization may modulate the photoemission intensity, thereby complicating the identification of competing interaction and symmetry-breaking effects in the electronic structure.

Importantly, the system retains symmetry across the xz mirror plane, indicating that the symmetry breaking is directionally dependent. In this configuration, magnetization along the y -axis breaks the yz mirror plane, resulting in asymmetric features along the orthogonal k_x direction. To clarify the symmetry breaking, surface high-symmetry points on opposite sides of the magnetization axis are denoted using a prime notation (e.g., $\bar{X}'$, $\bar{M}'$). This notation applies strictly to the discussion of the band structure and does not reflect changes in the underlying crystal structure. The electron-like bands forming the deformed square Fermi sheet exhibit clear asymmetry. Insets in Figures 6.1a and b highlight this behavior near $\bar{M}$ and $\bar{M}'$, particularly the asymmetric connections between $\bar{M}'$ and $\bar{X}'$.

This asymmetry becomes more apparent when comparing the local band structures at $\bar{M}$ and $\bar{M}'$. In the left inset (blue), a band crossing is observed in the $-k_x$ region, indicating a degenerate state. Conversely, in the right inset (red), this degeneracy is lifted in the $+k_x$ region, resulting in a gap labeled Point A. A similar feature is found near the $\bar{X}$ -points at an energy of 0.2 eV below E_F , where a discontinuity occurs only in the $-k_x$ region, labeled Point B.

Figure 6.1c shows the band dispersion along $\bar{M} \rightarrow \bar{\Gamma} \rightarrow \bar{M}'$, where three distinct bands can be seen near the Fermi level in the $+k_x$ region, while in the $-k_x$ region the separation is less distinct. The red and blue dotted lines highlight the band dispersion associated with the gap at Point A observed in the insets of Figure 6.1a.

Figure 6.1d presents the band dispersion, emphasizing the features at Point B.

Along $k_y = 0.25 \text{ \AA}^{-1}$, the dispersion reveals an avoided crossing in the $-k_x$ region and a preserved crossing in the $+k_x$ region, consistent with symmetry breaking across the yz -plane. The red and blue dotted lines mark the position of the gap, which can be attributed to SOC-induced hybridization, as previously observed in Pd in Chapter 4. The energy splitting at the avoided crossing near Point **B** is approximately 225 meV.

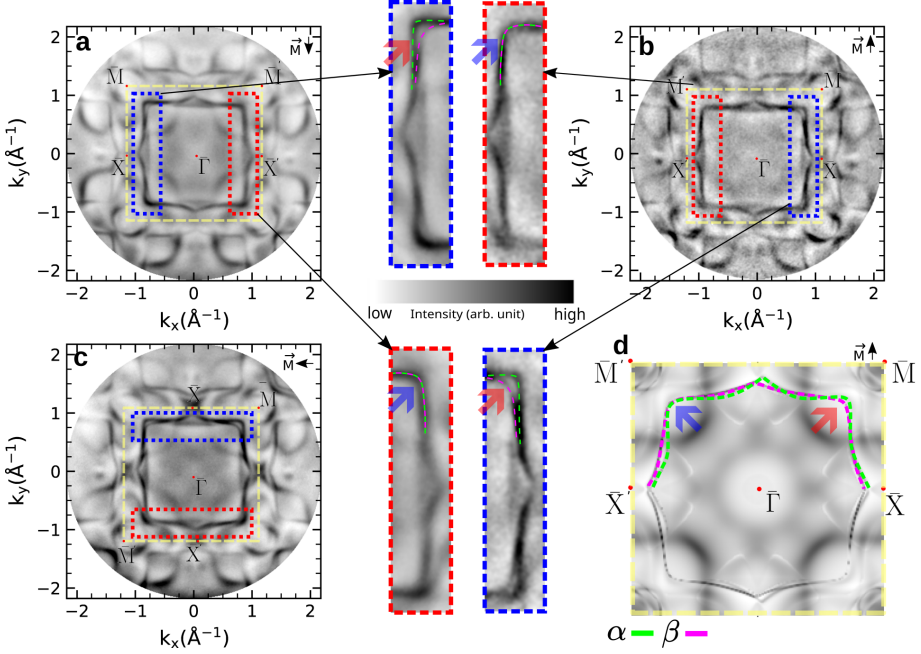


Figure 6.2: **a**, **b**, and **c** show experimental photoelectron momentum maps of the Fermi surface for two ML FePd/Pd(001), measured with p-polarized photons at a photon energy of 55 eV while the sample was magnetized along the $-y$, $+y$, and $-x$ directions, respectively. Insets highlight key asymmetric features. **d** displays a fully relativistic first-principles calculation of the Fermi surface of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ within its Brillouin zone for magnetization along $+y$, with bands α and β traced in color. The red and blue arrows denote the split and degenerate bands, respectively.

To corroborate the magnetization-induced symmetry-breaking features observed with s-polarized photons at 35 eV, complementary measurements were conducted at a photon energy of 55 eV using p-polarized light, as shown in Figure 6.2. At this photon energy with p-polarization, a square-like feature in the Fermi surface forms a closed contour, making it particularly effective for elucidating the distinctive topology of the Fermi surface and its symmetry characteristics in the two ML FePd/Pd(001).

Although p-polarized light can induce modulations in the photoemission intensity via linear dichroism (LD), leading to apparent asymmetries across the $\pm k_y$ directions, these effects originate from matrix element variations and do not correspond to a

breaking of mirror symmetry in the underlying electronic structure. LD-induced asymmetries affect only the intensity distribution and leave the symmetry of the band dispersion itself unaltered. Moreover, the LD contributions observed in the 55 eV data remain sufficiently weak so as not to obscure the interpretation of intrinsic symmetry-breaking effects arising from the interplay between SOC and exchange interaction.

Figures 6.2a–c present Fermi surface maps acquired under identical measurement conditions, differing only in the direction of the in-plane remanent magnetization: $-y$, $+y$, and $-x$, respectively. As described in Section 3.1, the thin film was magnetized before each measurement by positioning a permanent magnet near the sample surface and retracting it before data acquisition.

The analysis focuses on the square-like Fermi contour centered at $\bar{\Gamma}$, where two crisscrossing bands are distinctly visible in both experiment and theory. In the experimental data, asymmetries are highlighted by red and blue insets, following the convention introduced in Figure 6.1. For instance, in the blue insets near $\bar{M}$, gap openings are marked by red arrows, while the corresponding degenerate states near $\bar{M}'$ are denoted by blue arrows. Similarly, the red insets near $\bar{X}$ show gap openings, in contrast to the degenerate counterparts near $\bar{X}'$.

In Figures 6.1a and b, within the region spanning $\bar{M}-\bar{X}-\bar{M}$ (outlined by the blue dashed frame), a band degeneracy lifting is observed, as highlighted by the separate dashed lines. In contrast, within the mirror-reflected region $\bar{M}'-\bar{X}'-\bar{M}'$ (outlined by the red dashed frame), the bands appear continuous and degenerate. These findings provide further evidence of broken mirror symmetry across the yz -plane when the magnetization is aligned along the y -axis, with the symmetry being reversible upon antiparallel magnetization from $+y$ to $-y$ and vice versa.

In addition, the magnetization was reoriented along the x -axis in Figure 6.2c. In this configuration, the xz mirror plane is broken by magnetization, leading to observable asymmetries across the $\pm k_y$ directions. However, the yz mirror symmetry is preserved, as reflected in the symmetric band distribution across k_x . This serves as a cross-check, affirming that the asymmetries observed in Figures 6.2a and b originate from the intrinsic symmetry breaking induced by magnetization.

Figure 6.2d presents a fully relativistic density functional theory (DFT) calculation of the Fermi surface of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ with remanent magnetization along the $+y$ direction. The calculation reproduces the experimentally observed asymmetries, showing that the square-like Fermi surface is composed of two intersecting bands, labeled α (green) and β (purple). Notably, asymmetric features across the yz mirror plane are pronounced. For instance, a gap opening in the $+k_x$ region (indicated by the red arrow) contrasts with its degenerate counterpart in the $-k_x$ region (blue arrow), with the dashed lines corresponding to the α and β bands. Furthermore, the sharp edge of the Fermi sheet near $\bar{X}$ shifts in opposite directions for the two bands: for β , the tip moves toward $-k_x$, while for α , it shifts toward $+k_x$.

