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Electronic properties of topological semimetal candidates ACd_2Pn_2
($A = \text{Eu, Sr}$; $Pn = \text{As, Sb}$)

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Abstract

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Weyl semimetals have attracted significant attention due to their intriguing electronic properties arising from the presence of Weyl points. Among them, ideal magnetic Weyl semimetals, characterized by a single pair of Weyl points close to the Fermi level, have long been sought for exploring the intrinsic topological effects associated with Weyl fermions free from interference by other trivial energy bands. In the past few years, the antiferromagnetic layered compound $EuCd_2Pn_2$ ($Pn = \text{As, Sb}$) has been regarded as a potential platform to realize several different topological phases via tuning its magnetic order. Specifically, $EuCd_2As_2$ was proposed to be one of the leading candidates to realize an ideal magnetic Weyl semimetal. The earlier studies of magneto-transport and photoemission seem to agree with the existence of the Weyl semimetal phase, however, the direct observation of Weyl crossings of $EuCd_2As_2$ is lacking. In this study, through materials synthesis, materials characterization, and systematic magneto-transport and photoemission measurements, we not only reveal the trivial topological nature of ACd_2Pn_2 ($A = \text{Eu, Sr}$; $Pn = \text{As, Sb}$) but also distinguish the origin of the overestimation of the topological region in ACd_2Pn_2 .

In the first part of the study, we successfully synthesized highly insulating $EuCd_2As_2$ crystals with carrier density reaching as low as $2 \times 10^{15} \text{ cm}^{-3}$. The magnetotransport measurements revealed a progressive decrease of the anomalous Hall conductivity by several

orders of magnitude as the carrier density decreases. The behavior contradicts what is expected from the intrinsic anomalous Hall conductivity generated by the Weyl points, which is independent of carrier density as the Fermi level approaches the charge neutrality point. In contrast, the scaling relationship between AHC and longitudinal conductivity aligns with the characteristics of variable-range hopping insulators. Our results suggest that EuCd_2As_2 is a magnetic semiconductor rather than a topological Weyl semimetal. There is a significant discrepancy between DFT calculation prediction and experimental results.

In a very recent work, it was found there are two possible origins of the underestimation of the bandgap in EuCd_2As_2 , the choice of DFT functional and the size of the Hubbard potential $\mathbf{U}$. To elucidate the origin of the underestimation, we performed a comparative study of EuCd_2Pn_2 and SrCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$). transport and optical transmittance study of EuCd_2Pn_2 and SrCd_2Pn_2 . EuCd_2Sb_2 is the sister compound of EuCd_2As_2 with identical crystal structure and antiferromagnetic ground state. It was predicted that in the field-induced FM phase, EuCd_2Sb_2 is a type-II Weyl semimetal with five pairs of Weyl nodes. SrCd_2Pn_2 is a non-magnetic analog of EuCd_2Pn_2 . It has the same properties as EuCd_2Pn_2 but without Eu magnetic moments. Hence, SrCd_2Pn_2 is an ideal platform to separate the effect of 4f electrons on band structures. We successfully synthesized high-quality ACd_2Pn_2 ($\text{A} = \text{Eu}, \text{Sr}; \text{Pn} = \text{As}, \text{Sb}$) and conducted studies of electrical transport, optical transmittance, and DFT calculation of these samples. In the electrical transport measurement, we found that the temperature dependence of resistivity of RCd_2As_2 ($\text{R} = \text{Eu}, \text{Sr}$) shows an insulating behavior. We observed the Shubnikov-de Haas oscillation on the magneto- and Hall resistivity of RCd_2Sb_2 ($\text{R} = \text{Eu}, \text{Sr}$), and extracted the effective mass of carriers using the temperature dependence of the SdH oscillation. In the Fourier Transform Infrared spectroscopy (FTIR) measurement, we observed an electronic gap of ~ 0.74 eV, ~ 0.86 eV, ~ 0.48 eV, and ~ 0.54 eV for EuCd_2As_2 , SrCd_2As_2 , EuCd_2Sb_2 , and SrCd_2Sb_2 , respectively. Additionally, the extra drops on the transmission spectrum of EuCd_2Sb_2 and SrCd_2Sb_2 are in agreement with the

estimated values of plasma frequencies from the measured effective mass and carrier density. This further confirmed that EuCd_2Sb_2 and SrCd_2Sb_2 are hole-doped semiconductors. Our results suggest that the use of local functionals strongly overestimates the topological region in the prediction and design of topological phases in ACd_2Pn_2 .

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Chapter 1

INTRODUCTION

This chapter offers a comprehensive overview of the background knowledge essential to this thesis. It begins with an introduction to the band topology theory and magnetism in solids, followed by a focus on topological semimetals, including Dirac and Weyl semimetals. The chapter then delves into the signatures of topological semimetals in the transport measurements, including the surface state Shubnikov-de Haas effect, negative longitudinal magnetoresistance, and planar Hall effect. Finally, it introduces the topological semimetals candidates - RCd_2Pn_2 ($\text{R} = \text{Eu}, \text{Sr}$; $\text{Pn} = \text{As}, \text{Sb}$).

1.1 Topological band theory

The conventional band theory was established in the 1930s, relying mainly on Bloch's theorem, which characterizes the behavior of electrons in the periodic potential. The Fermi-Dirac statistics describe the filling of energy states at thermal equilibrium. It provided a foundational understanding of electronic properties in solids, classifying solids into insulators, semiconductors, and metals. In the 1980s, the experimental discovery of the integer quantum Hall effect in 2-dimensional electron gas challenged the traditional band theory and led to the discovery of the topological phase. The topological phase of 2D systems was proposed by Thouless et al. [73, 32, 37], characterized by a topological invariant that is robust under continuous deformations. In recent decades, with the development of the topological band theory, topological insulators, having an electronic band gap in the bulk but conductive states on the surface, and topological semimetals, having similar topological surface states, were proposed and subsequently realized.

1.1.1 Berry phase and Chern number

The Berry phase is one of the key concepts in the topological band theory. It described the cyclic adiabatic evolution of a quantum system. It was adapted to Bloch band theory to define the topological properties of electronic bands [5]. Within the independent electron approximation, the band structure of a crystal is determined by the following Hamiltonian for a single electron:

$$H = \frac{\hat{p}^2}{2m} + V(\mathbf{r}), \quad (1.1)$$

where $V(\mathbf{r} + \mathbf{a}) = V(\mathbf{r})$ is the periodic potential with Bravais lattice vector, $\mathbf{a}$. According to Bloch's theorem, the eigenstates of a periodic Hamiltonian satisfy the following boundary condition:

$$\psi_{n\mathbf{q}}(\mathbf{r} + \mathbf{a}) = e^{i\mathbf{q} \cdot \mathbf{a}} \psi_{n\mathbf{q}}(\mathbf{r}), \quad (1.2)$$

where n is the band index and $\hbar\mathbf{q}$ is the crystal momentum, which resides in the Brillouin zone (BZ). To comply with the general formalism of the Berry phase, the Hamiltonian is transformed to be q -dependent Hamiltonian:

$$H(\mathbf{q}) = e^{-i\mathbf{q} \cdot \mathbf{r}} H e^{i\mathbf{q} \cdot \mathbf{r}} = \frac{(\hat{\mathbf{p}} + \hbar\mathbf{q})^2}{2m} + V(\mathbf{r}). \quad (1.3)$$

The transformed eigenstate $u_{n\mathbf{q}}(\mathbf{r}) = e^{-i\mathbf{q} \cdot \mathbf{r}} \psi_{n\mathbf{q}}(\mathbf{r})$ is the cell-periodic part of the Bloch function. It satisfies the strict periodic boundary condition.

$$u_{n\mathbf{q}}(\mathbf{r} + \mathbf{a}) = u_{n\mathbf{q}}(\mathbf{r}). \quad (1.4)$$

If $\mathbf{q}$ is forced to vary in the momentum space, then the Bloch state will pick up a Berry phase as:

$$\gamma_n = \oint_{\mathcal{C}} d\mathbf{q} \cdot \langle u_n(\mathbf{q}) | i\nabla_{\mathbf{q}} | u_n(\mathbf{q}) \rangle, \quad (1.5)$$

where $\langle u_n(\mathbf{q}) | i\nabla_{\mathbf{q}} | u_n(\mathbf{q}) \rangle$ is regarded as Berry connection for n -th band. The path $\mathcal{C}$ must be closed to make Berry phase γ_n a gauge-invariant quantity with physical significance. The Berry curvature of the energy band as a gauge-field tensor in momentum space is then defined as:

$$\Omega_n(\mathbf{q}) = \nabla_{\mathbf{q}} \times \langle u_n(\mathbf{q}) | i\nabla_{\mathbf{q}} | u_n(\mathbf{q}) \rangle. \quad (1.6)$$

The Berry curvature describes the phase changes when the wave vector moves in the BZ. The presence of a non-zero Berry curvature indicates a non-trivial topology. The Berry curvature integrated over the entire BZ is quantized in the units of 2π and equals the net number of monopoles inside. This number is called the Chern number:

$$C_n = \frac{1}{2\pi} \oint_{\text{BZ}} \Omega_n(\mathbf{k}) d^2\mathbf{k}. \quad (1.7)$$

The Chern number C_n is a topological invariant associated with the topological classification of electronic bands in two-dimensional systems, which cannot change when the Hamiltonian varies smoothly.

1.1.2 Dirac and Weyl fermions

In 1928, P. A. M. Dirac proposed the Dirac equation in the context of particle theory. It was the first successful reconciliation of special relativity and quantum mechanics in describing electron motion [15]. The Dirac equation in d spatial dimension and effective speed of light $c = 1$ is

$$(i\gamma^\mu \partial_\mu - m)\psi = 0, \quad (1.8)$$

where ψ is the wave function of the particle, m is the mass of the particle. $\mu = 0, 1, \dots, d$ label time and space dimension, and the $d + 1$ gamma matrices satisfy the anticommutation relation $\{\gamma^\mu, \gamma^\nu\} = 0$ for $\mu \neq \nu$ and $(\gamma^0)^2 = -(\gamma^i)^2 = I$, where $i = 1, \dots, d$. I is a 2×2 unit matrix. The minimal-sized matrices that satisfy this property depend on the dimension and are $(2^{k+1} \times 2^{k+1})$ -dimensional matrices in both spatial dimensions $d = 2k + 1$ and $2k + 2$.

In 1929, the mathematician Hermann Weyl proposed a solution for the Dirac equation for massless particles in odd spatial dimensions [19]. Consider the simplest case that $d = 1$, the anticommuting two gamma matrices are the 2×2 Pauli matrices, $\gamma^0 = \sigma_z$ and $\gamma^1 = i\sigma_y$. Therefore, the Dirac equation in $1 + 1$ dimension involves a two-component spinor and can be written as

$$i\partial_t\psi = (\gamma^0\gamma^1 p + m\gamma^0)\psi, \quad (1.9)$$

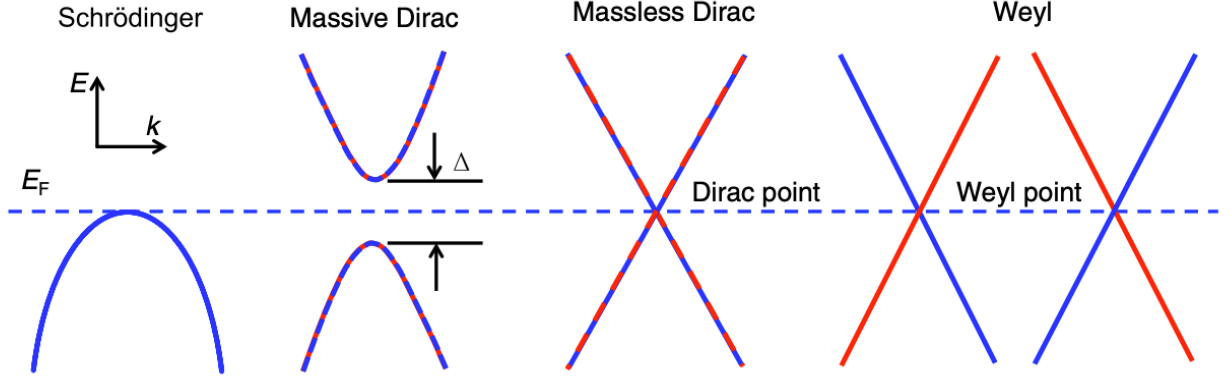


Figure 1.1: **Schematic plots of various band structures.** The band structures of Schrödinger, massive Dirac, massless Dirac, and Weyl fermions. The curves with mixed and uniform colors represent doubly degenerate and nondegenerate bands [40].

where $p = -i\partial_x$. Consider the massless particle $m = 0$, this equation can be further simplified by simply picking eigenstates of the Hermitian matrix $\gamma_5 = \gamma^0\gamma^1 = \sigma_x$ if $\gamma_5\psi_{\pm} = \pm\psi_{\pm}$. One then has the 1D Weyl equation

$$i\partial_t\psi_{\pm} = \pm p\psi_{\pm}. \quad (1.10)$$

The resulting dispersion is

$$E_{\pm}(p) = \pm p, \quad (1.11)$$

which denotes a right(left) moving particle with speed $c = 1$ which are termed Weyl fermions.

1.2 Topological semimetals

Semimetals are characterized by a small or vanishing density of states near the Fermi energy. Topological semimetals (TSMs) refer to the semimetals with the finite density of states caused by the crossing or touching of conduction and valence bands in three-dimensional BZ. Two of the most famous TSMs are Dirac semimetals (DSMs) and Weyl semimetals (WSMs) in which two doubly or single degenerated bands cross each other at discrete points near E_F , forming the fourfold Dirac points or twofold Weyl points.

In solids, the Schrödinger equation provides a successful description of nearly free quasi-particles with the Hamiltonian $H_s = p^2/2m^*$, where p is the momentum and m^* is the effective mass. The resulting electronic parabolic band structure is shown at the leftmost of Fig. 1.1. However, the realistic Dirac and Weyl equations are necessary as the effective mass of electrons approaches zero [23]. In a three-dimensional solid, the Dirac Hamiltonian has the following form:

$$H_D = \nu_F \boldsymbol{\sigma} \cdot \mathbf{k} + \beta m \nu_F^2 = \begin{pmatrix} \nu_F \boldsymbol{\sigma} \cdot \mathbf{k} & m \nu_F^2 \\ m \nu_F^2 & -\nu_F \boldsymbol{\sigma} \cdot \mathbf{k} \end{pmatrix}, \quad (1.12)$$

where $\mathbf{k} = (k_x, k_y, k_z)$ represents the momentum, ν_F is the Fermi velocity and m is the effective mass. Equation 1.12 has the same form as the Dirac Hamiltonian in high-energy physics, with the effective speed of light c replaced by the Fermi velocity. The Dirac fermions in a solid obey the relativistic energy-momentum relation

$$E_{\pm} = \pm \sqrt{m^2 \nu_F^4 + k^2 \nu_F^2}, \quad (1.13)$$

which leads to spectral gap $\Delta = 2m\nu_F^2$ at $k = 0$. The excitations on the electrons are massive Dirac fermions and the materials with such 3D band crossings are called massive DSMs (Fig. 1.1).