Figure 6.3 presents energy–momentum dispersions of the band structure for two ML $\text{FePd}/\text{Pd}(001)$ along the high-symmetry path $\bar{M}-\bar{\Gamma}-\bar{M}'$ (marked by the yellow dashed line in Figures 6.1a,b). A particular local $\bar{k}$ -region near $\bar{M}'$, indicated by a yellow dashed box near the corner of the square-like Fermi contour, serves as a refer-

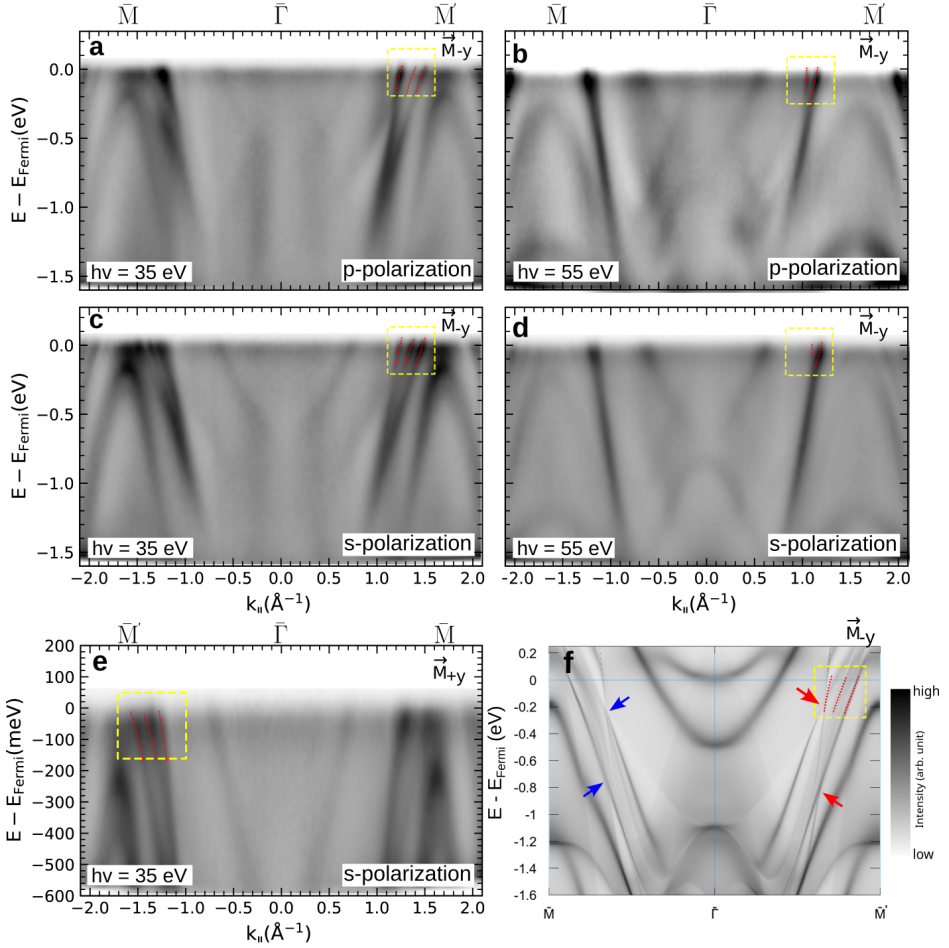


Figure 6.3: Experimental band structure of two ML of FePd/Pd(001) along the high-symmetry direction $\bar{M}-\bar{\Gamma}-\bar{M}'$ (yellow dashed line in Figures 6.1a,b). Panels a–d show energy–momentum cuts measured with a,b p-polarized and c,d s-polarized photons at a,c 35 eV and b,d 55 eV, under remanent magnetization along the $-y$ direction. Panel e displays the band structure under the same conditions as c but with the magnetization reversed to $+y$. Red dashed lines serve as guides to the eye for band identification. Panel f presents the corresponding fully relativistic band structure calculation for $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ with magnetization in $-y$ direction. Red and blue arrows highlight features that break mirror symmetry, specifically crossing and anti-crossing point pairs across the yz mirror plane.

ence point to highlight band asymmetries associated with mirror symmetry breaking. Across all panels, despite differences in photon energy and light polarization (35 eV and 55 eV; s- and p-polarized), the band structure remains consistent, as expected for a two-dimensional thin film. However, variations in spectral weight and intensity are observed due to matrix element effects. Figures 6.3a and c display three distinct bands, highlighted by red dashed lines, near the boxed $\bar{M}'$ region (point B in Figure 6.1). In contrast, the corresponding region near $\bar{M}$ shows a weaker band separation, with bands converging around 0.7 eV binding energy. Meanwhile, the $\bar{M}'$ -side features converge closer to 0.8 eV, indicating a clear asymmetry across the yz mirror plane induced by the magnetization.

In Figures 6.3b and d, measured with 55 eV photons, the separation between the interwoven Fermi sheets becomes more evident. In the $\bar{M}'$ region (yellow box), a sharply defined band appears near the Fermi level, shown as two red dashed lines, whereas the corresponding bands in the $-k_x$ region near $\bar{M}$ remain degenerate. Figure 6.3e provides a direct comparison with reversed magnetization in the $+y$ direction, under otherwise identical conditions to c. Notably, the three distinctly separated bands observed near $\bar{M}'$ in c now shift to the opposite side ($-k_x$), consistent with the reversal of the magnetization vector. This shift reflects the intrinsic nature of the magnetization-induced symmetry breaking at the Fermi surface.

Theoretical results in Figure 6.3f, obtained from fully relativistic DFT calculations for $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$ with $-y$ magnetization, qualitatively reproduce the experimental features. Within the yellow dashed box, the theory predicts multiple band splittings and unequal spectral weight distribution. The two green dashed rectangles, mirrored about the k_y axis, display notable asymmetries in the dispersion along $\bar{M}-\bar{\Gamma}$ versus $\bar{\Gamma}-\bar{M}'$, supporting the experimentally observed mirror symmetry breaking. Furthermore, the calculations predict several anti-crossing features (blue arrows), consistent with possible SOC-induced hybridization gaps observed experimentally (e.g., Figure 6.1d). Meanwhile, red arrows highlight their degenerate counterparts in the $+k_x$ region.

In summary, a key result is the magnetization-dependent momentum distribution of states under different magnetizations. This behavior reflects the breaking of mirror symmetry in the electronic structure, while the mirror plane orthogonal to the magnetization direction remains preserved. Although the momentum asymmetry of individual bands—particularly the α and β states near the Fermi level—has been discussed in detail, the observed asymmetry extends beyond these specific features. It represents a global property of the spin-split electronic structure in the ferromagnetic two ML $\text{FePd}/\text{Pd}(001)$ system. Notably, the observed pair of band crossings and avoided crossings upon magnetization reversal may have profound consequences for the transport properties, as they reflect symmetry-protected degeneracies and SOC hybridization gaps that can strongly influence the transport properties.

6.1.1 Symmetry transformation induced by magnetization

The experimental results, supported by fully relativistic theoretical calculations, reveal a distinct transformation in the symmetry of the electronic structure upon remanent in-plane magnetization of the two ML FePd/Pd(001) film. This transformation is most evident in the Fermi surface and the band structure, where the momentum distribution of the avoided crossing and crossing pairs depends on the magnetization direction. These observations collectively signal a departure from the non-magnetic plane group symmetry $p4mm$ and the emergence of a reduced magnetic symmetry.

In the absence of magnetization, the system nominally exhibits a two-dimensional $p4mm$ plane group symmetry, consistent with the square symmetry of the Pd(001) substrate and the pseudomorphic growth of the FePd alloy [111, 133]. This group includes fourfold rotational symmetry and mirror planes along both the x - and y -axes. In this configuration, the electronic states are expected to be symmetric under reflection through both the xz and yz mirror planes.