In the special case of vanishing effective mass ($m \rightarrow 0$), the Dirac Hamiltonian becomes

$$H_D^{m=0} = \begin{pmatrix} \nu_F \boldsymbol{\sigma} \cdot \mathbf{k} & 0 \\ 0 & -\nu_F \boldsymbol{\sigma} \cdot \mathbf{k} \end{pmatrix}. \quad (1.14)$$

As a result, the spectrum of this massless Dirac Hamiltonian is gapless at $k = 0$, giving rise to a fourfold-degenerate node with linear dispersion in all the k_x , k_y , and k_z directions, known as the Dirac point. The corresponding low energy excitations at the Dirac point are massless Dirac fermions and materials with such 3D Dirac band crossings near E_F are called DSMs (Fig. 1.1).

When $m = 0$, the upper two components (ψ_+) and the lower two components (ψ_-) are no longer coupled. The Bloch diagonal H_D can be written in a simple 2×2 form

$$H_{\pm} = \pm \nu_F \boldsymbol{\sigma} \cdot \mathbf{k}. \quad (1.15)$$

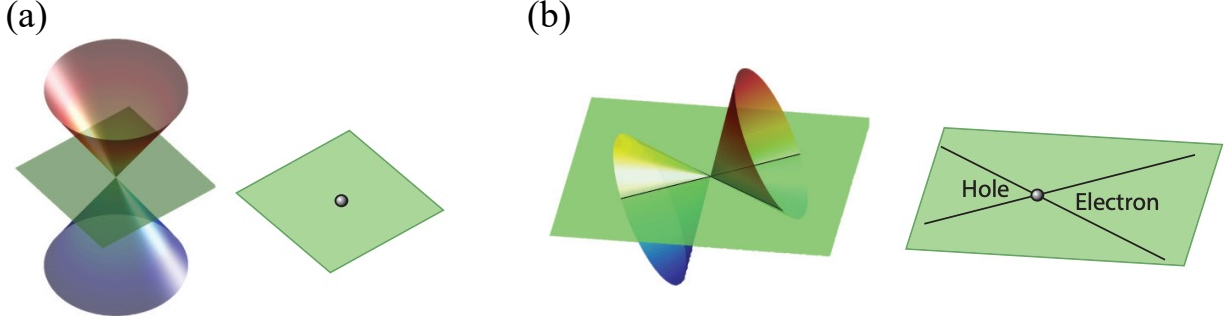


Figure 1.2: **Two types of Weyl semimetals.** (a) The type-I WSM. The Fermi surface shrinks to zero at the Weyl points when the Fermi energy is sufficiently close to the Weyl points. (b) The type-II WSM. Due to the strong tilting of the Weyl cone, the Weyl point acts as the touching point between electron and hole pockets in the Fermi surface [85].

This is the Weyl Hamiltonian of condensed-matter systems, and $\pm$ corresponds to the different chirality of the massless Weyl fermions. Either H_+ or H_- has two eigenvalues,

$$E = \pm v_F |k|, \quad (1.16)$$

which implies that the spectra of the Weyl Hamiltonian are also gapless, and two linearly dispersed and nondegenerate bands cross each other at $k = 0$ and form a twofold point, called the Weyl point. The three-dimensional solids with Fermi points existing are WSMs (Fig. 1.1). A fourfold-degenerate Dirac point can be considered the composite of two Weyl points of opposite chirality. Therefore, once the spin degeneracy is lifted by breaking either the inversion symmetry ($\mathcal{P}$) or time-reversal symmetry ($\mathcal{T}$) in DSMs, one Dirac point is split into a pair of Weyl points separated in the momentum space.

1.2.1 Type-I and type-II Weyl semimetals

The realistic Dirac fermions and Weyl fermions in solids imported from particle theory should respect Lorentz invariance, which gives rise to an isotropic Dirac or Weyl cone with linear band dispersion in all momentum directions. However, band crossings in crystals are con-

strained by the symmetries of the space groups, giving rise to the possibility of finding titled band crossings [1]. In general, according to the configuration of the band crossing, WSMs can be classified into two types by the energy dispersions near the Weyl points – type-I and type-II. Adding a tilting term to the simplest 2×2 Weyl Hamiltonian [40].

$$H = \pm \nu_0 \boldsymbol{\sigma} \cdot \mathbf{k} + \mathbf{t} \cdot \mathbf{k} I_2, \quad (1.17)$$

where $\mathbf{k} = (k_x, k_y, k_z)$, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ and t is the tilt vector. Consider the right-handed fermion and assume the vector t is along the k_z direction. The Hamiltonian can then be further written as

$$H = \nu_0 \begin{pmatrix} k_z(1 + t/\nu) & k_x - ik_y \\ k_x + ik_y & -k_z(1 - t/\nu_0) \end{pmatrix}. \quad (1.18)$$

The resulting two branches of the energy spectrum are:

$$\epsilon_{\pm}(k) = \pm \nu_0(k_x + k_y) \pm \nu_0(1 \pm \frac{t}{\nu_0})k_z. \quad (1.19)$$

These two energy branches cross each other and form a Weyl node at $k = 0$. The $\nu_0 k$ and tk_z can be viewed as the kinetic and potential energy, respectively. When $t/\nu_0 < 1$ ($tk_z < \nu_0 k$), the two linearly dispersed Weyl bands always have opposite velocities along any k direction, and $\epsilon(k) = 0$ only occurs at $k = 0$ point. The band crossing obeys the Lorentz invariance. The WSMs having such band crossing are classified as type-I WSMs. However, if $t/\nu_0 > 1$, potential energy exceeds the kinetic energy, the Weyl cone is tipped along the k_z direction. At a particular region in BZ, the equation of $\epsilon(k) = 0$ has solutions not only at $k = 0$ but also at certain other nonzero k_z points. The WSMs having this tilted band crossing are classified as type-II WSMs. When Weyl points at the Fermi level, Type-I WSMs have the Fermi surface shrinking at zero while type-II WSMs have the Weyl point acting as the touching point between electron and hole pockets 1.2.

1.2.2 Topological aspects

We have understood the topology nature and classification of WSMs. Here we explore some of the remarkable phenomena in WSMs associated with their topological band including the

Berry curvature monopoles [16, 83], surface states [4, 75, 83], and chiral anomaly [52, 24, 31].

Berry curvature monopoles

The topological invariant Chern number can be used to characterize the previously discussed nontrivial electronic structure of WSMs:

$$n_m = \frac{1}{2\pi} \oint \Omega_n d^2\mathbf{k} = \pm 1. \quad (1.20)$$

This equation reveals that a Weyl point is a singularity of the Berry curvature, which is a close analog of the magnetic field in momentum space. Therefore, a pair of Weyl points of opposite chirality can be regarded as the monopole and antimonopole of Berry curvature in momentum space. Moreover, to satisfy the periodic BZ boundary condition, the Berry curvature must begin and end within the BZ, that is the Weyl points should always come in pairs of opposite chirality so that the total monopole charge integrated over the one BZ is zero. The only way to eliminate the Weyl points without breaking charge conservation is to annihilate them pairwise, which happens only if one can move them to the same k point. Thus, the Weyl points are topologically protected in k space.

Finally, we note the difference between the $\mathcal{T}$ -breaking WSMs and $\mathcal{P}$ -breaking WSMs. In the $\mathcal{T}$ -breaking WSMs, the presence of $\mathcal{P}$ symmetry ensures that $\mathbf{\Omega}(k) = \mathbf{\Omega}(-k)$, implying that Weyl points at k and $-k$ should have opposing monopole charges. These $\mathcal{T}$ -breaking WSMs can have a minimum of one pair of Weyl points at k and $-k$ of opposite chirality. In the $\mathcal{P}$ -breaking WSMs, for a Weyl point at k , there must be another Weyl point with the same chirality $-k$, due to the $\mathcal{T}$ invariance imposing the condition that the Berry curvature at the k and $-k$ are negatives of each other, $\mathbf{\Omega}(k) = -\mathbf{\Omega}(-k)$. The vanished net chirality requires another pair with the opposite chirality, making the total number of Weyl points in $\mathcal{P}$ -breaking WSMs a multiple of four. While the $\mathcal{T}$ -broken WSMs can ideally have only one pair of Weyl points, the $\mathcal{P}$ -broken WSMs, without the complications of magnetism, possess properties that are simpler under a strong magnetic field. Additionally, they are more compatible with angle-resolved photoemission spectroscopy (ARPES).

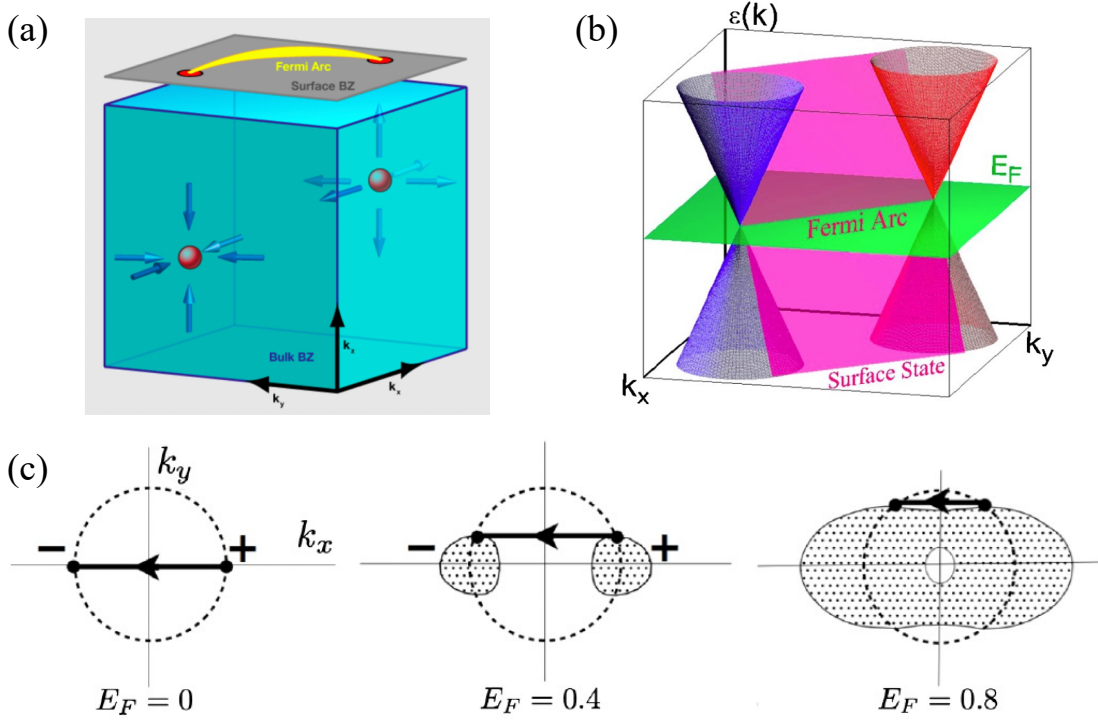


Figure 1.3: **Fermi arc surface states.** (a) A schematic of Weyl points and surface arcs. (b) Connection of surface states to bulk Weyl points. (c) Evolution of the Fermi arc with chemical potential in a particular microscopic model on raising the chemical potential from the nodal energy ($E = 0$). Fermi arcs are tangent to the bulk Fermi surface projections and may persist even after they merge into a trivial bulk Fermi surface [20, 75, 4].

Fermi-arc surface states

One of the most striking consequences of the fact that the Weyl nodes behave as monopoles of the Berry curvature is the appearance of unique surface states. Consider the simplest example of WSMs in which only one pair of Weyl nodes existed at $(0, 0, \pm k_0)$, and trivial states are far away from the E_F . Therefore, slices not containing the Weyl points in BZ are gapped 2D insulators. If the slices lie between two Weyl points, the net Berry flux accumulated across the slices leads to Chern insulators with a nonzero Chern number, which carries chiral edge states. If the slices stay far away from the two Weyl points, they are

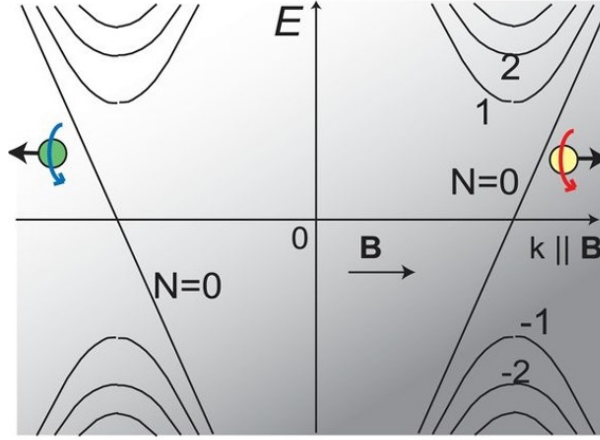


Figure 1.4: **Chiral anomaly.** (a) Schematic of chiral charge pumping between two Weyl cones with opposite chiralities under parallel magnetic and electric fields. [82].

trivial 2D insulators. Thus, the chiral edge states exist only between these two Weyl points and assemble a topological Fermi surface - Fermi arc. As shown in Fig. 1.3 (b), both surface (pink) and bulk and projected to the surface BZ. The Fermi arc is tangent to the projection of the bulk states onto the surface BZ.

When $E_F = 0$, the Fermi arc appears as a straight line on the surface BZ, connecting the projected points of Weyl nodes, as shown in Fig. 1.3 (c). As E_F deviates from the Weyl nodes, the bulk Fermi surface encloses a nonvanishing volume and its projection onto the surface BZ is a pair of filled disks that encloses the Weyl points. The Fermi arc is displaced by its finite velocity and becomes a contour tangent to a closed contour of the Weyl point. As E_F continues to move away, the projection of the bulk surface evolves into a dumbbell shape. The Fermi arc remains tangent to the bulk Fermi surface projection until merges into a trivial bulk Fermi surface.

Chiral anomaly

The Weyl node as a chiral magnetic monopole could lead to another extraordinary phenomenon: the chiral anomaly [52, 31, 24, 55]. In the presence of a strong magnetic field, the energy states of the WSMs condensed into Landau levels, and the zeroth Landau levels can be expressed as $\pm\hbar v_F \mathbf{k} \cdot \mathbf{B}$. Once the magnetic field is large enough, all electrons will be condensed into two zeroth LLs with opposite chirality, χ . Now, if an external electric field $\mathbf{E}$ is applied parallel to $\mathbf{B}$. The electrons are accelerated at a rate of eE in the $-\mathbf{E}$ direction, leading to a charge pumping between right-moving and left-moving zeroth LLs, and resulting in the following modified charge continuity equation for each Weyl node of opposite chirality:

$$\frac{\partial \rho_\chi}{\partial t} = \chi \frac{e^3}{4\pi^2 \hbar^2} \mathbf{E} \cdot \mathbf{B}, \quad (1.21)$$

where ρ_χ is the charge density of χ chirality Weyl fermions. The charge flow of individual Weyl point results in an imbalance of chiral charge within an individual Weyl point. This is known as the chiral anomaly (Fig. 1.11 (a)). Since the Weyl nodes are separated in momentum space, the pumped charge is then relaxed by the scattering process and reaches a steady state. The final chiral imbalance can thus be expressed as:

$$\frac{\partial}{\partial t}(\rho_+ - \rho_-) = -\frac{e^3}{2\pi^2 \hbar^2} \mathbf{E} \cdot \mathbf{B} \cdot \tau_{int}. \quad (1.22)$$

where τ_{int} is the intervalley relaxation time. Equ. 1.11 refers to an extra electric current along the magnetic field. In a sufficiently clean system, the backscattering of electrons of opposite chirality is suppressed, resulting in a large τ_{int} that is nearly independent of the magnetic field in a certain range. Consequently, the longitudinal conductivity along the applied magnetic field is large and proportional to the square of B , the resistivity decreases with increasing magnetic field.

1.3 Magnetism in solids

This chapter introduces the concept of magnetism in solids. Magnetism in a solid originates from magnetic moments generated by the motion of electrons in the atoms of this solid.

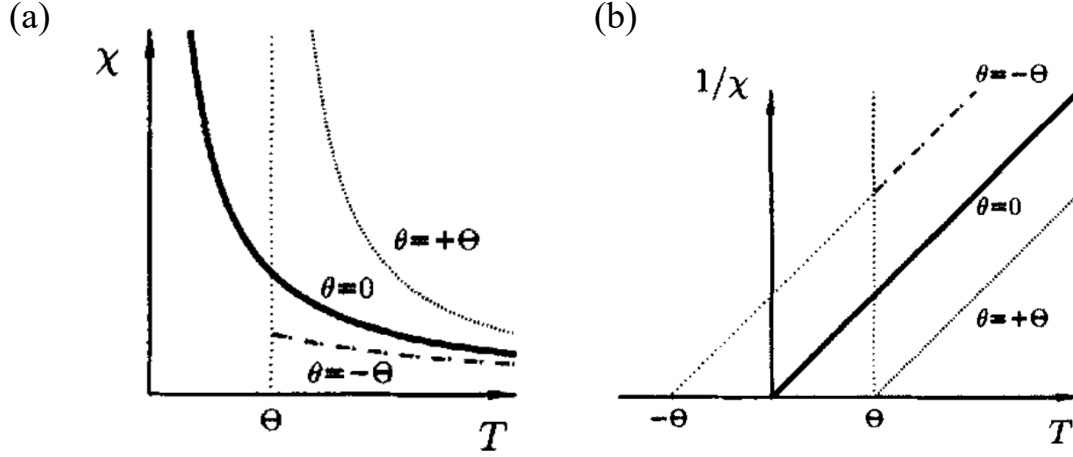


Figure 1.5: **The Curie-Weiss law** (a) The susceptibility χ versus temperature T for paramagnet ($\theta = 0$), ferromagnet ($\theta = 0$) and antiferromagnetic ($\theta = 0$). (b) The inverse susceptibility, $1/\chi$ against T for paramagnet, ferromagnet, and antiferromagnet with the intercept on the temperature axis yielding $\theta = 0$, $\theta = T_C$, and $\theta = T_N$, respectively.

The orbital and spin motion of an electron together gives rise to the magnetic moment of an atom. However, the magnetism in a solid is not a simple summation of the magnetic moments of atoms. For the magnetic atoms in certain crystal structures, a magnetic moment interacts with the neighboring magnetic moments or with their immediate environment. These interactions finally produce various long-range magnetic orders in solids, including ferromagnetism, antiferromagnetism, ferrimagnetism, and so on.

Before the introduction of spontaneous long-range magnetic orders from the interactions of magnetic moments, we start with paramagnetism in which the magnetic moments are independent of each other and the environment. Paramagnetism in a solid is due to at least one unpaired electrons in its orbit shell which gets magnetized in a magnetic field. The magnetic moment in an atom is associated with its total angular momentum $\mathbf{J}$ which is a sum of the orbital angular momentum $\mathbf{L}$ and the spin angular momentum $\mathbf{S}$:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (1.23)$$

An increase in applied magnetic field will tend to align the moments while an increase in temperature will tend to disorder them. The Brillouin function is used to describe the magnetization of an ideal paramagnet in the presence of a magnetic field:

$$\mathbf{B}_J(y) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}y\right) - \frac{1}{2J} \coth\frac{y}{2J} \quad (1.24)$$

where $y = g_J \mu_B \mathbf{J} \mathbf{B} / k_B T$, g_J is the Landé g factor and μ_B is the Bohr magneton.

In the limit of the small magnetic field, the Brillouin function can be reduced to:

$$B_J(y) = \frac{(J+1)y}{3J} + O(y^3). \quad (1.25)$$

Hence, the susceptibility is expressed by

$$\chi = \frac{M}{H} \approx \frac{\mu_0 M}{B} = \frac{n \mu_0 \mu_{eff}^2}{3k_B T} \quad (1.26)$$

where $\mu_{eff} = g_J \mu_B \sqrt{J(J+1)}$.

The susceptibility we discussed above is evaluated in the limit of vanishing applied magnetic field and given by μ_{eff} . However, at high applied magnetic fields, the magnetization saturates to M_s which is equivalent to a moment of $g_J \mu_B J$ per ion.

Ferromagnetism in a solid refers to a spontaneous parallel alignment of magnetic moments in the absence of an applied field due to exchange interactions. For a ferromagnet in the presence of applied magnetic field $\mathbf{B}$, the Hamiltonian can be expressed as:

$$\hat{H} = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g \mu_B \sum_j \mathbf{S}_j \cdot \mathbf{B}. \quad (1.27)$$

The first term is the Heisenberg exchange energy, where J_{ij} is the exchange constant for the nearest neighbors and is positive for ferromagnets, and $\vec{S}_i$ and $\vec{S}_j$ are the spin vectors of electrons at sites i and j . The second term is the Zeeman energy from the applied field. Here, the orbital angular momentum is ignored to keep things simple. To solve equ. 1.30, an effective molecular field at the i th site is estimated by:

$$\mathbf{B}_{mf} = - \frac{2}{g \mu_B} \sum_j J_{ij} \mathbf{S}_j. \quad (1.28)$$

The exchange interaction between the i th spin and its neighbours become

$$-2\mathbf{S}_j \cdot \sum_j J_{ij}\mathbf{S}_j = -g\mu_B \mathbf{S}_I \cdot \mathbf{B}_{\text{mf}}. \quad (1.29)$$

Then, the effective Hamiltonian can now be written as:

$$\hat{H} = g\mu_B \sum_i \mathbf{S}_i \cdot (\mathbf{B} + \mathbf{B}_{\text{mf}}). \quad (1.30)$$

Assuming that $\mathbf{B}_{\text{mf}} = \lambda\mathbf{M}$, where λ is a constant that parameterizes the strength of the molecular field as a function of the magnetization. We are now able to treat this problem as if the system were a simple paramagnet placed in a magnetic field $\mathbf{B} + \mathbf{B}_{\text{mf}}$.

The temperature above which ferromagnetic materials lose their permanent magnetization and become paramagnetic is known as the Curie temperature, T_c . The the Curie temperature T_c is defined by:

$$T_c = \frac{g_J\mu_B(J+1)\lambda M_s}{3k_B} = \frac{n\lambda\mu_{eff}^2}{3k_B}. \quad (1.31)$$

Applying a small $\mathbf{B}$ field at $T > T_C$ will lead to a small magnetization so that the reduced form of Brillouin function near zero field limit can be used (Equ. 1.25). Thus

$$\frac{\mathbf{M}}{\mathbf{M}_s} \approx \frac{g_J\mu_B(J+1)}{3k_B} \left(\frac{\mathbf{B} + \lambda\mathbf{M}}{T} \right). \quad (1.32)$$

So that the magnetic susceptibility is

$$\chi = \lim_{B \rightarrow 0} \frac{\mu_0 M}{B} \propto \frac{1}{T - T_C} \quad (1.33)$$

If the exchange interaction is negative, $J < 0$, the molecular field is oriented such that it is favorable for nearest neighbor magnetic moments to align antiparallel to one another. This is antiferromagnetism. The antiparallel magnetic moments can be considered as two interpenetrating sublattices, on one of which the magnetic moments point up and on the other of which they point down. The molecular field on each sublattice is

$$\begin{aligned} \mathbf{B}_+ &= -|\lambda|\mathbf{M}_-, \\ \mathbf{B}_- &= -|\lambda|\mathbf{M}_+ \end{aligned} \quad (1.34)$$

Néel temperature is known

$$T_N = \frac{g_J \mu_B (J+1) |\lambda| M_s}{3k_B} = \frac{n |\lambda| \mu_{eff}^2}{3k_B}. \quad (1.35)$$

By expanding the Brillouin function $B_J(y) = (J+1)y/3J + O(y^3)$, the results in the magnetic susceptibility χ is given by:

$$\chi = \lim_{B \rightarrow 0} \frac{\mu_0 M}{B} \propto \frac{1}{T - T_N}. \quad (1.36)$$

In the Curie-Weiss model,

$$\chi \propto \frac{1}{T - \theta}, \quad (1.37)$$

θ is the Weiss temperature. If $\theta = 0$, the material is a paramagnet. If $\theta > 0$, the material is a ferromagnetic and $\theta = T_C$. If $\theta < 0$, the material is an antiferromagnetic and $\theta = T_N$. In a temperature dependence of magnetic susceptibility measurement, T_C or T_N can be determined by the intercept of $\frac{1}{\chi}$ at $T = 0$ (Fig. 1.5 (b)).

If the two sublattices with magnetic moments point up and on are not equivalent, a solid will then have a net magnetization. This phenomenon is known as ferrimagnetism. The spontaneous magnetization of each sublattice is different and thus will have quite different temperature dependence. One sublattice can dominate the magnetization at low temperature but another dominates at higher temperature. In this case, the net magnetization can be zero and change sign at a temperature known as the compensation temperature. The temperature dependence of magnetic susceptibility of ferrimagnets therefore does not follow the Curie Weiss law.

1.4 Transport signatures of topological semimetals

In the last few decades, experimental studies have shown that relativistic fermions can result in a rich variety of extraordinary transport properties, including extremely large magnetoresistance, intrinsic anomalous Hall conductivity, negative longitudinal magnetoresistance, and planar Hall effect. These relativistic fermion-associated properties have great potential for future electronic and spintronic applications and also serve as a powerful tool in identifying

topological semimetals. In this section, this signature of topological semimetals and their corresponding underlying mechanisms will be introduced in the following.

1.4.1 Quantum oscillation

The de Haas-van Alphen (dHvA) and Shubnikov-de Haas (SdH) effects describe the oscillatory behavior of a material's magnetization and resistivity, respectively, as a function of the applied magnetic field at low temperatures. The observation of these oscillations, which are periodic in the reciprocal magnetic field, is a powerful way to reveal the physical properties of the material, such as the cross-sectional area of the Fermi surface, effective mass, and Fermi velocity. Therefore, these effects are extensively used to study topological semimetals.

The dHvA and SdH effects in a solid stem from the Landau quantization of electronic states under a high magnetic field. With the conduction band condensates into Landau levels (LLs), the density of state at the Fermi level is periodically modulated by the magnetic field, leading to periodic oscillations in resistivity or magnetization. Figure 1.6 (a) shows a parabolic electronic band for nonrelativistic electrons. The Hamiltonian for free electrons is

$$\hat{H} = \frac{\hat{p}_x^2}{2m_e} + \frac{\hat{p}_y^2}{2m_e} + \frac{\hat{p}_z^2}{2m_e}. \quad (1.38)$$

In the presence of magnetic field $\mathbf{B} = (0, 0, B)$, the magnetic vector potential $\mathbf{A} = (0, Bx, 0)$ is imported. The Hamiltonian becomes

$$\hat{H} = \frac{\hat{p}_x^2}{2m_e} + \frac{(\hat{p}_y + eB\hat{x})^2}{2m_e} + \frac{\hat{p}_z^2}{2m_e}. \quad (1.39)$$

The energy spectra under a magnetic field is the quantized LLs energy

$$\epsilon_n = (n - 1/2) \hbar\omega_c + \frac{\hat{p}_z^2}{2m_e}, (n = 1, 2, \dots), \quad (1.40)$$

where $\omega_c = \frac{eB}{m_e}$ is the cyclotron frequency and n is the non-negative LL index. The energies of LLs are field-dependent and evenly spaced by $\hbar\omega$. The lowest LL has finite energy $\hbar\omega_c/2$ (Fig. 1.6 (b) and (c)).

For the relativistic fermions on the linear dispersive band (Fig. 1.6 (d)), the LL quantization is also formed but with a different structure. Equation 1.15 describes the Hamiltonian of the relativistic fermions. By introducing a magnetic field $\mathbf{B} = (0, 0, B)$, the energy is quantized into energies:

$$\epsilon_n = \text{sgn}(n)\mu_F\sqrt{e\hbar|B|n + (\hbar k_z)^2}, (n = 0, \pm 1, \dots), \quad (1.41)$$

where $\text{sgn}(n)$ is the sign function of n , μ_F is the Fermi velocity and n is an integer. As shown in Fig. 1.6 (c) and (e), in relativistic fermions, the LLs are no longer equally spaced. The space between two levels depends on the magnetic field and LL index, $\epsilon_n \propto \sqrt{B|n|}$. Notably, there is a field-independent zeroth LL with finite energy, $\hbar v_F k_z$ located at the band crossing point ($\epsilon_0 = 0$). For a 3D WSM with topological-protected bands, the LL quantization yields energy spectra of

$$\epsilon_n = \text{sgn}\epsilon_{n,k} = \begin{cases} v_F \text{sgn}(n)\sqrt{2e\hbar|B||n| + \hbar^2 k_z^2}, & \text{if } n \neq 0, \\ \chi \hbar v_F k_z & \text{if } n = 0, \end{cases} \quad (1.42)$$

where $\chi = \pm 1$ represents the chirality of the Weyl points.