Upon applying an in-plane remanent magnetization, the system undergoes a magnetic symmetry reduction. Specifically, magnetization along the $+y$ or $-y$ direction breaks the mirror symmetry with respect to the yz -plane (i.e., across $\pm k_x$) while preserving the symmetry with respect to the xz -plane. Since magnetization is an axial vector, only one mirror plane exists. In this case, it is the xz mirror plane. As demonstrated in Figures 6.2 and 6.3, the Fermi surface and band structure show asymmetric features across the k_y axis in the yz plane, such as gap openings near $\bar{M}$ but not near $\bar{M}'$, and momentum shifts of band edges upon magnetization reversal. These signatures directly reflect the lifting of degeneracies and the removal of mirror planes, both hallmarks of reduced symmetry due to magnetic ordering.

This selective symmetry breaking transforms the plane group symmetry to $p2'mm'$, a magnetic space group that retains only twofold rotational symmetry and mirror symmetries combined with time-reversal [133]. Here, we can associate the time-reversal operation($'$) with the reversal of the magnetization direction and spin polarization of states in the experiments. Specifically, $p2'mm'$ includes:

- A two-fold rotation about the z -axis in combination with a time-reversal operation ($2'$),
- A preserved mirror symmetry in the xz -plane, denoted by the first m ,
- A broken mirror symmetry in the yz -plane, replaced by a combined mirror symmetry operation and time reversal operation. This is denoted by the second m' character.

The directionality of the magnetization vector determines which mirror symmetries of the crystal are preserved and which are only retained through a combined operation of mirror reflection and time-reversal symmetry. Specifically, for a given in-plane magnetization, the magnetic point group symmetry is reduced, and only a subset of the original symmetries is maintained.

As illustrated in Figure 6.2, the features in the blue inset of panel **a** are transformed into those in the red inset by reflection across the yz mirror plane. If this mirror operation is subsequently followed by a time-reversal transformation, reversing the magnetization vector, the resulting pattern corresponds to the measurement shown in the blue inset of Figure 6.2b, where the magnetization is reversed. This operation is also referred to as an anti-mirror symmetry. Similarly, one can arrive at the same observation via $p2'$ operations by performing a two-fold rotation operation followed by time reversal. When the magnetization is instead oriented along the x -axis, the roles of the xz and yz mirror planes are reversed, as clearly seen in Figure 6.2c, further validating the role of magnetic symmetry operations in defining the observable features in momentum space. The observed correspondence between the electronic features under opposite magnetizations confirms the role of such anti-mirror operations in the magnetically reduced symmetry group of the system.

The presence of SOC plays a pivotal role in enabling this symmetry reduction. SOC couples the magnetization direction to the crystal lattice. The gap openings observed at Points **A** and **B** (Figures 6.1 and 6.2) are direct consequences of such SOC-induced hybridization under broken mirror symmetry. A notable lack of pronounced asymmetry in the electronic structure of Fe(001) in Figure 3.5d can be attributed to its relatively weak SOC. In contrast, the FePd alloy exhibits significantly stronger SOC due to Pd, leading to more prominent symmetry-breaking features and band splittings in both experiment and theory.

In summary, the combined experimental and theoretical evidence establishes that remanent in-plane magnetization induces a symmetry transformation of the two-dimensional electronic structure from $p4mm$ to the magnetic plane group $p2'mm'$. This transformation is manifested in momentum-resolved features such as asymmetric Fermi contours, lifted degeneracies, SOC-induced hybridization gaps, and magnetization-dependent band shifts. Such control over symmetry via magnetization has significant implications for spin-dependent transport phenomena and the engineering of symmetry-protected topological states in ultrathin magnetic heterostructures.

6.2 Momentum Distribution of Circular Dichroism

CD in photoemission serves as a qualitative probe of the orbital character of electronic states. While a detailed quantitative analysis of orbital wavefunctions necessitates extensive theoretical modeling, the symmetry of the momentum-resolved CD signal provides valuable insight into mirror symmetry breaking induced by magnetization. This symmetry breaking can be linked to the SOC through the orbital characters of the bands. In the presence of SOC, the electron's spin couples with its orbital angular momentum, thereby influencing the electronic structure's symmetry and reflecting this in the CD signal.

In the following, we analyze how magnetization-induced symmetry-breaking is reflected in the CD signal. Figures 6.4a and b display the momentum distribution of CD across the Fermi surface, measured under remanent magnetization along the $\pm y$

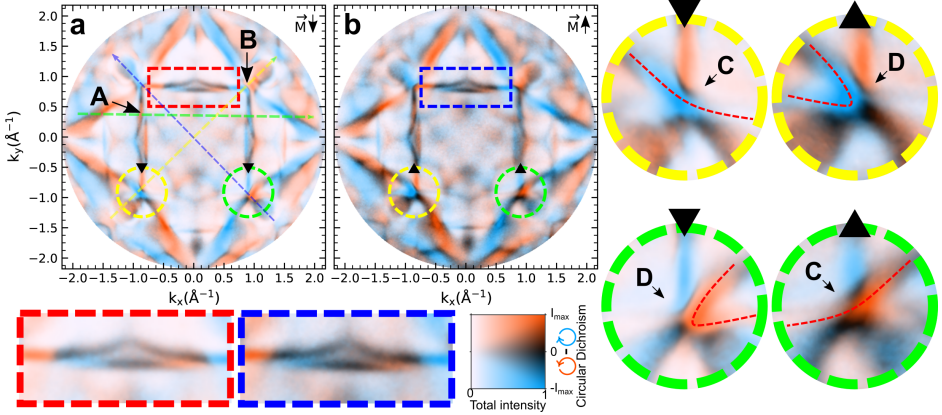


Figure 6.4: Momentum distribution of CD across the Fermi surface of two ML FePd/Pd(001) obtained at different remanent magnetization directions of **a** -y and **b** +y, respectively. The measurements are taken at a photon energy of 35 eV. The insets highlight the enlarged momentum space corresponding to the colored dashed lines. Black triangles are markers for the respective magnetization direction. The red dotted lines serve as eye guides.

directions. Firstly, the CD of two local regions near the $\bar{M}$ - and $\bar{M}'$ - points, located at the edges of the square-like Fermi contours, are compared. Here, features **C** and **D** are the respective identical features shown in the circular inset of Figure 6.4 by red-dotted lines. Feature **C** crosses the edge as a curved line, whereas feature **D** looks more like a "V"-shape. The insets highlight the reversal of asymmetric $\vec{k}$ -points upon mirror symmetry operation, observed through the inversion of the remanent magnetization vector.

Secondly, the sides of the square-like contours near the $\bar{X}$ -point along the mirror plane, which appear to be shifted in $\pm k_x$ depending on the parallel or anti-parallel magnetization in y , also feature a dependence on the magnetization direction. In the rectangular inset of Figure 6.4, we can see that the local points (red arrows) where the CD switches along the square-like Fermi contour are shifted to the right (left) when magnetized in the in $-y$ ($+y$) direction, with respect to the crystalline mirror plane (k_y -axis marked with dotted dashed line).

Thirdly, we explore the energy-momentum dispersion of the CD along two "opposing" cuts of $\bar{M}$ - $\bar{X}$ - $\bar{M}'$ (yellow dashed line in Figure 6.4a) and $\bar{M}'$ - $\bar{X}$ - $\bar{M}$ (blue dashed line in Figure 6.4a) in Figures 6.5a and b, respectively. Here, we not only observe the expected sign reversal of the CD across the mirror plane but also notice an asymmetry in the CD energy dispersion. The CD dispersions extending from the Fermi surface features **C** and **D** are distinctly asymmetrical. By tracing the crossing point of the CD signals (black), we observe that the dispersion extending from feature **D** has a sharper and steeper slope at lower binding energy, while feature **C** has a mellower and

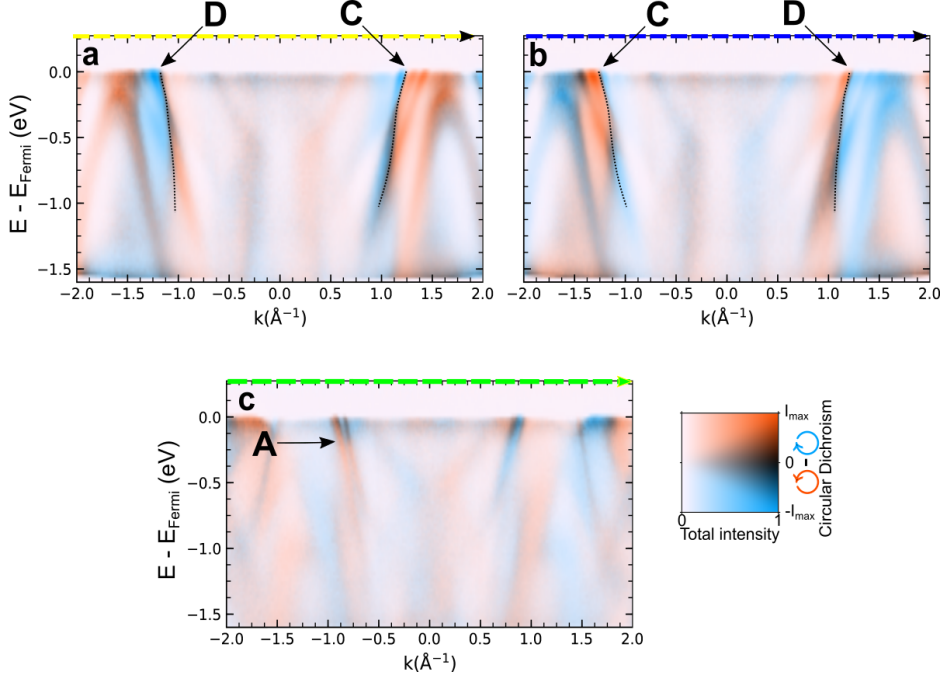


Figure 6.5: Energy dispersions of CD of two ML FePd/Pd(001), measured at a photon energy of 35 eV, along **a** $\bar{M}-\bar{X}-\bar{M}'$, **b** $\bar{M}'-\bar{X}-\bar{M}$, and **c** a line cut along k_x at $k_y = 0.25 \text{ \AA}^{-1}$ denoted as dashed yellow, blue and green lines, respectively, in Figure 6.4. The film is remanently magnetized in the $-y$ direction. The black dotted lines are eye-guides where the CD switches.

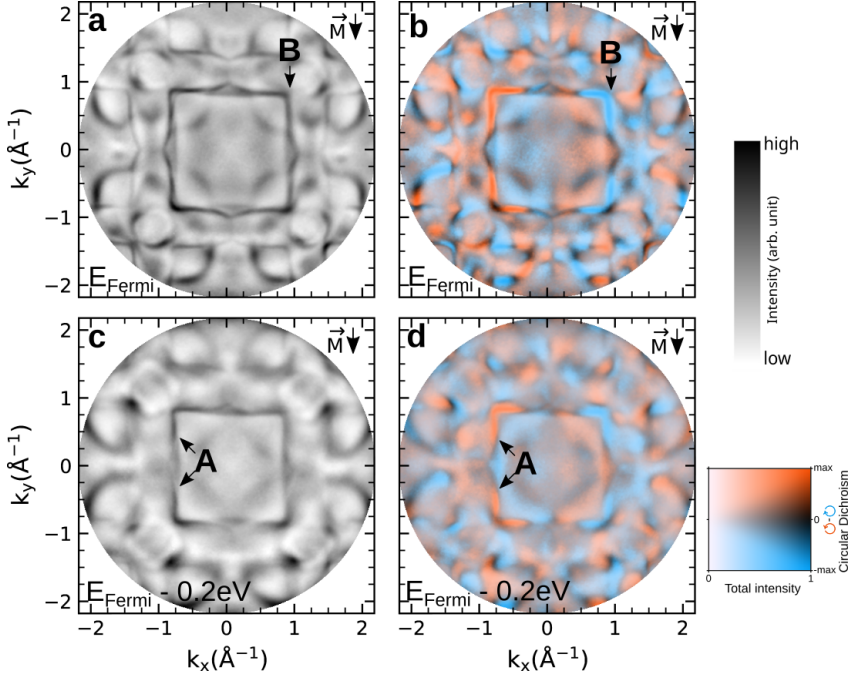


Figure 6.6: Momentum distribution of **a** total photoemission response and **b** CD across the Fermi surface of two ML FePd/Pd(001), obtained using circularly polarized photons at a photon energy of 55 eV. **c,d** show their respective counterparts at 0.2 eV below the Fermi level. The dash-dotted line indicates the crystal mirror plane along the magnetization and also the plane of incidence of the photons. The red arrow shows the local inversion points of interest.

more gradual slope at higher binding energy. Although these two energy-momentum cuts correspond to the features observed in Figure 6.4, the CD is mixed with the LD due to the experimental geometry.

Therefore, Figure 6.5c shows an extracted energy-momentum cut along k_x at $k_y = 0.25 \text{\AA}^{-1}$, similar to the data presented in Figure 6.1d, to exclude the LD contribution. Close to the gap at 0.2 eV below the Fermi energy, denoted as point **A** in Figure 6.5, we observe that the CD switches between the two bands, similar to its degenerate counterpart in the $+k_x$ direction. This observation connects the orbital character of the electronic states in two ML FePd/Pd(001) to the asymmetry induced via magnetization.

Figure 6.6 shows the momentum distribution of the CD of the Fermi surface obtained with photons of $h\nu = 55$ eV. Attention is focused on the interweaving of the α and β bands along the deformed square. We observe that the crossing points between the two bands are reflected as CD inversion points across the Fermi surface.

In Figures 6.4 and 6.6, the local CD inversion points along the square-like Fermi contours coincide with the theoretical crossing points of the α and β bands shown in Figure 6.2d.

Figure 6.4 presents the total photoemission response, obtained by summing the photocurrents from right- and left-circularly polarized photons. At first glance, the mirror symmetry across the crystalline mirror plane of the k_y axis and across k_x appears to be broken. The crossing points between the theoretical α and β bands are manifested as local inversion points in the momentum distribution of CD, even though they are not apparent in the total photocurrent in Figure 6.2. These inversion points are marked by the red arrows in Figure 6.6b and d. Furthermore, across the crystalline mirror plane, the inversion point on the $-k_x$ side is closer to the yz -plane along the k_y -axis, while its mirror-reflected counterpart on the $+k_x$ side is shifted further away from the mirror plane.

The CD momentum maps display distinct asymmetric features, which complement the momentum maps obtained using linearly polarized photons. This observation is further supported by the reversal of the circular photoemission responses upon inversion of the remanent magnetization vector, highlighting the dependence of these asymmetric features on the magnetization orientation. This suggests an asymmetry in the orbital character of the electronic states due to the presence of SOC and time-reversal symmetry breaking. A more comprehensive theoretical understanding of the orbital character of the band structure, along with photoemission calculations, is required for further analysis. In summary, our experiments demonstrate a magnetization-dependent broken mirror symmetry in the band structure of two ML FePd/Pd(001), arising from the interplay between exchange interaction and SOC.

6.3 Non-Collinear Spin Texture of two ML FePd/Pd(001)

To investigate the spin texture of the Fermi surface of two ML FePd/Pd(001) in more detail, spin-resolved momentum microscopy is employed under four distinct magnetization orientations $\pm x$ and $\pm y$, while keeping all other experimental parameters, such as photoemission geometry, photon energy, and polarization, constant. This approach enabled a direct comparison of spin polarization behavior across different magnetization directions, analogous to changing the spin quantization axis, providing a comprehensive view of the overall spin texture of the Fermi surface.

Figures 6.7a and b display the spin-resolved momentum maps of the Fermi surface obtained using 55 eV photons for magnetizations along $\pm y$, with the spin-quantization axis, S_y , aligned in the same direction. In excellent agreement with our spin-resolved results in Figure 5.2, obtained using 35 eV photons, the spin polarization follows the magnetization vector, leading to a predominantly half-metallic spin texture.