As we introduced, the dHvA and SdH effects share the same underlying mechanism - LL quantization. Here, we will focus on the SdH effect in which the resistivity oscillates against the applied magnetic field. The experimental observed SdH oscillation can be well described using the Lifshitz-Kosevich (LK) formula [28, 22, 47]:

$$\Delta\rho \propto R_T R_D \cos \left[2\pi \left(\frac{F}{B} + \frac{1}{2} + \beta \right) \right]. \quad (1.43)$$

Here, $\Delta\rho$ is the oscillatory amplitude of resistivity, F is the resistivity oscillation frequency, and $2\pi\beta$ is the Berry phase. R_T is the temperature damping factor defined as:

$$R_T = \frac{\alpha T m^*}{B \sinh(\alpha T m^*/B)}, \quad (1.44)$$

where $\alpha = 2\pi^2 k_B m_e / e\hbar$, and m_e is the effective mass of electrons on the Fermi level. R_D is the Dingle factor:

$$R_D = \exp - \frac{\alpha T_D m^*}{B}, \quad (1.45)$$

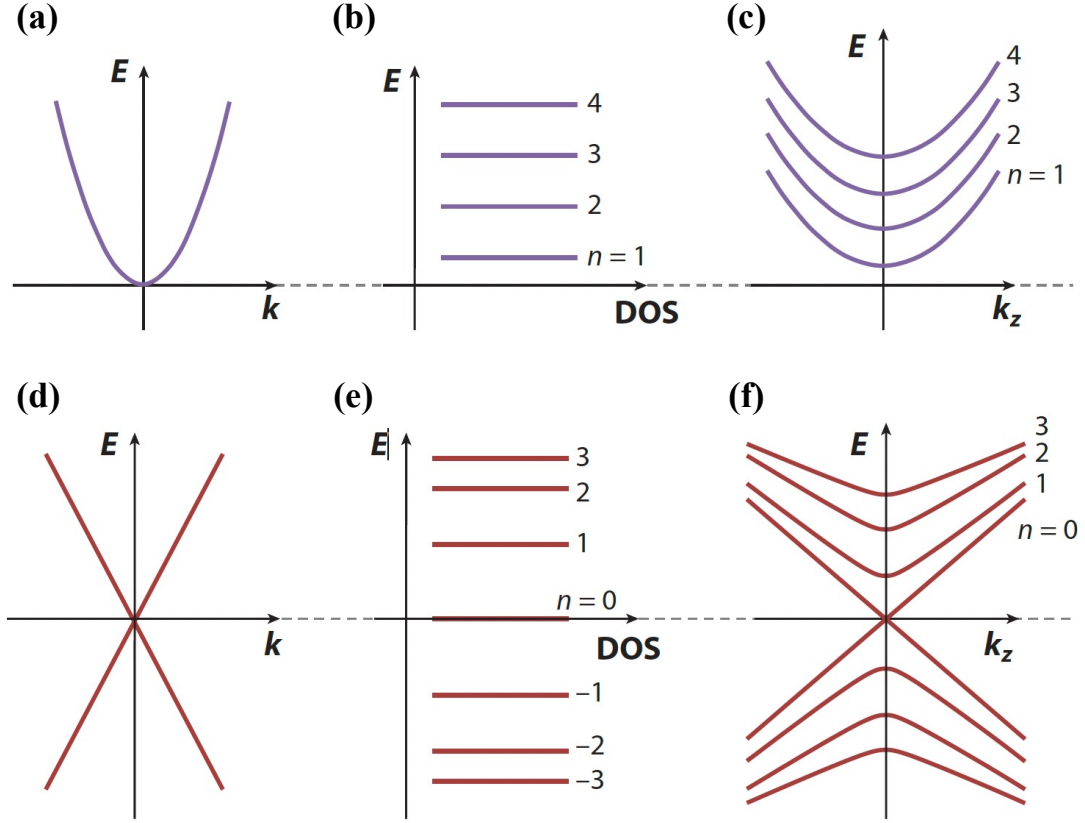


Figure 1.6: **Landau levels quantization.** Schematics for energy-momentum dispersions of (a) nonrelativistic and (c) relativistic electrons. Landau spectra for the 2D spinless (b) nonrelativistic and (d) relativistic electrons. Landau spectra for the three-dimensional spinless (e) nonrelativistic and (f) relativistic electrons as the magnetic field along the k_z direction [25].

where $T_D = \hbar/2\pi k_B \tau_q$ is the Dingle temperature and τ_q is the cyclotron relaxation time.

The SdH measurement is powerful in revealing various physical parameters of a solid, including the cross-sectional area of the Fermi pocket, electron scattering time, the effective mass of fermions at the Fermi level, and the Berry phase. These parameters can be extracted from the period, temperature, and field dependence of the oscillation amplitude, and phase of the SdH oscillation. The oscillation frequency F of oscillation can be obtained using the Fast Fourier Transform (FFT) analysis of the oscillatory component of resistivity versus inverse

magnetic field. The cross-sectional area of the Fermi pocket normal to the applied field, A_F , is then obtained via the Onsager relation using the oscillation frequency:

$$F = (\hbar/2\pi e)A_F. \quad (1.46)$$

The corresponding Fermi momentum, k_F , can be extracted by assuming a circular Fermi surface cross-sectional area via $A_F = \pi k_F^2$. The effective mass of electrons at the Fermi level, m^* , is estimated by fitting the temperature dependence of the oscillation amplitude using Equ. 1.44.

The nontrivial π Berry phase, a distinct feature of topological semimetals, can also be extracted from the SdH oscillation. In general, any closed cyclotron orbit is quantized under an external magnetic field, according to the Lifshitz-Onsager quantization rule:

$$A_F \frac{h}{eB} = 2\pi \left(n + \frac{1}{2} + \beta + \delta \right) = 2\pi(n + \gamma) \quad (1.47)$$

where n is the LL index, $2\pi\beta$ is the Berry phase, and $2\pi\delta$ is the additional phase shift resulting from the curvature of the Fermi surface in the k_z direction. δ equals 0 for a two-dimensional cylindrical Fermi surface and $\pm 1/8$ (+ for hole and $-$ for electrons) for a corrugated three-dimensional Fermi surface. The quantity $\gamma = \frac{1}{2} + \beta + \delta$ can be experimentally accessed by analyzing the LL fan diagram of the SdH oscillation. The LL indexes are plotted with the inverse magnetic field with peaks of the oscillation assigned to integers and valleys assigned to half integers. The intercept in the limit $1/B \rightarrow 0$ is the value of γ . In the SdH measurement of Cd_3As_2 [22], the nontrivial π Berry phase ($\beta = -1/2$) was detected by fitting the Landau index versus the inverse magnetic field using Lifshitz-Onsager rule.

Besides the bulk states, the SdH oscillation can also detect the topological surface states, such as Fermi arcs of Dirac/Weyl semimetals. In a simple case, assuming that a WSM has only one pair of Weyl points along the k_z direction, the Fermi-arc surface states are thus expected on the top and bottom (010) surfaces (Fig. 1.7 (a)), on which the projections of the two Weyl points are well separated in the k space. In the presence of a magnetic field perpendicular to the (010) surface, the surface electrons may propagate between the top and

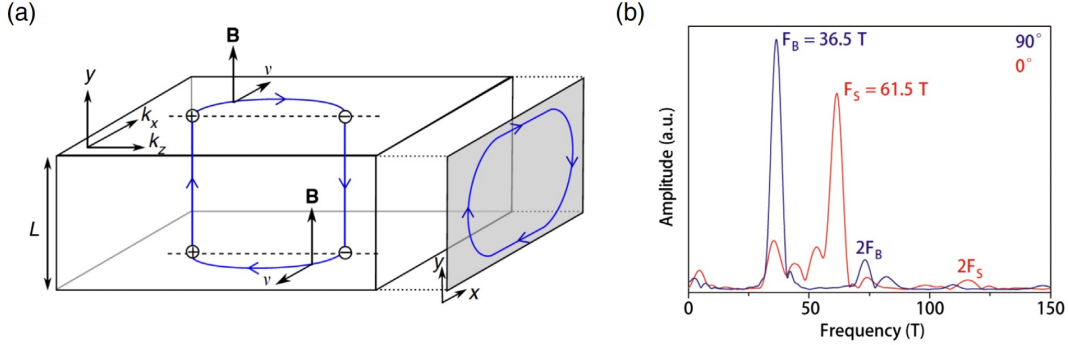


Figure 1.7: **Shubnikov-de Hass oscillation of Fermi arc.** (a) Weyl orbits in a slab of a WSM of a finite thickness (L) in the presence of a perpendicular magnetic field. (b) Fourier transform of magnetoresistance measured on the Cd_3As_2 microplates at 2 K, with magnetic field parallel (blue curve) and perpendicular (red curve) to the (010) surface, respectively.

bottom surfaces via the bulk states if the propagation distance is smaller than the quantum mean free path of the electron and an oscillation. Therefore, a DSM or WSM with finite thickness under a magnetic field perpendicular to the Weyl orbit would have an additional oscillation strongly depending on the sample thickness and the angle of the magnetic field (Fig. 1.7).

In the presence of a magnetic field strong enough to push all LLs above E_F except for the lowest LL, all electrons are condensed to the lowest LL; such a state is generally referred to as a quantum limit. In the quantum limit, a new type of resistivity oscillation is periodic in $\log(B)$ emergent, which is believed to be associated with the discrete scale invariance and formation of the two-body quasi-bound state [81, 39].

1.4.2 Intrinsic anomalous Hall effect

The intrinsic anomalous Hall effect (AHE) is another important transport feature for the topological semimetals. Consider a $\mathcal{T}$ -breaking magnetic WSM with a pair of Weyl nodes along the z direction separated by a distance Δk in the momentum space. In this situation, the region between the two Weyl points with opposite chiralities can be seen as a collection

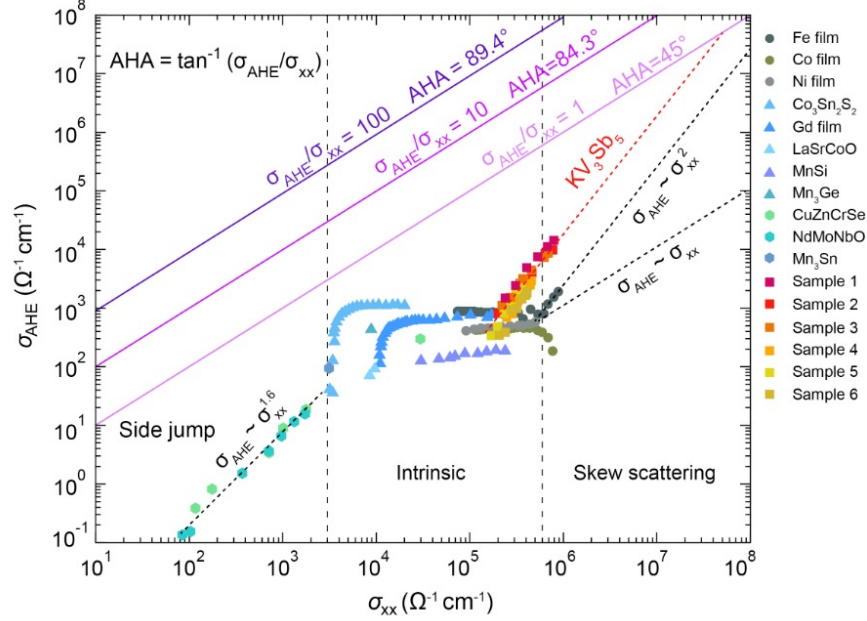


Figure 1.8: **Mechansims of anomalous Hall effect.** σ_{xy}^{AH} versus σ_{xx} for a variety of materials spanning the three AHE regimes from the side-jump mechanism through the intrinsic and skew scattering [88].

of 2D Chern insulators. Each Chern insulator has a chiral edge mode near the Fermi energy contributing a Hall conductance e^2/h . Therefore, the total intrinsic anomalous Hall conductivity (AHC) when the Fermi level is at the Weyl nodes should be given by the integral of the z component of the Berry curvature over all occupied states:

$$\sigma_{xy}^{A.int} = \frac{1}{2\pi} \int_{-\pi}^{\pi} \sigma_{xy}(k_z) dk_z = (e^2/2\pi h) \Delta k. \quad (1.48)$$

When the Fermi level slightly moves away from the Weyl points, the intrinsic AHC attains a universal value determined by Δk (the plateau shown in Fig. 1.9 (b)), the linear dispersion sufficiently close to Weyl nodes is a topological property, thus the intrinsic AHC follows directly and exclusively from the existence of a nonzero topological charge. As the Fermi level moves away, there are also intrinsic and extrinsic contributions to the AHC from the free carriers. However, for an untilted type-I Weyl semimetal the sum of these contributions

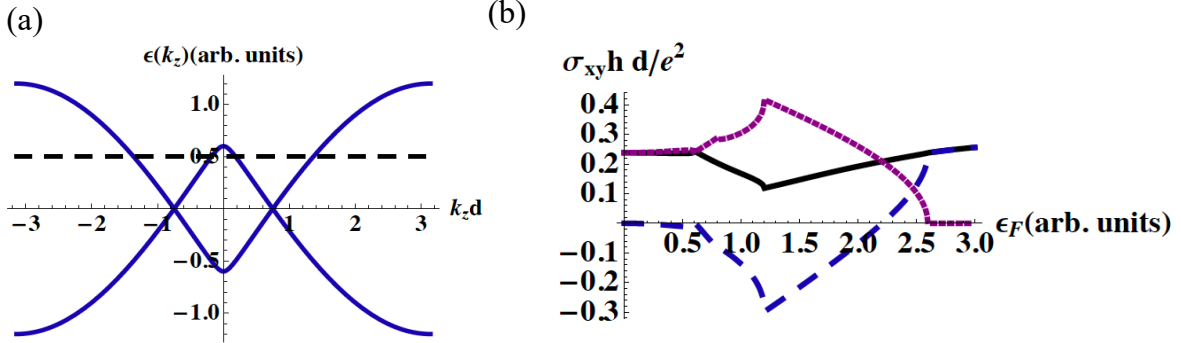


Figure 1.9: **Intrinsic anomalous Hall effect** (a) Band edges along the z -direction in the momentum space for the two bands that touch at the Weyl points. The dashed line denotes the Fermi energy. (b) Total anomalous Hall conductivity (solid line) versus the Fermi energy. The plateau-like feature in σ_{xy} correlates with the range of the Fermi energies, for which the Fermi surface consists of two separate sheets, each enclosing a single Weyl node. When the Fermi surface enclosing two Weyl points merge, the intrinsic AHC contributed by the existence of Weyl points vanishes [7].

is equal to zero[7].

Unlike the type-I WSMs discussed above, the type-II WSMs have a tilted conical spectrum around the Weyl points. The intrinsic AHC of a type-II WSM with a pair of Weyl points is not universal and can change signs as a function of the tilting parameters [93]. Moreover, for the $\mathcal{P}$ -breaking Weyl semimetal, the intrinsic anomalous Hall effect principally diminishes because a $\mathcal{P}$ -breaking Weyl semimetal possesses at least two pairs of Weyl points in the Brillouin zone, and the total Berry phase contributed by the two Weyl pairs cancel each other.