In the previous section, we discussed the momentum distribution of the electronic structure of two ML FePd/Pd(001). A similar momentum-dependent variation in

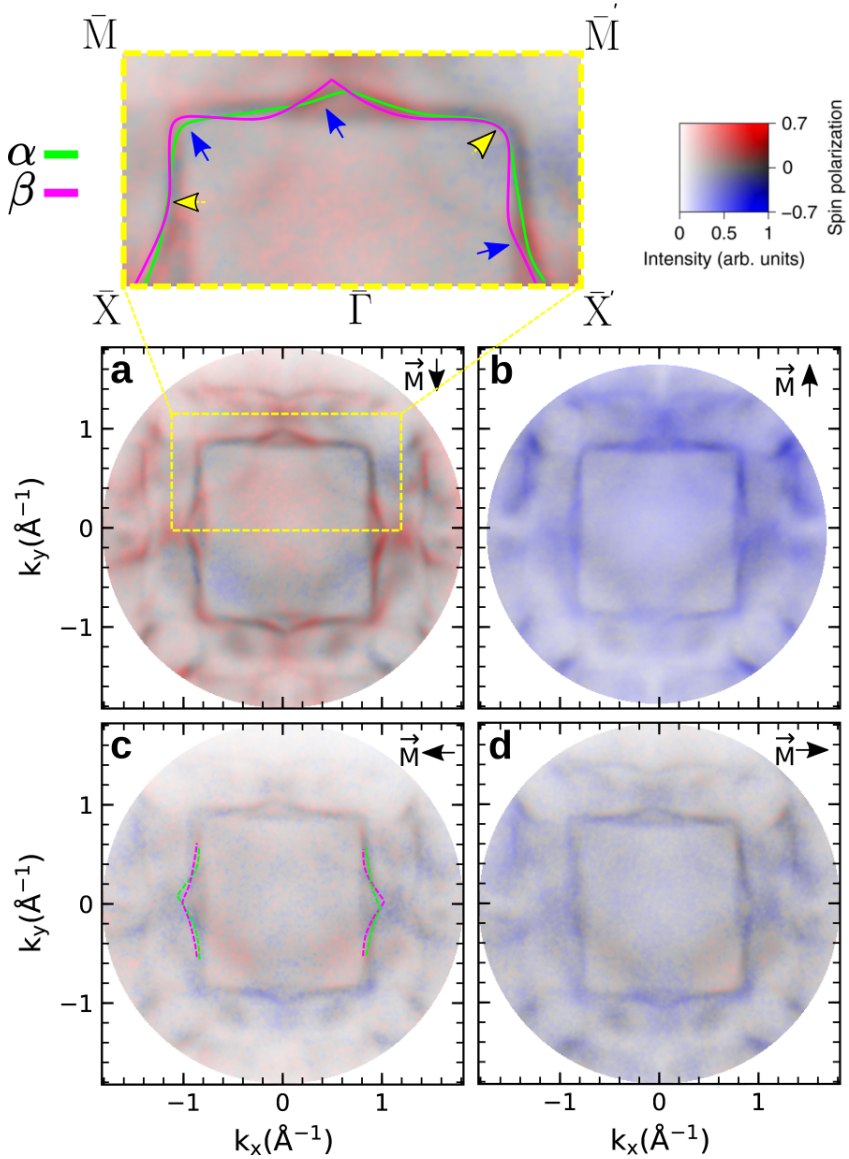


Figure 6.7: Spin-resolved photoelectron momentum maps of the Fermi surface of two ML FePd/Pd(001) obtained with p-polarized photons of 55 eV, under in-plane remanent magnetization in (a) $-y$, (b) $+y$, (c) $-x$, and (d) $+x$ directions, with the experimental spin-quantization axis aligned along the y -axis. The inset shows a magnified view of the region of interest in a, along with the overlay of theoretical α and β bands. The blue arrows denote splitting between the two contours, while the yellow arrows denote their crossing points.

spin polarization across the Fermi surface is evident in both Figures 5.2a,c and Figures 6.7a,b. Specifically, Figure 6.7a reveals an asymmetric spin polarization distribution across the yz -plane when the sample is magnetized along the $-y$ direction. Similar to the electronic structure, this spin polarization distribution is anti-mirrored under an antiparallel magnetization along the $+y$ direction, exhibiting the characteristic of plane group symmetry $p2'mm'$.

To enhance visualization, the inset in Figure 6.7 presents a magnified view of Figure 6.7a, overlaid with the theoretically calculated Fermi sheets α and β . This comparison is made because the theoretical map closely aligns with the spin-integrated experimental results shown in Figure 6.2, where the two interwoven Fermi sheets are identified. In the inset, yellow arrows mark the $\vec{k}$ -points at which the two bands intersect, while blue arrows indicate band splittings.

A closer examination reveals that the spin polarization is reduced at the intersection point marked by the yellow arrows. Meanwhile, the band splittings indicated by the blue arrows exhibit strong spin polarization. In general, the observed trend suggests that spin polarization decreases at band intersections and increases at band splitting points.

In addition to analyzing the momentum-resolved spin polarization under remanent magnetization along the $\pm y$ directions, we further investigate the case of magnetization along the $\pm x$ directions. In this configuration, like Figure 6.2c, the mirror symmetry with respect to the zx plane (i.e., reflection across the x -axis) is broken, while the mirror symmetry with respect to the yz -plane is preserved.

Throughout the measurements, the spin quantization axis was fixed along the y -direction. When the sample is magnetized along $\pm x$, this configuration becomes sensitive to spin polarization components orthogonal to the magnetization and spin quantization axes—specifically, the S_x component of the electronic structure, as in the case for a sample magnetized along y . This geometry enables the detection of transverse spin components arising from non-collinear spin configurations and provides a more comprehensive view of the spin texture.

In a conventional collinear ferromagnet, in-plane magnetization along $\pm x$ is expected to align spin polarization with the magnetization direction, yielding distinct majority (spin-up) and minority (spin-down) bands. With the spin quantization axis aligned along y , the transverse spin polarization component should ideally vanish in the absence of spin canting. However, the strong anisotropy and asymmetry in the momentum distribution of the electronic states and their CD signals indicate a significant interplay between SOC and exchange interaction.

Thus, magnetization along the $\pm x$ directions serves as an effective probe for detecting spin canting or non-collinear spin textures induced by SOC. This is consistent with the mechanism illustrated in Figure 2.4, which highlights how the interplay between exchange interaction and SOC may generate spin components transverse to both the magnetization and the spin quantization axes. In the case of a half-metal, the emergence of such transverse spin components across momentum space would be a direct signature of SOC-driven spin mixing in the absence of minority-spin states at the Fermi level.

The two-ML FePd/Pd(001) film was remanently magnetized along the $\pm x$ direction, which is orthogonal to the spin quantization axis (S_y). Remarkably, a nonzero, momentum-dependent spin polarization emerges across the Fermi surface, as illustrated in Figures 6.7c,d. This behavior reflects a clear deviation from conventional spin alignment in a ferromagnet. It corroborates the symmetry-broken electronic structure observed in Figure 6.2, which reveals pronounced asymmetries attributable to SOC and lowered crystalline symmetry.

Under magnetization along $\pm x$, the Fermi surface exhibits a markedly reduced net spin polarization compared to the configuration with magnetization along $\pm y$. More significantly, the spin polarization becomes strongly momentum-dependent, with spin-up and spin-down contributions distributed non-uniformly across the Brillouin zone. Notably, regions of relatively high spin polarization are localized along the square-like Fermi surface contours. This pronounced momentum-space modulation stands in stark contrast to the more uniform spin polarization observed under $\pm y$ magnetization, where the spin quantization and magnetization axes are collinear.

Figure 6.7 shows that the measured spin texture cannot be reconciled with a purely collinear spin configuration. Rather, the data suggest that two ML FePd/Pd(001) hosts a non-collinear spin texture at the Fermi level, which is modulated by the SOC-related effect at specific k -points.

While the experimental results are reproducible across multiple measurements, we note that the remanent magnetization was achieved via proximity to a permanent magnet, which introduces potential uncertainties in the exact orientation and homogeneity of the in-plane magnetic field. Therefore, although the observed features strongly indicate the presence of a non-collinear spin structure, we regard these conclusions as preliminary. Future experiments employing *in situ* magnetization using a controllable vector magnet would enable a more rigorous examination of the anisotropic spin response and disentangle contributions from field misalignment.

To supplement the experimental findings, we compare them with fully relativistic first-principles calculations of the spin-resolved electronic structure of Fe_{0.9}Pd_{1.1}/Pd(001). The theoretical results presented in Figure 6.8a show the Fermi surface of Fe_{0.9}Pd_{1.1}/Pd(001) under remanent magnetization along the $-y$ direction, whereas Figure 6.8b depicts the corresponding Fermi surface under magnetization along the $-x$ direction. In Figure 6.8a, the momentum distribution of spin polarization exhibits only weak polarization along the square-like Fermi contours. In contrast, Figure 6.8b reveals pronounced orthogonal spin polarization components (S_x) along these contours, particularly at points of band degeneracy or hybridization. In addition, the dispersions highlighted in the insets of Figure 5.5, where the hybridization gap emerges, correspond to parts of the square-like Fermi contours.