In the practical measurements of the AHC, the WSMs are not always ideal as assumed, the trivial electronic band around E_F also contributes to the AHC, σ_{xy}^A , like the extrinsic contribution, including the skew scattering, and side-jump. Therefore, the experimental measured σ_{xy}^A can be expressed by

$$\sigma_{xy}^{AH} = \sigma_{xy}^{AH_{int}} + \sigma_{xy}^{AH_{skew}} + \sigma_{xy}^{AH_{sj}}. \quad (1.49)$$

Each of the mechanisms is governed by different relationships between longitudinal resistivity and anomalous Hall resistivity. The longitudinal resistivity, σ_{xx} is divided into three regimes

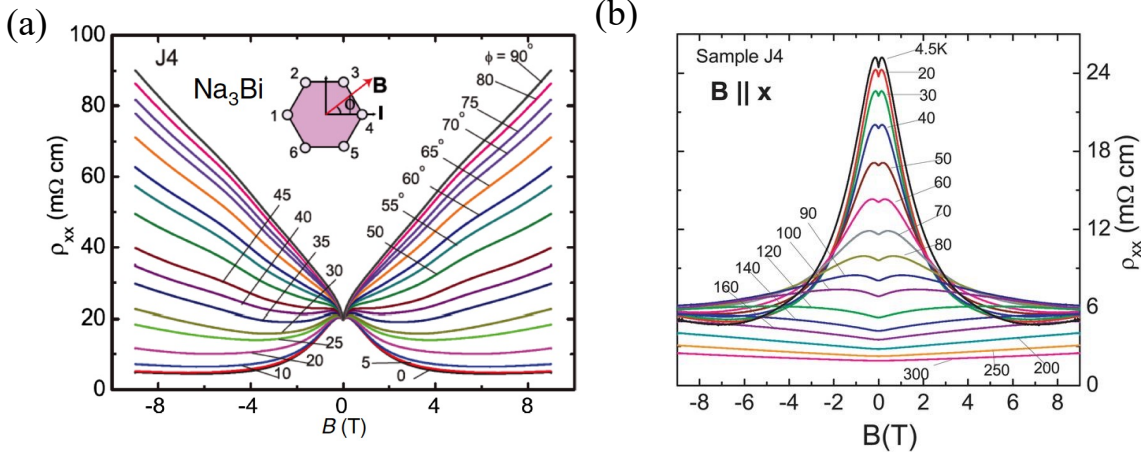


Figure 1.10: **Negative longitudinal magnetoresistance (NLMR)**. (a) Resistivity ρ_{xx} versus B at the selected field-tilt angle ϕ to the x axis. For $\phi = 90^\circ$, ρ_{xx} displays a B-linear positive MR. However, as $\phi \rightarrow 0^\circ$ ($B \parallel I$, σ_{xx} is strongly suppressed). (b) Longitudinal magnetoresistance ρ_{xx} at various temperatures measured with B parallel to E and perpendicular to x axis for Na_3Bi . Negative longitudinal MR is observed at lower temperatures [82].

that have been identified when surveying a large body of experimental data for diverse materials. As shown in Fig. 1.8. Within each regime, difference mechanisms contribute the total AHE, σ_{xy}^{AH} . In the high conductivity regime ($\sigma_{xx} > 10^6 \Omega^{-1}\text{cm}^{-1}$), a linear contribution to $\sigma_{xy}^{AH} \propto \sigma_{xx}$ due to skew scattering dominates σ_{xy}^A and the normal Hall conductivity contribution can be significant. In the mediate conductivity regime ($10^4 \Omega^{-1}\text{cm}^{-1} < \sigma_{xx} < 10^6 \Omega^{-1}\text{cm}^{-1}$), the σ_{xy}^{AH} is intrinsic and thus roughly independent of σ_{xx} . In the bad metal regime ($\sigma_{xx} < 10^4 \Omega^{-1}\text{cm}^{-1}$), σ_{xy}^{AH} decreases with decreasing σ_{xx} following the power law, $\sigma_{xy}^{AH} \propto \sigma_{xx}^\alpha$ ($\alpha = 1.6$) [48]. The mechanism of AHE in this region is side-jump.

1.4.3 Negative longitudinal magnetoresistance

The negative longitudinal magnetoresistance (NLMR), a decrease of longitudinal resistivity when the magnetic field $\mathbf{B}$ is parallel to the electrical field $\mathbf{E}$, related to the chiral anomaly has been regarded as one of the most prominent transport features of topological semimetals. In a sufficiently clean system, the backscattering of electrons of opposite chirality is suppressed,

resulting in a large τ_{int} that is nearly independent of the magnetic field in a certain range and an NLMR versus magnetic field.

However, in a solid, the NLMR is not a universal behavior of chiral anomaly. The quantum limit condition requires that no other states cross E_F , otherwise, the zeroth LLs contribution would be smeared out. Moreover, in a strong magnetic field, the relaxation time can be proportional to $|B|^{-1}$, which cancels out the dependence on the current induced by the chiral anomaly [40]. Therefore, a semiclassical approach based on the Boltzmann equation was developed to describe the NLMR in TSMs [31]. By describing the scattering channels using the semi-classical equation of electron motion, the electrical current is solved as:

$$J = ne\vec{r} = ne \left(1 + \frac{e}{c}\vec{B} \cdot \vec{\Omega}_p\right)^{-1} \left\{ \frac{\vec{p}}{m} + e\vec{E} \times \vec{\Omega}_p + \frac{e}{mc}(\vec{\Omega}_p \cdot \vec{p})\vec{B} \right\}. \quad (1.50)$$

After several straightforward steps derivations, the NLMR under a small magnetic field can be expressed in:

$$\sigma(B) = (1 + C_w B^2) \cdot \sigma_{\text{WAL}} + \sigma_n, \quad (1.51)$$

where σ_{WAL} is the conductivity from weak anti-localization corrections associated with intra-node scattering and σ_n is that from conventional Fermi surface contribution. $C_w B^2$ with a positive value of C_w is from the topological $E \cdot B$, driven by the parallel $\mathbf{E}$ and $\mathbf{B}$ under the influence of Berry curvature [31]. The chiral anomaly-induced NLMR described by the equation above has been observed in both Na_3Bi (Fig. 1.11 (b)) and Cd_3As_2 single crystals [82, 27, 91].

In type-I WSMs, the chiral anomaly-induced NLMR always appears, regardless of the direction of the parallel magnetic field. In contrast, in type-II WSMs, the chiral anomaly shows a different situation. Given the strongly tilted Weyl cones in such WSMs, Landau quantization sensitively depends on the orientation of the magnetic field, and the Landau spectrum is gapped for some field directions. Therefore, their negative longitudinal MR is strongly anisotropic [70, 74, 89].

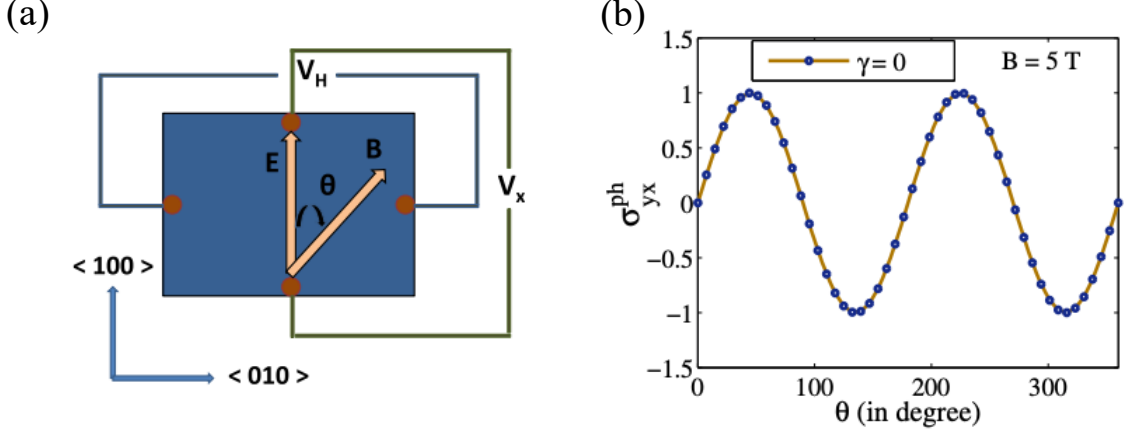


Figure 1.11: **Planar Hall effect (PHE)**. (a) Illustration for the planar Hall effect measurement setup (V_H is the in-plane Hall voltage). (d) The angular dependence of planar Hall conductivity for $B = 5\text{T}$ [50].

1.4.4 Planar Hall effect

Recent advances reveal that the chiral anomaly in WSMs can lead to another key effect, the planar Hall effect (PHE), which refers to the appearance of transverse Hall resistivity when the coplanar electric and magnetic fields are not perfectly aligned [8, 50]. Figure. 1.11 (c) shows the configuration of the PHE measurement. The Hall resistivity ρ_{xy}^{AHE} of PHE in a pure WSM can be described as:

$$\rho_{xy}^{AHE} = (\rho_{\perp} - \rho_{\parallel}) \sin \theta \cos \theta, \quad (1.52)$$

where θ is the angle between the current flow and the magnetic field orientation, $\rho_{\perp}$ and $\Delta\rho_{\parallel}$ are the resistivity with the planar magnetic field perpendicular and parallel to the current, respectively. The planar Hall conductivity follows $\cos \theta \sin \theta$ dependence is depicted in Fig. 1.11 (d). Notably, unlike the conventional Hall effect, the PHE is not antisymmetry as the magnetic field since the origin is not the Lorentz force. This face can be used to isolate PHE in experiments by taking measurements with both positive and negative B . On the other

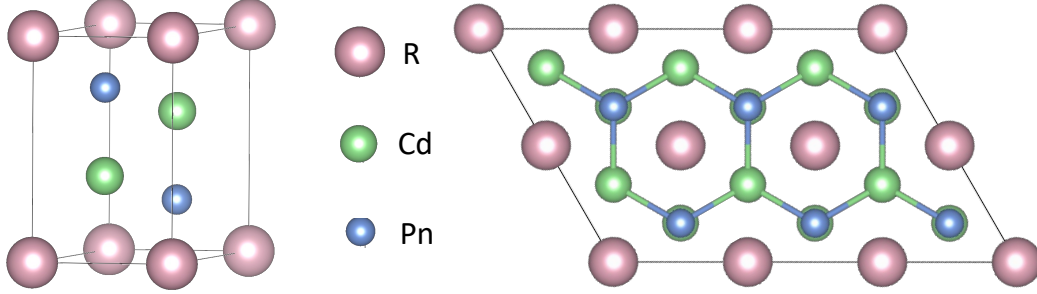


Figure 1.12: **Crystal structure of RCd_2Pn_2 ($\text{R} = \text{Eu}, \text{Sr}$; $\text{Pn} = \text{As}, \text{Sb}$).** RCd_2Pn_2 has a hexagonal unit cell with space group $P\text{-}3m1$.

hand, the PHE can be distinguished from the anomalous Hall effect by taking measurements with both $B = 0$ and $B \neq 0$ and subtracting the background ($B = 0$) contribution [50].

1.5 RCd_2Pn_2 ($\text{R} = \text{Eu}, \text{Sr}$; $\text{Pn} = \text{As}, \text{Sb}$)

In the last few decades, significant progress has been made in the field of WSMs. Weyl states and associated extraordinary phenomena have been observed in several material systems using various experimental techniques. However, the study of Weyl fermions in a solid so far has been hindered by (1) the non-negligible distance between Weyl nodes and E_F , (2) the presence of trivial bands surrounding the Weyl points, and (3) the existence of multiple Weyl points. Consequently, a direct study of the fundamentals of Weyl fermions is still lacking. The realization of an ideal WSM with only one pair of Weyl points close to the E_F without other trivial electronic bands surrounding is demanding.

In recent years, the magnetic layered materials family, EuCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$), was proposed to be a platform to realize several topological phases. For example, a topological DSM phase can be realized in EuCd_2Pn_2 in a c -axis oriented layered AFM order (c -AFM). When the spin easy axis lies in the plane, the same AFM state leads to a band gap due to a broken C_3 symmetry. The gapped phase is expected to be an axion insulator, which shows a

half-quantum Hall effect [45]. c -axis oriented FM phase is predicted to be a magnetic WSM with one pair of Weyl points, where the breaking of time-reversal symmetry splits the Dirac node to one pair of Weyl nodes [68, 78, 41].

EuCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$) crystalize in the CaAl_2Si_2 structure of space group D_3 (Fig. 1.12). They can be considered as the layered analog of the well-known 3D DSM Cd_3As_2 with Cd_3As_2 layers separated by trigonal Eu/Sr layers. At a temperature of 7.2 K and 9.5 K, the localized magnetic moments of Eu atoms develop a long-range magnetic order, with moments ferromagnetically coupled within layers and antiferromagnetically coupled between layers for EuCd_2Sb_2 and EuCd_2As_2 , respectively [90, 69, 58, 65]. Application of a 3.2 T and 2 T magnetic field saturates all magnetic moments along the c axis at low temperature, stabilizing a field-induced FM state in EuCd_2Sb_2 and EuCd_2As_2 , respectively. Previous studies suggest the field-induced FM order leads a phase transition of small gap topological insulator to an FM Weyl semimetals with five pairs of Weyl points in EuCd_2Sb_2 and only one pair of Weyl points free from interference by other trivial energy bands in EuCd_2As_2 [71, 68, 78, 41].

SrCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$), with Sr replacing Eu in EuCd_2Pn_2 , is a non-magnetic analog of EuCd_2Pn_2 . It has a qualitatively similar crystal structure and electronic band structure to EuCd_2Pn_2 but lacks ordered magnetic moments. Hence, SrCd_2Pn_2 can be thought of as a platform to reveal the topology nature and explore the interplay of magnetism and topology in the proposed magnetic Weyl semimetal, EuCd_2Pn_2 . Previous works proposed that SrCd_2As_2 is a small electronic gap semiconductor and the negative hydrostatic pressure can reduce the band gap of SrCd_2As_2 , inducing the band inversion between Cd s and As p orbitals along the Γ - A direction to form a pair of Dirac points [14]. SrCd_2Sb_2 with the increased nearest neighbor Cd-Pn distance from the larger Sb atomic size is as SrCd_2As_2 under negative hydrostatic pressure. Therefore, SrCd_2Sb_2 was expected to be a DSM.

The main focus of this thesis is to investigate the electronic properties and determine the topological properties of these Dirac and Weyl semimetal candidates. As we will show, the DFT calculations that are widely used by the community seriously underestimate the

bandgap of these materials, and therefore incorrectly predict their topological properties.

Chapter 2

EXPERIMENTAL METHOD

This chapter introduces the experimental methods used in the works presented in this thesis. It starts with a detailed introduction of the synthesis procedure for single crystal RCd_2Pn_2 ($\text{R} = \text{Eu, Sr}$; $\text{Pn} = \text{As, Sb}$). It then introduces the techniques used for characterizing the synthesized single crystals. Finally, it presents the methods for measuring physical properties, including electrical transport, magnetic properties, and heat capacity.