Another key agreement between the calculation and the spin-resolved momentum microscopy data is the pronounced enhancement of the S_x transverse spin component at band-crossing and anti-crossing regions, particularly along the square-shaped Fermi surface contours. These features are resolved in Figure 6.7c, where localized enhancements in spin polarization are observed under in-plane magnetization along $\pm x$. In contrast, a more uniform spin polarization across the Brillouin zone is seen

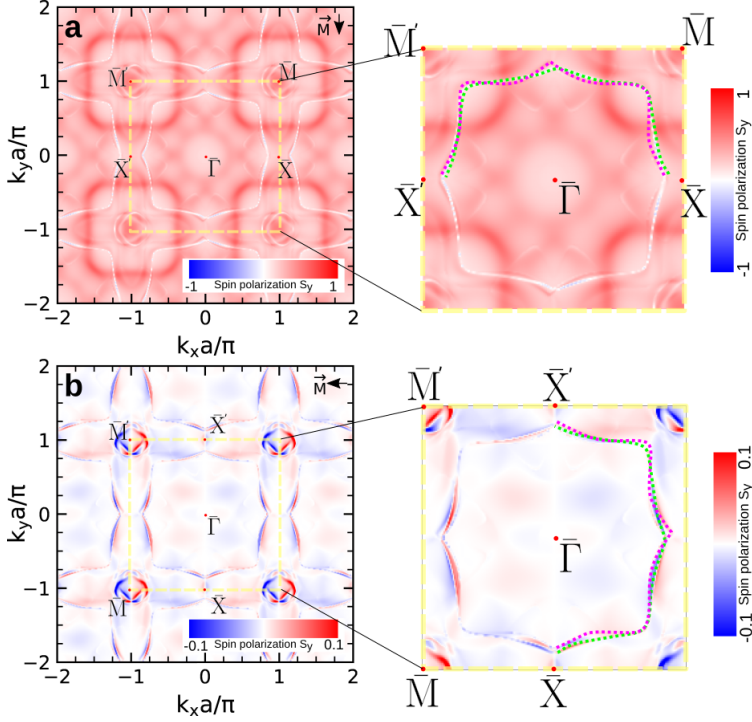


Figure 6.8: **a** The calculated spin-resolved Fermi surface of $\text{Fe}_{0.9}\text{Pd}_{1.1}/\text{Pd}(001)$, with the spin quantization axis along the y -axis, under in-plane remanent magnetization in **a** $-y$ direction and **b** in $-x$ direction, overlaid with the α and β bands. The insets show a magnified view of the Brillouin zone of **a** and **b**. The dotted lines are the overlay of the square-like Fermi contours.

for magnetization along $\pm y$, consistent with the collinearity of the spin quantization axis and magnetization direction in that configuration. These results provide direct evidence for a momentum-dependent, non-collinear spin texture.

This momentum distribution of spin polarization is especially prominent at band intersections, where spin mixing is due to SOC hybridization. These regions act as spin-mixing hotspots, where the interplay between exchange splitting and SOC leads to a breakdown of simple collinear spin configurations. Notably, the observed spin polarization cannot be attributed solely to the α and β bands near the Fermi level. Instead, it emerges from hybridization effects at avoided crossings, suggesting a coupling of spin and orbital character across the Fermi surface.

Complementary insights are provided by the CD measurements, which probe the orbital angular momentum distribution. Although CD does not directly measure the spin and orbital components of the states, its momentum dependence indicates the

orbital texture of the electronic states, which SOC strongly influences. The correspondences in momentum distributions between features in the CD maps and spin-resolved data suggest a coherent picture of SOC-driven band hybridization along the interwoven Fermi contours. These results reinforce the interpretation of SOC-mediated spin-mixing at critical $\vec{k}$ -points, further validating the emergence of a non-collinear spin texture in this system.

In summary, these findings demonstrate that even in a half-metallic FePd/Pd(001) system, a spin texture in its electronic structure can emerge due to SOC. SOC induces significant spin canting and facilitates local spin-mixing effects, particularly at band-crossing and anti-crossing points. The observation of non-collinear spin textures and spin-mixing hotspots highlights the pivotal role of SOC-driven band hybridization in shaping the electronic structure of a two-dimensional ferromagnet.

7 Discussion

The interplay between exchange interaction and spin-orbit coupling (SOC) fundamentally shapes the electronic band structure of magnetic materials and is central to their potential in spintronic applications. In this thesis, spin-resolved photoelectron momentum microscopy combined with a tunable synchrotron radiation source is employed as the principal experimental technique. This approach enables comprehensive access to the full Brillouin zone with high momentum and energy resolution, providing details of the electronic structure.

Ultrathin FePd/Pd(001) serves as a platform for investigating the competing effects of exchange interaction and SOC in a two-dimensional ferromagnet. This system exhibits a unique combination of properties arising from the interplay between strong exchange interaction among the valence electrons of Fe, an elemental ferromagnet, and Pd, which lies near the threshold of ferromagnetism according to the Stoner criterion, along with substantial SOC contributions from 4d Pd. Moreover, the electronic structure of the alloy can be systematically tuned by adjusting the nominal stoichiometry and alloy composition. These characteristics render the FePd system particularly suitable for *in situ* exploration of competing SOC and exchange interaction in an ultrathin ferromagnet.

This thesis unfolds in three stages. First, the role of SOC in shaping the Fermi surface topology is addressed through a comparative study of single-crystalline Pd and Rh, highlighting the effect of SOC-induced degeneracy lifting. These experimental results are interpreted in conjunction with relativistic band structure calculations. Second, ultrathin FePd films are investigated to resolve spin-polarized band structures and the emergence of two-dimensional half-metallicity in two monolayers (ML) FePd alloy on Pd(001). Finally, the combined effects of SOC and exchange interaction are explored by observing mirror symmetry breaking and complex spin textures under systematically varied in-plane magnetization directions, along with the fundamental symmetry reductions arising from time-reversal symmetry breaking in the presence of strong SOC.

In Chapter 4, we investigated the influence of SOC on the bulk band structure of Pd and Rh in the complete 3D Brillouin zone. Our results show how SOC significantly modifies the electronic bands in the 4d transition metals by lifting degeneracies at high-symmetry points, creating local gaps, and forming distinct features, such as a hole pocket near the L-point. These effects are particularly pronounced near the Fermi level, where SOC induces shifts in the band structure in the so-called "jungle-gym" Fermi sheets of Pd. These sheets, characterized by their complex connectivity and multiple pockets, provide a foundation for investigating phenomena such as Fermi surface nesting and its potential role in enhancing electronic correlations [35]. Fur-

thermore, the SOC-driven restructuring of the band structure pushes certain bands towards flatter dispersions. In the case of Pd, such an SOC-driven effect may contribute to its high-density states at the Fermi level and its nearly ferromagnetic state based on the Stoner criterion.

The influence of SOC on the electronic states not only modifies band dispersion and lifts degeneracies but also introduces geometric properties into the band structure that are pivotal for understanding topological and transport phenomena. Among these is the intrinsic spin Hall effect, wherein SOC induces a transverse spin current in response to an applied longitudinal electric field without requiring extrinsic scattering mechanisms [134, 135]. This intrinsic mechanism arises from the Berry curvature, a geometric property of Bloch states in momentum space, which acts analogously to a magnetic field in $\vec{k}$ -space and exerts an anomalous velocity on electrons depending on their spin [136].

Geometric quantities, such as the Berry curvature, are derived from the momentum-space structure of the wavefunctions and encode the topological response of the electronic system [136, 137]. In particular, the Berry curvature plays a central role in the intrinsic spin Hall effect by mediating spin-dependent anomalous transport in systems with strong SOC. In the context of bulk Pd, our experimental observations, including local gap openings, hole-pocket formations, and band splitting near the Fermi level, reflect strong SOC-induced band restructuring. These band features may contribute to an enhanced Berry curvature near avoided crossings and degeneracy points [138]. The enhanced Berry curvature in local k -points may be the driving mechanism for the intrinsic spin Hall effect in systems such as Pd and Rh. Our momentum-resolved studies of the Fermi surface topology and band dispersions in Pd and Rh, therefore, offer insight into the origin of the spin Hall conductivity in these $4d$ transition metals.

Furthermore, the ability to access the full three-dimensional Brillouin zone using photoelectron momentum microscopy enables a detailed investigation of the surface and bulk sensitivity of photoemission, particularly as a function of photon energy. In this study, we present comprehensive two-dimensional momentum-resolved maps of the Fermi surface of single-crystalline Pd across a wide photon energy range. These measurements reveal pronounced deviations from the free-electron final-state approximation, particularly at photon energies below 200 eV, where the photoemission process becomes strongly influenced by the presence of evanescent final states. Such states emerge when the emitted photoelectron cannot couple to a propagating, bulk-like final state—especially in regions of the Brillouin zone where local band gaps exist in the unoccupied band structure, such as near the zone boundaries. In these momentum regions, the absence of available final states forces the photoelectron into a non-propagating, exponentially decaying (evanescent) channel, significantly altering the measured spectral intensity in Fermi surface tomography.

Our experimental results demonstrate that at photon energies above approximately 200 eV, the free-electron final-state approximation becomes increasingly valid. In this regime, the Fermi surface tomography shows systematic intensity suppression near the Brillouin zone boundaries, consistent with the absence of accessible final states, namely the onset of final-state band gaps where the free-electron final state becomes

evanescent. By contrast, at lower photon energies (below 200 eV), strong anomalies appear in the Fermi surface maps, including enhanced spectral weight in symmetry-forbidden regions and apparent photon energy-dependent band “stretching” in the spectra. These features, manifesting as waterfall-like dispersions across photon energies, are not captured within the conventional free-electron final-state model and instead reflect the damping and interference effects introduced by evanescent channels due to finite photoelectron escape depth.

To interpret these deviations, we collaborated with Dr. Ján Minár’s group to perform one-step photoemission calculations incorporating the complex final-state band structure. These calculations reveal that, at sub-200 eV photon energies, the photoemission process involves transitions into evanescent final states—complex wavevector states characterized by finite decay lengths into the crystal. Such states dominate when the initial state is excited to a band gap of the final state, particularly near the zone boundaries. Notably, we identify that these evanescent states can give rise to “ghost” zone boundaries in the momentum-resolved intensity maps and artifacts stemming from the overlap of initial states with non-propagating final states. This effect may introduce distortions in the experimental observations, such as a reconstructed Fermi surface, and must be carefully considered when interpreting experimental data.

A similar experimental pipeline was conducted on a Rh single crystal to verify the reproducibility and generality of these observations. The results reaffirm the high efficiency of momentum microscopy-based Fermi surface tomography while also emphasizing the importance of accounting for final-state effects in quantitative photoemission analyses. In particular, we identify and evaluate several limitations of the free-electron final-state approximation, emphasizing conditions under which its applicability breaks down due to the emergence of evanescent final states. Such deviations can compromise the interpretation of electronic structure, especially near Brillouin zone boundaries or in regions of the unoccupied band structure where local gaps inhibit coupling to propagating final states. These effects are most pronounced at lower photon energies (typically below 200 eV), where the kinetic energy of the photoelectrons is insufficient to access extended bulk-like states.

However, when these limitations are recognized and the conditions under which the free-electron model remains valid are well-defined, such as at higher photon energies where final-state dispersions are evenly distributed and weakly structured, the approximation provides insight into the bulk band structure, like the Fermi surface. Accordingly, these findings underscore the need for careful photon energy selection and consideration of final-state effects when extracting reliable information about bulk electronic properties. Complementary approaches, such as soft X-ray photoemission or one-step photoemission calculations, are indispensable for validating the interpretation of bulk electronic structure.

Following the detailed analysis of Pd(001) and Rh(001), we now focus on the findings presented in Chapter 5, which explore exchange-driven spin polarization in ultrathin FePd alloy films grown epitaxially on Pd(001). Our experimental results from spin-resolved momentum microscopy reveal the emergence of a two-dimensional half-metallic electronic structure. This is evidenced by a fully spin-polarized Fermi surface

in the two ML FePd alloy, where the minority spin bands are gapped at the Fermi level, resulting in a Fermi surface exclusively populated by spin-up electrons.

The observed half-metallicity in the two-ML FePd alloy on Pd(001) is a direct consequence of exchange engineering, achieved through stoichiometric control of Fe and Pd constituents in the two ML FePd alloy. The nominal Fe content of 0.9 ML is carefully tuned to optimize the exchange splitting between majority and minority spin channels and the SOC hybridization gap at the Fermi level. Within the alloy, Fe atoms contribute local magnetic moments that induce spin polarization of the electronic states via exchange interaction with neighboring Fe and Pd atoms. Crucially, in the two-ML FePd alloy on Pd(001), the exchange splitting between the majority and minority bands is sufficient to position the onset of the minority spin bands below the Fermi level, thereby suppressing minority spin-down channel conduction. This results in a Fermi surface populated exclusively by spin-up electrons - a hallmark of half-metallic behavior.

Concurrently, owing to their heavy *4d* character, Pd atoms provide substantial SOC, enabling band hybridization and opening local gaps near the Fermi level. A particularly striking feature of this system is the suppression of the free electron-like spin-down minority bands, which are often difficult to exclude from the Fermi level due to their large bandwidth and extended dispersion across the Brillouin zone. In typical itinerant systems, these delocalized states tend to cross the Fermi level even in the presence of strong exchange interaction. However, in the two ML FePd alloy with nominal 0.9 ML Fe content, the SOC hybridization plays a decisive role by inducing local hybridization points that gap the free-electron-like spin-down states at the Fermi energy. In concert with the exchange splitting, this SOC-driven gap leads to a complete suppression of the minority channel over the entire momentum-resolved Fermi surface.

In addition, the system's proximity to the Pd substrate introduces an important interfacial effect. Theoretical modeling reveals that the third atomic layer, constituted by the topmost layer of Pd(001), undergoes proximity-induced polarization. This results in a band structure with opposite polarization to that of the overlying FePd alloy film. The anti-parallel spin alignment in the Pd layer can partially reintroduce minority carriers near the Fermi level, thereby destroying the ideal half-metallicity. This underscores a critical challenge: the half-metallic character is inherently sensitive to interfacial polarization and hybridization.

To overcome this limitation and preserve half-metallicity, we propose an epitaxial two-dimensional half-metallic film on an insulating substrate with minimal electronic interactions with the film near the Fermi level. Such a configuration would eliminate the proximity-induced polarization band interaction, thereby preserving the gap in the minority spin channel. The system could be subsequently integrated into spintronic device architectures, where its intrinsic half-metallicity could be exploited for efficient spin injection and spin filtering.

The application prospects of this system are substantial. In particular, a half-metallic film with in-plane magnetic anisotropy and high Curie temperature, as demonstrated for the two ML FePd alloy, can serve as a robust spin filter or a

spin injector in magnetic tunnel junctions or all-metallic spin valves. Furthermore, the strong SOC provided by the Pd component may enable additional functionality, such as spin-orbit torque or spin-charge interconversion, when interfaced with non-magnetic layers [139]. The discovery of tunable two-dimensional half-metallicity in ultrathin FePd/Pd(001) films, together with the insights on proximity-induced depolarization, opens a clear pathway for developing heterostructured FePd-based spin filters. This work establishes this alloy system as a promising candidate for scalable spintronic technologies.

Chapter 6 first investigates the intricate interplay between SOC and exchange interaction in ultrathin FePd/Pd(001) films by emphasizing the symmetry reduction and the resulting anisotropies in the electronic structure. By systematically varying the in-plane remanent magnetization directions with respect to the crystalline mirror plane, we uncover a pronounced magnetization-induced asymmetry in the momentum-resolved electronic band structure. This broken mirror symmetry is consistent with a reduction of the $p4mm$ plane group symmetry of Pd(001) to the magnetic plane group $p2'mm'$, reflecting the impact of time-reversal symmetry breaking in the presence of SOC.