2.1 *Materials synthesis*

RCd_2Pn_2 ($\text{R} = \text{Eu, Sr}$; $\text{Pn} = \text{As, Sb}$) single crystals were synthesized via the flux method [30]. For RCd_2Sb_2 , mixtures of stoichiometric Eu or Sr lump (Ames Laboratory), Cd, and Sb shots with 4 times atomic mass Sn shots were used as start materials; While for RCd_2As_2 , mixtures of stoichiometric Eu or Sr lump, Cd, and As shots with 10 times atomic mass Sn shots were used. The mixtures were then ground, mixed, and loaded in the bottom of a Canfield crucible [56]; then the crucible was loaded in a quartz tube. To avoid oxidization, grind, and load were conducted in the glove box filled with argon, and the ball valve was used to keep input materials from the air when transferring them out of the glove box to the seal station. The mixture was then sealed in an evacuated quartz tube and placed in a box furnace. The mixture was heated to 900 °C over 12 h, held for 24 h, then slowly cooled over 200 h to 550 °C for RCd_2As_2 , and to 450 °C for RCd_2Sb_2 . The tube was quickly removed from the furnace and spun in a centrifuge to remove the Sn flux. This process yields plate-like single crystals with a hexagonal shape up to a few millimeters in size (Fig. ??).

For EuCd_2As_2 , we discovered that the residual carrier density of crystals is highly sensitive to the ratio of Sn flux in the starting materials. The stoichiometric Eu pieces and Cd and

As shots were mixed with 10 to 25 times atomic mass Sn shots as starting materials, which yielded EuCd_2As_2 crystals with hole carrier density spanning from 10^{15} to 10^{16} cm^{-3} . This allowed us to use various carrier densities as a convenient knob to study the electronic band structure of EuCd_2As_2 .

2.2 Materials characterization

2.2.1 Energy-dispersive spectroscopy

Energy-dispersive spectroscopy (EDS) is used to determine the chemical composition of crystals. The high-energy electron beam (0.5 - 20 kV) strikes the sample surface and knocks out a deeply localized electron in an atom. The emission occurs as the outer electrons relax into the inner hole. Each element emits x-ray at specific energies unique to its atomic structure. The emitted x-rays from all the elements are finally collected by the detector and used for qualitative determination of the elemental ratio.

The EDS measurement was carried out on a clean crystalline surface using a Sirion XL30 scanning electron microscope mounted on a scanning electron microscope. For each crystal, measurements were made at several locations on each sample to obtain an averaged chemical composition and composition ratio variations.

2.2.2 X-ray diffraction spectroscopy

X-ray diffraction spectroscopy (XRD) is used to observe the space group and lattice constants of crystals. The XRD was performed at room temperature using a Rigaku MiniFlex diffractometer either on a flat crystalline surface of a single crystal or on the ground crystal powder.

In powder XRD measurement, the sample is ground into a fine powder to ensure every crystalline orientation is represented equally; the powder is then pressed on the sample to ensure a flat surface. Figure 2.2 is the powder XRD diffraction spectrum measured on EuCd_2As_2 , along with the calculated intensity made via FullProf [61]. Each peak corresponds

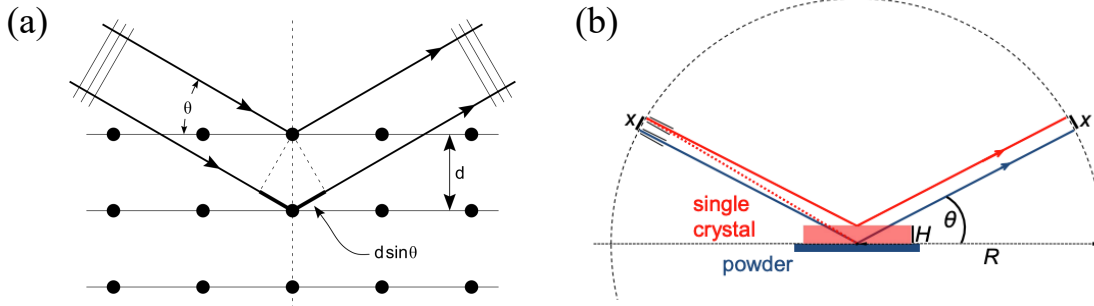


Figure 2.1: **X-ray diffraction.** (a) Bragg's condition for constructive interference that gives the Bragg peak in the powder XRD spectrum. (b) The x-ray path for an ideally aligned sample is indicated by the blue line. For a single crystal with a thickness of H (sample height), the peak position is shifted as shown by the red line.

to a specific lattice plane where the distance between the two parallel planes is an integer multiple of the incident wavelength (2.1 (a)). The relationship between the distance of a specific crystalline plane d and the diffraction angle 2θ is described by Bragg's law

$$n\lambda = 2d \sin \theta \quad (2.1)$$

where λ is the wavelength of incidents. By analyzing the diffraction spectrum, one can obtain the space group and lattice constants of a crystal. Further, the Rietveld refinement of the spectrum can be used to reveal more detailed crystalline information, including types of crystal defects and inner strain inside crystals using the FullProf suite [61].

The single-crystal XRD measurement allows the checking of the lattice constants along a specific direction. The single-crystal XRD on the ab plane of SrCd_2As_2 is shown in Fig. 2.2. The red triangles mark the peaks refracted from the ab plane of crystal, reflecting the lattice space along the c axis according to Equ. 2.1. However, for a single crystal with a thickness H , the peak position shifted as shown in 2.1 (b). The effect of the sample height on the peak position is given by

$$\Delta 2\theta_{\text{disp}} = S \cdot \cos \theta \quad (2.2)$$

where $S = 2 \cdot \frac{H}{R}$, H is the sample height and R is the diffractometer radius. The displacement results in a modified Bragg equation can be written as:

$$2c \cdot \sin(\theta - S \cdot \cos \frac{\theta}{2}) = \lambda \quad (2.3)$$

By subtracting θ corresponded with peaks and fitting it with H , R , and λ into Equ. 2.3, one can obtain the precise value of constant c .

2.2.3 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) technique is used to determine the electronic band gap of crystals. FTIR was conducted using a Hyperion 2000 system from Bruker Inc at room temperature. The measurement was performed in the transmission mode, employing an infrared globar source and a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. To ensure optimal signal transmission, a bulk crystal sample is polished down to a thin plate with a thickness under $100 \mu m$. Finally, a thin plate crystal with a flat and clean surface was utilized. Additionally, a reference measurement was conducted using a silicon wafer.

2.3 Physical properties measurement

2.3.1 Electrical transport measurement

The magnetotransport measurements were carried out in a 14 T physical property measurement system (PPMS), or a 31 T resistive magnet at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL. The magnetic field is out-of-plane along the c -axis of the crystal if not otherwise noted. The magnetic field angle dependence of magnetotransport measurement was carried out using a sample holder board attached to the horizontal rotator probe. The magnetic field rotates from out-of-plane to in-plane perpendicular to the current direction.

In sample preparation, the single crystal was cut into a rectangular plate using a wire saw and then made into a standard six-probe contact configuration with the current direction

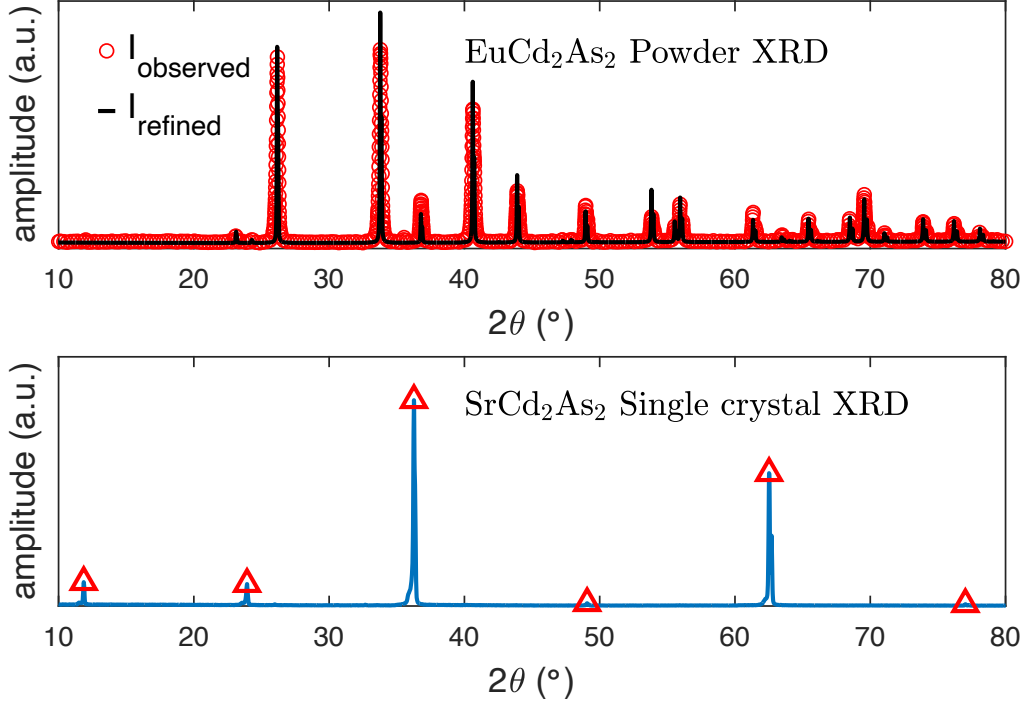


Figure 2.2: **Powder and single crystal XRD of RCd_2As_2** (a) The observed x-ray diffraction spectrum (red circles) of EuCd_2As_2 and the refined intensity (black line) gained by the Rietveld refinement using FullProf suite [61]. (b) The x-ray diffraction spectrum is measured on the ab crystalline plane of SrCd_2As_2 single crystal. The red triangles mark the condition where the diffracted beam constructively interferes, corresponding to the c lattice constant.

in-plane and the magnetic field out of plane (Fig. ??). Electrical contacts were made to the sample by sputtering gold pads on the sample surface using a hand-made paper mask and gold sputterer with argon atmosphere (108 Manual Sputter Coater, Cressington Scientific Instruments). Electrical leads in the form of 25-micron diameter gold adhered gold to the pre-patterned contacts using silver paste (EPO-TEK H20E, Ted Pella, Inc). For high-insulating samples, the contact resistance of samples was limited to a few hundred Ω . We utilized a Keithley2450 as the current source and voltmeter for measuring the $\text{G}\Omega$ level resistance, benefiting from the high impedance resistance of the Keithley2450. The current source and measured voltage range should be adjusted accordingly to get a better signal as

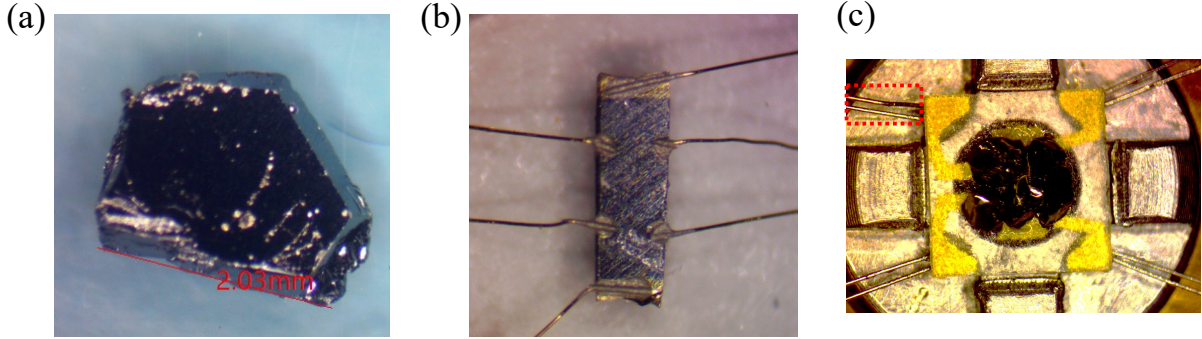


Figure 2.3: **Single crystal and samples for transport measurements.** (a) Single crystal of EuCd_2As_2 . (b) The sample of EuCd_2As_2 with six-probe contact configuration for the magnetotransport measurement. (c) The heat capacity puck with single crystals mounted with grease. The red dot frame marks the supporting wires on the puck to transfer heat from the mounted sample.

the resistivity changes a few orders of magnitude as the temperature decreases in a short time. For metallic or semimetallic samples, the SRS860 Lock-in amplifier is used to supply the current source and record the voltage between electrical leads. To eliminate any effects from contact misalignment, the magnetoresistance and Hall resistance were symmetrized and antisymmetrized, respectively.

2.3.2 Magnetic properties measurement

Magnetization measurements were performed using the vibrating sample magnetometer (VSM) module of the 14 T PPMS. In the VSM mode, the measurement is accomplished by oscillating the sample at a frequency between 10 and 60 Hz near a detection coil which synchronously detects the voltage induced. The magnetization resolution is less than 10^{-6} emu. In preparation for the measurement, a small amount of GE varnish was used to glue the sample plate on a low background quartz rod, which was then placed in a brass sample holder.

Two principal magnetic measurements were performed: magnetization as a function of

temperature and applied magnetic field. For the temperature dependence of magnetic susceptibility measurement, two cooling modes are used, zero-field cooled (ZFC) and field cooled (FC). In the ZFC mode, the sample is first cooled across the magnetic ordering temperature under zero field, then the magnetic field is switched on and data are taken while the sample is warmed from base to room temperature. In the FC mode, the sample is cooled with the field on, and data of the sample are recorded while warming. For the field dependence of magnetization measurements, the up to ± 14 T magnetic field is applied either along the sample plane or perpendicular to the sample plane.

The raw magnetization data is measured in the unit of emu, and then converted to Bohr magnetons per formula unit ($\mu_B/f.u.$) or emu/oe mol using the weight of the measured sample and the EDS-determined composition and corresponding formula mass. To eliminate the background effect from the sample holder, two sets of measurements are conducted on the empty sample holder with the same amount of grease and with the sample added, respectively. The final results are the magnetization of samples deducted by the magnetization of the background.

2.3.3 *Heat capacity measurement*

The heat capacity measurements were performed using the heat capacity option of the 9 T PPMS. The heat capacity puck with single crystal mounted is shown in Fig. 2.1. A pulse of heat is applied to the sample, then gradually lost to the environment through the supporting wires. The temperature of the sample is recorded throughout the process as it relaxes back to equilibrium. By fitting the recorded temperature to an exponential decay function, the relaxation time constant is determined at each temperature. To increase the accuracy, the relaxation process is repeated three times at each temperature. To obtain the sample heat capacity, the empty puck measured without the sample was subtracted from the data measured under identical conditions with the sample present.

In the sample preparation for the measurement, a sample with a mass at least of ~ 100 mg is needed to guarantee measurement quality. For one big sample, the sample surface

in contact with the platform needs to be flat to ensure good thermal contact with the calorimeter puck. For a few small pieces of samples, the orientation of the pieces needs to be aligned in the same orientation. Then Apiezon N grease is applied to cover the samples to further enhance the thermal contact between the sample and the puck. The PPMS chamber is pumped to a high vacuum during the measurement to minimize the thermal dissipation to surrounding gas.