For instance, as shown in the experimental data presented in Figure 6.1, distinct asymmetries are observed in the form of gapped and degenerate band features across the yz mirror plane, which cannot be explained by structural symmetry alone. These features are indicative of SOC-mediated band hybridization, which is further modulated by magnetization direction. Notably, the reversal of the in-plane magnetization in panel **a** and **b** of Figure 6.2 leads to a corresponding reversal in the asymmetry of the band structure, highlighting the crucial role of magnetization direction in modifying the electronic properties of the system.

Such magnetization-induced modifications to the band structure have profound implications for the anisotropic transport properties of the system, including anisotropic magnetoresistance and intrinsic anomalous Hall effect. These modifications are intricately linked to the symmetry-breaking mechanisms dependent on the magnetization vector. By changing the magnetization vector, the geometric properties of the electronic wavefunctions—specifically the Berry curvature—are also modified due to the resulting asymmetry in the electronic structure.

Next, the interplay between SOC and exchange interaction was studied using circular dichroism (CD) of the electronic structure. CD indirectly probes the orbital character of the electronic states. In this sense, CD can serve as an indirect probe of Berry curvature signatures in the band structure [108, 140]. The experimental results reveal several crossing points in the CD spectra, where sharp transitions are observed. These points correspond to significant changes in the orbital character of the electronic states, which are indicative of loci for large Berry curvature. These transitions can be linked to regions where the SOC induces strong hybridization between the electronic bands, leading to an abrupt modification of the orbital character. At the avoided crossings, the SOC-driven hybridization of otherwise non-interacting bands results in abrupt changes in orbital character. These features may indicate locally enhanced Berry curvature, as established in analogous systems [141, 142].

The observed momentum distribution of the CD variable with magnetization suggests that the underlying wave function geometry, potentially including Berry curvature, is sensitive to symmetry-breaking. While the connection between CD and Berry curvature is not a direct correspondence, our results may point to a route for manipulating the geometric properties of the electronic structure via magnetization.

Given the central role of Berry curvature in the intrinsic anomalous Hall effect [12, 143], particularly in systems with broken time-reversal symmetry, the observed magnetization-induced band asymmetries may contribute to transverse transport phenomena. Such asymmetries, potentially linked to modifications in the Berry curvature [141], underscore the importance of symmetry-breaking in engineering spintronic functionalities. The capacity to modulate electronic structure via magnetization offers a promising route for controlling spin and charge transport, crucial for applications such as magnetic memory and spin-based logic devices [144].

However, the precise influence of magnetization on Berry curvature and the resulting Hall responses in the FePd alloy thin films remains to be established. These results point to compelling directions for future research, combining spin-resolved photoemission, theoretical modeling, and transport measurements to establish how symmetry-breaking and SOC can be harnessed to control spin and charge dynamics in ferromagnetic thin films.

Another key finding of this chapter is the emergence of spin textures and the formation of local spin-mixing hotspots within the fully spin-polarized Fermi surface bands of the half-metallic ultrathin FePd film. These spin-mixing hotspots, concentrated around the square-like Fermi contours, are prominent in the momentum distribution and have profound implications for the spin dynamics of the system. At these hotspots, spin-flip transitions occur, where electron spins experience mixing between different spin states due to SOC [145, 146]. This facilitates a switching channel for the spin polarization, which directly influences the transport properties.

The ultrafast demagnetization process is intricately tied to the spin-mixing hotspots and can lead to non-equilibrium states where the system's band structure undergoes transient changes. These dynamics, occurring on femtosecond to picosecond timescales, introduce time-dependent effects into the electronic structure, resulting in a transient alteration of the Fermi surface and the spin-polarized states [147, 148]. Notably, this provides a direct avenue for k -dependent ultrafast magnetic switching via spin-orbit torque, where the spin-mixing hotspots serve as the channel for the ultrafast demagnetization and switching processes.

Interestingly, the coexistence of strong SOC from the 4d Pd substrate and ferromagnetic order from the half-metallic ultrathin FePd creates a platform akin to a prototypical spin-orbit torque device setup [149, 150], with Pd as the heavy metal substrate and FePd alloy as the ferromagnetic thin film. Such configurations are of great interest as building blocks for spintronic devices, enabling efficient ultrafast current control of the magnetic state and dynamics of the half-metallic ferromagnet. Such a platform may open new avenues for developing a switchable ultrafast spin valve for spintronic applications.

8 Conclusion and Outlook

This thesis investigates the role of spin-orbit coupling (SOC) in Pd(001) and Rh(001), and its interplay with exchange interactions in ultrathin FePd alloys on Pd(001), with a main focus on their electronic structure. Chapter 4 demonstrates the impact of SOC on the band structure of Pd(001), including gap openings at high-symmetry points and Fermi surface modifications. In Chapter 5, spin-resolved momentum microscopy reveals tunable exchange interactions and SOC-driven half-metallicity in two-monolayer FePd. Chapter 6 examines magnetization-dependent band asymmetries and non-collinear spin textures in the Fermi surface, highlighting the consequences of time-reversal symmetry breaking. Collectively, these studies provide fundamental insights into competing SOC and exchange interaction in a $3d$ - $4d$ hybrid alloy system, supported by theoretical calculations from collaborative groups.

The findings of this study contribute to a broader understanding of SOC-driven phenomena and their influence on the magnetic and electronic properties of low-dimensional systems. Firstly, the reshaping of the Fermi surface by SOC provides a pathway for tuning transport properties, such as the anomalous Hall effect. Secondly, the demonstrated control over magnetization-dependent band structures offers insights into designing materials with tailored spintronic functionalities compatible with contemporary industrial thin-film processes. Thirdly, the exploration of half-metallicity in an ultrathin film opens new avenues for 2D spin filters and spin-injection devices in spintronic applications. Furthermore, the experimental identification of spin-mixing hotspots across the Fermi surface of an ultrathin ferromagnet lays the groundwork for investigating $\vec{k}$ -dependent ultrafast (de-)magnetization mechanisms.

Building upon our findings, several directions for future research can be explored. We propose extending the study of two monolayers (ML) of FePd alloy on Pd(001) to investigate temperature-dependent properties and their impact on spin dynamics and transport. In addition to the techniques used in this thesis, scanning probe techniques and magneto-optical measurements are suited for this endeavor. While we have theoretically examined the effects of disorder, chemical composition, and interface interactions in a two ML FePd alloy on Pd(001), further experimental refinements are necessary to precisely tune its electronic structure. On the theoretical front, advanced approaches such as dynamical mean-field theory could be employed to capture electron correlation effects on the band structure of hybrid ferromagnetic films. Additionally, to support the interpretation of the observed dichroic signals and their potential relation to Berry curvature, it would be valuable to explicitly compute the Berry curvature in the vicinity of degenerate points and avoided crossings identified in the Brillouin zone. Such calculations would enable a more rigorous connection to the intrinsic anomalous Hall conductivity and help elucidate the role of symmetry

breaking and spin–orbit coupling in shaping the electronic structure.

This study into the spin-resolved electronic structure of ultrathin FePd alloys and the relevant systems provides a broader framework for investigating the interplay of exchange interactions and SOC. Beyond the reported findings, the experimental and theoretical approaches employed here offer a model setup for exploring electronic structures and spin-dependent phenomena in other systems of interest. For instance, Fermi surface tomography used in Chapter 4 can be used to explore flat-band phenomena [151–153] that enhance electronic correlations in bulk systems, potentially leading to exotic phases like superconductivity or spin liquids. Similarly, the hybridization effects observed in FePd suggest the potential for studying heavy fermion systems [154], where SOC and exchange effects create highly tunable electronic structures. On the other hand, the access to the spin-resolved band structure of the FePd ultrathin alloy in its entire Brillouin zone allows us to probe the magnetization-dependent symmetry-breaking phenomena and the momentum distribution of spin-mixing hotspots. This can be applied to the study of contemporary systems of high interest, such as strongly correlated oxides [62], topological semimetals [155], 2D van der Waals materials [156], and complex magnetic order, such as non-collinear magnets and altermagnetic phases [8], which may reveal new paradigms in spin-texture engineering and magnetotransport phenomena.

This thesis ultimately lays a robust foundation for future explorations into the physics of complex electronic systems and hybrid materials. By integrating state-of-the-art photoemission techniques with first-principles theoretical modeling, it offers a rigorous framework for unraveling the effects of SOC and exchange interactions in low-dimensional quantum materials.

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