Chapter 3

COLOSSAL NEGATIVE MAGNETO-RESISTIVITY AND CARRIER DENSITY DEPENDENCE OF ANOMALOUS HALL CONDUCTIVITY IN EuCd_2As_2

3.1 Abstract

The antiferromagnetic layered compound EuCd_2As_2 is widely considered a leading candidate of ideal Weyl semimetals, featuring a single pair of Weyl nodes in its field-induced ferromagnetic state. Nevertheless, this view was recently challenged by an optical spectroscopy study, which suggested that it is a magnetic semiconductor. In this study, we successfully synthesized highly insulating EuCd_2As_2 crystals with carrier density reaching as low as $2 \times 10^{15} \text{ cm}^{-3}$. The magnetotransport measurements revealed a progressive decrease of the anomalous Hall conductivity (AHC) by several orders of magnitude as the carrier density decreases. This behavior contradicts what is expected from the intrinsic AHC generated by the Weyl points, which is independent of carrier density as the Fermi level approaches the charge neutrality point. In contrast, the scaling relationship between AHC and longitudinal conductivity aligns with the characteristics of variable-range hopping insulators. Our results suggest that EuCd_2As_2 is a magnetic semiconductor rather than a topological Weyl semimetal.

3.2 Introduction

Weyl semimetals have attracted significant attention due to their intriguing electronic properties arising from the presence of Weyl points [3, 85]. Among them, ideal magnetic Weyl semimetals, characterized by a single pair of Weyl points close to the Fermi level, have long been sought for exploring the intrinsic topological effects associated with Weyl fermions free from interference by other trivial energy bands. In the past few years, the layered mag-

netic compound EuCd_2As_2 was proposed to be one of the leading candidates to realize an ideal magnetic Weyl semimetal in its field-induced ferromagnetic (FM) state [68, 78, 41]. EuCd_2As_2 has a hexagonal unit cell with space group $P\bar{3}m1$ [No.164; Fig. 3.1(a)]. At a temperature of 9.5 K, the localized magnetic moments of Eu develop a long-range magnetic order, with moments ferromagnetically coupled within layers and antiferromagnetically coupled between layers [77, 59, 66]. Nevertheless, the magnetic ground state appears to be highly tunable and depends on the growth method and the application of a small amount of hydrostatic pressure [30, 18, 72]. Application of a 2 T magnetic field saturates all magnetic moments along the c axis at low temperature, stabilizing a field-induced FM state. Previous density functional theory (DFT) calculations suggested that Cd s and As p orbitals are inverted near the Γ point in the energy bands of EuCd_2As_2 [26, 59], leading to an antiferromagnetic (AFM) topological insulator. Once the moments are fully saturated along the c axis in the FM state, the Zeeman splitting lifts the band degeneracy and gives rise to a single pair of Weyl points [78, 41, 68].

In previous works, a high magnetic field quantum oscillation study revealed a small Fermi surface with a light effective mass in the field-induced FM state of EuCd_2As_2 [68]; a Hall resistivity study presented a large anomalous Hall conductivity at low temperatures presumably related to the topological state of EuCd_2As_2 [84, 10, 62, 68], and angle-resolved photoemission spectroscopy experiments observed the quasilinear dispersion of the valence band in the AFM state and the band degeneracy splitting at a temperature right above the Néel temperature due to the existence of strong spin fluctuations [79, 43, 41]. All of these observations seem to agree with the existence of the Weyl semimetal phase. Nevertheless, the direct observation of Weyl crossings of EuCd_2As_2 is not possible because all the samples synthesized so far are p type with a Fermi level below the valence band top. In contrast, a recent study employing optical conductivity and pump-probe photoemission suggested that EuCd_2As_2 is, in fact, a semiconductor with an electronic gap of 0.77 eV instead of a Weyl semimetal [63]. Furthermore, a systematic investigation on the DFT calculation of the materials family EuCd_2X_2 ($\text{X}=\text{P}, \text{As}, \text{Sb}, \text{Bi}$) revealed that the topological states of the

materials in this family are sensitive to the choice of functional and the value of Hubbard U ; hence, the conduction and valence bands might not even be inverted in EuCd_2As_2 [13].

A well-known prediction for a type-I Weyl semimetal is that the anomalous Hall conductivity (AHC) is solely determined by the distance between the Weyl nodes in the momentum space when the Fermi level is exactly at the Weyl crossings [86, 7]. Therefore, the AHC is expected to approach a finite and constant value as carrier density decreases to zero, which serves as direct evidence to distinguish Weyl semimetals from other trivial electronic states. In this work, we successfully synthesize EuCd_2As_2 single crystals with carrier density ranging from 10^{15} to 10^{16} cm^{-3} in the field-induced FM state and conducted a systematic study of the transport behaviors of these samples. We find that the temperature dependence of resistivity of all samples shows an insulating behavior and the resistivity dramatically decreases by several orders of magnitude as Eu moments are fully saturated by a c axis magnetic field. We find the AHC decreases by several orders of magnitude as the carrier density decreases, far below the value expected from previous DFT calculations that predicted a Weyl semimetal phase in this system. In contrast, the scaling analysis shows good agreement with the AHC in the variable-range hopping regime. The optical transmittance measurement further confirms a finite optical gap of 0.74 eV, consistent with previous studies. An *ab initio* calculation to compute the Hubbard U parameter of EuCd_2As_2 is also performed in this work, revealing that previous calculations significantly underestimate the value of Hubbard U , highlighting the importance of correlation when determining the topological phase of magnetic semiconductors.

3.3 Results

3.3.1 Transport and magnetic characterization

EuCd_2As_2 single crystals were synthesized via the Sn flux method [30]. We discovered that the residual carrier density of crystals is sensitive to the Sn flux ratio. The stoichiometric Eu pieces and Cd and As shots are mixed with 10 to 25 times atomic mass Sn shots as

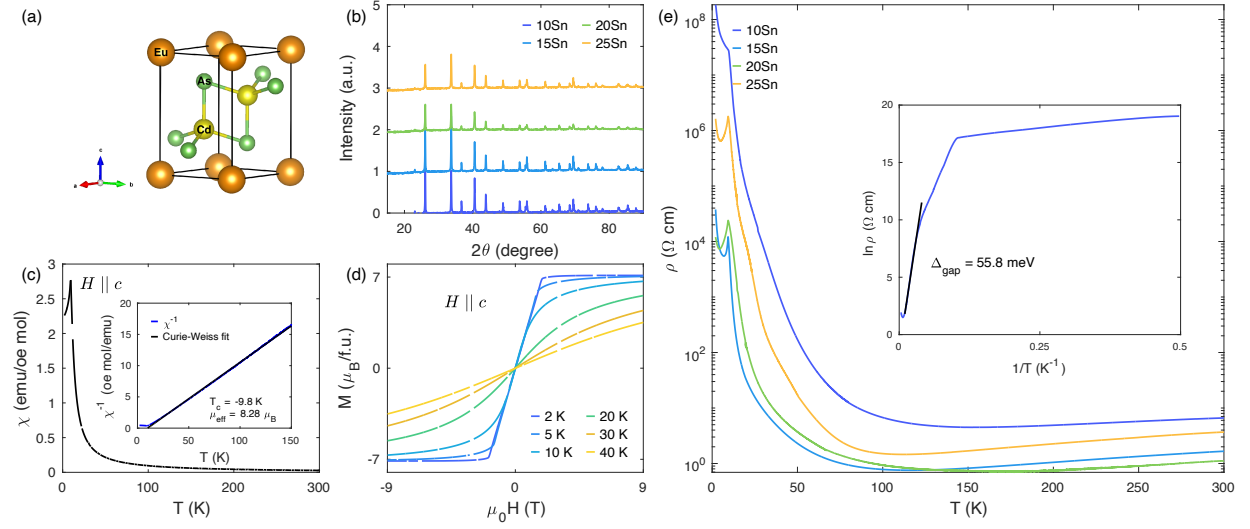


Figure 3.1: **Transport and magnetic characterizations of EuCd₂As₂.** (a) Crystal structure of EuCd₂As₂ with the *P*-3*m*1 space group. (b) Powder x-ray diffraction of EuCd₂As₂ at room temperature. (c) Temperature dependence of magnetic susceptibility χ with 0.1 T magnetic field applied along the *c* axis. The inset shows the inverse susceptibility versus temperature and the Curie-Weiss fitting. (d) Magnetization versus field at different temperatures. The saturated magnetization is $\sim 7\mu_B$ per Eu atom at the base temperature 2 K. (e) Temperature dependence of the electrical resistivity $\rho(T)$ between 2 and 300 K. The inset shows $\ln \rho$ versus the inverse of temperature $1/T$ of the sample from 10Sn. The transport activation gap $\Delta_{gap} = 55.8$ meV is obtained by fitting $\ln \rho$ versus $1/T$ in the temperature range of 30-100 K.

starting materials, which yielded EuCd₂As₂ crystals with the hole carrier density spanning from 10^{15} to 10^{16} cm⁻³. While it is unclear how the Sn flux ratio alters the defect density, the wide range of carrier density offers us a convenient knob to tune the transport properties of EuCd₂As₂.

Figure 3.1(b) shows the powder x-ray diffraction of EuCd₂As₂ samples from batches using 10, 15, 20, and 25 Sn flux ratios (labeled 10Sn, 15Sn, 20Sn, and 25Sn). All diffraction patterns and extracted lattice constants are identical to the previous report [30], indicating that the change in the Sn flux ratio has a minimal effect on structural properties. Similarly, the magnetic properties of samples from different batches show no measurable difference

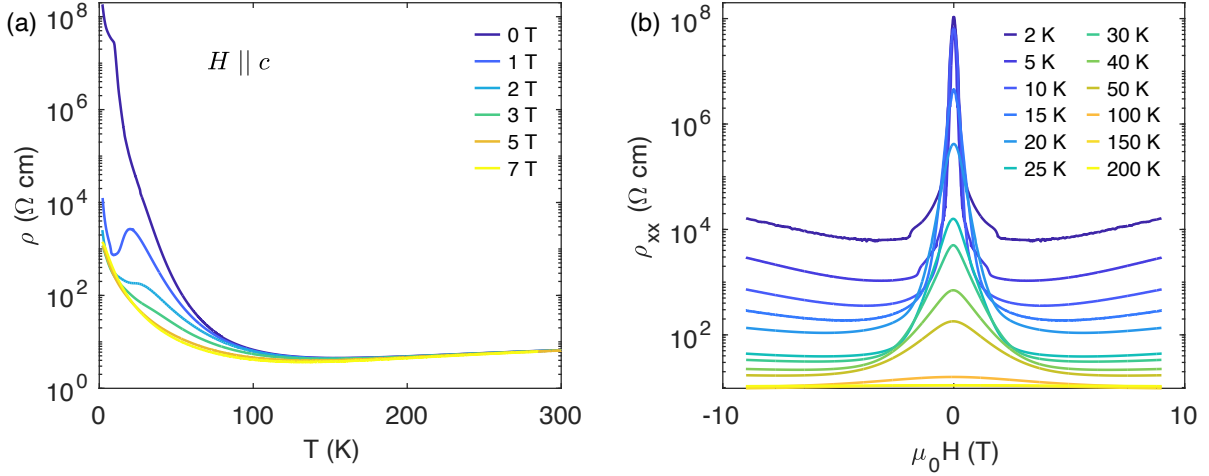


Figure 3.2: **Colossal magnetoresistance of EuCd_2As_2 .** (a) Temperature dependence of resistivity $\rho(T)$ under different magnetic fields applied along the c axis. (b) Resistivity ρ_{xx} versus magnetic field at temperatures between 2 and 200 K.

and agree with previous studies [41]. The representative data of a sample from 10Sn are summarized in Fig. 3.1. As shown in Fig. 3.1(c), the temperature dependence of c axis magnetic susceptibility χ follows the Curie-Weiss temperature dependence, with a kink at 9.5 K indicating the onset of AFM order. Fitting the high-temperature susceptibility with the Curie-Weiss law yields a Weiss temperature of -9.8 K and an effective magnetic moment of $8.28\mu_B$. Figure 3.1(d) shows the magnetization $\mathbf{M}$ as a function of the field measured at different temperatures. At the base temperature of 2 K, $\mathbf{M}$ increases linearly before reaching the saturated value of $\sim 7\mu_B$ per Eu atom, in agreement with the magnetic moment of a divalent Eu with half-filled $4f$ orbitals.

Unlike the structural and magnetic properties, the electrical transport of EuCd_2As_2 is very sensitive to the Sn flux ratio. Figure 3.1(e) shows the temperature dependence of in-plane resistivity $\rho(T)$ for samples selected from different batches. All samples show an insulating behavior below 100 K, where resistivity increases by 3 to 7 orders of magnitude as the temperature decreases. This is very different from the semimetal behavior reported in

previous studies [68, 84, 10], with the exception of the most recent works [63, 80]. The kink in resistivity at 9.5 K is consistent with the AFM transition determined from the magnetic susceptibility. Below 9.5 K the resistivity of the sample from 10Sn continuously increases, while samples from 15Sn, 20Sn, and 25Sn initially decrease before increasing again as the temperature cools further down to 2 K. The inset in Fig. 3.1(e) shows $\ln \rho$ versus $1/T$ of the sample from 10Sn. The black solid line denotes the linear fit of $\ln \rho$ versus $1/T$ in the temperature range between 30 and 100 K, which allows us to extract the activation energy $\Delta_{gap} \sim 55.8$ meV using the relationship $\ln \rho = \frac{\Delta_{gap}}{2K_B T}$. We note that in a disordered semiconductor the activation energy extracted from resistivity is often related to the energy of impurity levels, which is much lower than the band gap.

3.3.2 Colossal magnetoresistance

The insulating resistivity of EuCd_2As_2 can be strongly modulated by the application of magnetic fields. The magnetoresistance (MR) of the sample from 10Sn is summarized in Fig. 3.2. The results are qualitatively similar to samples from other batches. Figure 3.2(a) shows the temperature dependence of the resistivity $\rho(T)$ under different magnetic fields from 0 to 7 T. The exponential increase of resistivity is suppressed by the external magnetic field, resulting in a dramatic decrease of resistivity by almost 5 orders of magnitude. As the magnetic field increases, the kink at the Néel temperature is smeared, and a bump like feature at ~ 20 K emerges for 1 T magnetic field and then shifts to the higher temperatures. For temperatures higher than 100 K, where resistivity no longer follows the thermally activated temperature dependence, the magnetoresistance becomes negligible.

Figure 3.2(b) shows the magneto-resistivity ρ_{xx} as a function of field at a fixed temperature between 2 and 200 K. It can be seen that at low temperatures resistivity abruptly drops by several orders of magnitude as magnetic field increases, followed by a kink at the saturation field, above which the resistivity increases again when magnetic moments are fully aligned with the field. As temperature increases, the drop in resistivity becomes more gradual and the kink is smeared out, which is highly correlated with the field dependence

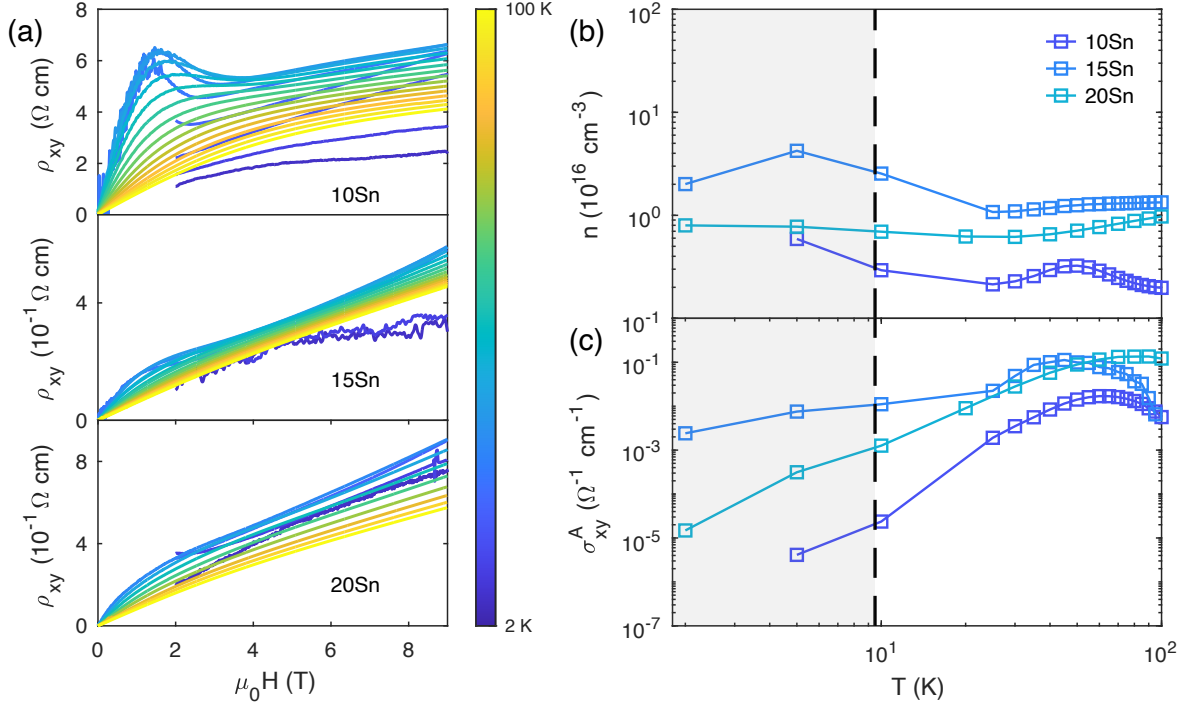


Figure 3.3: **The temperature dependence of the carrier density and anomalous Hall conductivity of EuCd_2As_2 .** (a) Hall resistivity ρ_{xy} versus magnetic field for samples from 10Sn, 15Sn, and 20Sn at temperatures between 2 and 100 K. (b) Carrier density n and (c) anomalous Hall conductivity σ_{xy}^A versus temperature obtained by fitting from ρ_{xy} in (a) (see text for details of the fitting). Vertical lines mark antiferromagnetic transition temperature $T_N = 9.5 \text{ K}$.

of magnetization at higher temperatures [Fig. 3.1(d)]. This was also reported in a recent work [80], and is consistent with the decrease in band gap induced by the saturation of magnetization reported in Ref. [63]. $\text{MR} = 100\% \times [\rho_{xx}(9\text{T}) - \rho_{xx}(0\text{T})]/\rho_{xx}(0\text{T})$ reaches -90% at $T < 50 \text{ K}$. Such a colossal negative MR was also observed in several Eu-based semiconducting materials, a property that might be of interest for spintronics applications [60, 76].

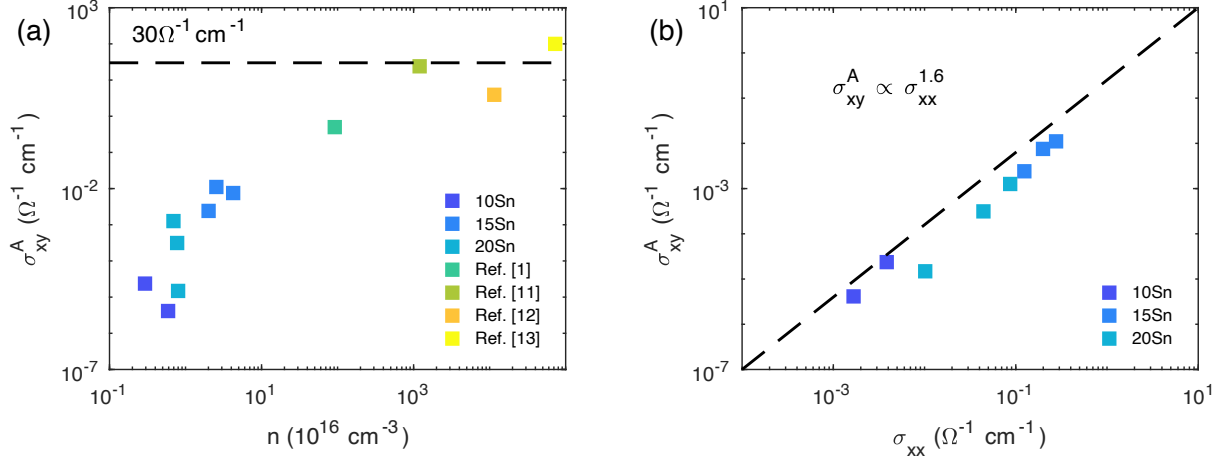


Figure 3.4: **Carrier density dependence and the scaling relationship of the anomalous Hall effect in EuCd_2As_2 .** (a) Anomalous Hall conductivity σ_{xy}^A versus carrier density n measured from samples 10Sn, 15Sn, and 20Sn and semi metallic EuCd_2As_2 reported in previous works [68, 84, 10, 62]. The expected value of σ_{xy}^A (black dashed line) is for an ideal Weyl semimetal with only one pair of Weyl nodes separated by 0.52 nm^{-1} [68]. (b) Anomalous Hall conductivity σ_{xy}^A versus longitudinal conductivity σ_{xx} in log-log scale. The dashed line marks the power law $\sigma_{xy}^A \propto \sigma_{xx}^{1.6}$.

3.3.3 Anomalous Hall effect

The Hall resistivity ρ_{xy} is shown in Fig. 3.3(a) for samples from 10Sn, 15Sn, and 20Sn. Similar to the longitudinal resistivity ρ_{xx} , ρ_{xy} is strongly affected by the magnetism. As temperature decreases, the field dependence of ρ_{xy} becomes highly nonlinear and resembles that of the magnetization, a clear sign of the anomalous Hall effect (AHE). For temperatures below 10 K, ρ_{xx} becomes too large (approximately $\text{M}\Omega\text{cm}$) for magnetic fields below 2 T, so antisymmetrization becomes too difficult to extract ρ_{xy} , and hence, only data above 2 T are presented. To quantitatively understand the temperature and carrier density dependence of the AHE, we extract the anomalous Hall resistivity ρ_{xy}^A and the ordinary Hall effect $R_0\mu_0H$ from the linear fit of ρ_{xy} in the field range of 3 to 9 T using the expression $\rho_{xy} = R_0\mu_0H + \rho_{xy}^A$. The ordinary Hall coefficient R_0 allows us to calculate the carrier density n . The anomalous

Hall resistivity ρ_{xy}^A is converted to the AHC σ_{xy}^A via the expression $\sigma_{xy}^A = \rho_{xy}^A / (\rho_{xy}^A{}^2 + \rho_{xx}^2)$, where the values of ρ_{xx} are taken at 9 T, at which the magnetic moments are most aligned along the c axis. Using ρ_{xx} at different fields results in minor changes in the absolute values of the AHC but does not change its dependence on carrier density or longitudinal conductivity. Figures 3.3(b) and 3.3(c) show the temperature dependence of the carrier density n and AHC σ_{xy}^A between 2 and 100 K. Intriguingly, the carrier densities of all three samples show a nonmonotonic temperature dependence, which is in contrast to the thermally activated behavior where carrier density decreases monotonically with temperature. This is likely due to the interplay between the thermal activation of carriers and the change in magnetic configurations at elevated temperatures due to moment fluctuations. Regardless of the origin, the carrier density and the AHC measured across three samples show a substantial variation for $T < T_N$, providing us an opportunity to systematically investigate the carrier density dependence of AHC of EuCd_2As_2 in the field-induced FM state.

In a Weyl semimetal, the Weyl nodes are the source and sink of Berry curvature flux in the momentum space. In an ideal time-reversal symmetry-breaking Weyl semimetal, the single pair of Weyl nodes forms a Berry curvature dipole and gives rise to an intrinsic AHE solely depending on the separation of the Weyl nodes, $\sigma_{xy}^A = (e^2/2\pi h \Delta k)$. This σ_{xy}^A is topological and independent of the Fermi level position; hence, we should expect a constant AHC even if the carrier density approaches zero. Here, we compile the data of σ_{xy}^A and n extracted below 10 K in the field range of 3–9 T when EuCd_2As_2 is in the field-induced FM state from Figs. 3.3(b) and 3.3(c) and plot the result in Fig. 3.4(a) on a log-log scale. In addition to the data collected in this work (blue squares), the AHC measured from higher carrier density samples in previous works are also included [68, 84, 10, 62]. The horizontal black dashed line indicates the value of the intrinsic AHC, $30 \Omega^{-1}\text{cm}^{-1}$, from a single pair of Weyl points separated by 0.52 nm^{-1} in ferromagnetic EuCd_2As_2 predicted by previous DFT calculations [68, 78]. As shown in Fig. 3.4(a), the observed σ_{xy}^A has a strong dependence on carrier density n and decreases dramatically as n decreases. As the carrier density approaches $\sim 10^{15}\text{cm}^{-3}$, the AHC reaches a value that is 5 orders of magnitude smaller than the AHC expected for

an ideal Weyl semimetal.

To gain insight into the underlying mechanism of the AHE in EuCd_2As_2 , σ_{xy}^A versus σ_{xx} [$\sigma_{xx} = \rho_{xx}/(\rho_{xy}^2 + \rho_{xx}^2)$] is plotted in Fig. 3.4(b). Note that we use the values of resistivity tensors at $\mu_0 H = 9$ T for all conversions since both longitudinal and Hall resistivities depend strongly on the magnetic fields. As shown in Fig. 3.4(b), all longitudinal conductivities σ_{xx} fall below the value of $1 \text{ } \Omega^{-1}\text{cm}^{-1}$, which belongs to the insulating regime, where conduction and the AHE are governed by the variable-range hopping or activated hopping process. Moreover, the AHC versus longitudinal conductivity can be well fitted by a power law relation, $\sigma_{xy}^A \propto \sigma_{xx}^\alpha$, with $\alpha = 1.6$ (black dashed line). This is consistent with previous experimental results and theoretical models of the AHE in the insulating regime [48]. Thus, the observed AHC is fully consistent with EuCd_2As_2 being a magnetic semiconductor.

3.3.4 Optical transmittance

As a final confirmation, the optical transmittance spectrum of sample 10Sn was measured using the Fourier transform infrared spectroscopy (FTIR) technique at room temperature. As shown in Fig. 3.5, EuCd_2As_2 remains transparent up to a wave number of 6000 cm^{-1} (equivalent to ~ 0.74 eV), followed by a sharp drop in transmittance at higher wave numbers. This is consistent with the presence of an ~ 0.74 eV band gap, which is in agreement with the optical study reported in Ref. [63].

3.4 Discussion

The comprehensive anomalous Hall effect and optical transmittance measurements presented above clearly support the conclusion that EuCd_2As_2 is a magnetic semiconductor. One remaining question is why most of the previous first-principles calculations identified ferromagnetic EuCd_2As_2 as a Weyl semimetal. We note that recent calculations by Cuono *et al.* [13] showed that electron correlation effects can significantly alter the electronic and topological behaviors of EuCd_2As_2 . In particular, within the standard generalized gradient approximation (GGA) functional, AFM EuCd_2As_2 can exhibit a vanishing electronic band

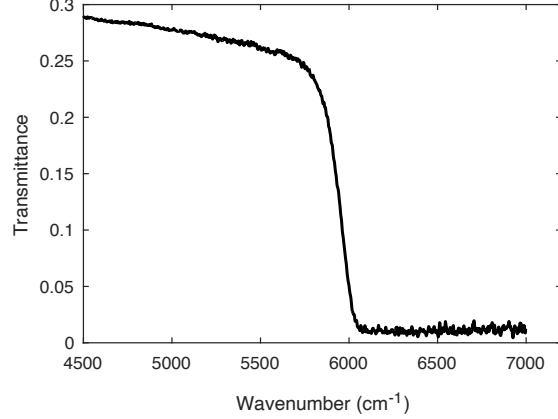


Figure 3.5: **Transmittance spectrum of EuCd_2As_2 .** Transmittance versus incident light wave number of sample 10Sn measured by FTIR at room temperature. The incident lights with a wave number larger than 6000 cm^{-1} are fully absorbed, consistent with a band gap of 0.74 eV.

gap and nontrivial band topology only when Eu's on-site Hubbard repulsion $\mathbf{U}$ is less than $\sim 6 \text{ eV}$ [13]. Previous theoretical and experimental studies considered $\mathbf{U}$ values in the range of $\sim 3\text{-}5 \text{ eV}$ [26, 43, 41, 35, 59, 92], which could tend to lead to the conclusion that EuCd_2As_2 is topologically nontrivial. Since the Hubbard repulsion plays a critical role, it is important to more accurately estimate the $\mathbf{U}$ value.

Here, we employ the linear-response ansatz by Cococcioni and de Gironcoli to determine the Hubbard $\mathbf{U}$ from first principles [12]. In this approach, the $\mathbf{U}$ value is derived by measuring the change in the Eu f orbital occupation as a response to external perturbation of an on-site potential. Specifically, after an initial DFT ground state calculation, the self-consistent response χ and non-self-consistent response χ_0 are constructed by computing the orbital occupation change with and without DFT charge density updates, respectively. Afterward, $\mathbf{U}$ is determined by subtracting the inverse of the self-consistent response from the non-self-consistent one: $\mathbf{U} = \chi^{-1} - \chi_0^{-1}$. Figure 3.6(a) shows the corresponding calculation on a five-atom EuCd_2As_2 unit cell in the external potential range -0.20 to 0.20 eV . When the perturbation is small, both response functions show a linear trend, so χ^{-1} and χ_0^{-1} can be

obtained directly from the linear slopes. With a larger perturbation, the response functions may exhibit a nonlinear behavior. In this case, the linear response approach can still be applied by using a nonlinear fit and then taking the derivative near the zero potential [36]. The result is essentially equivalent to that of a linear fit in a smaller perturbation regime.

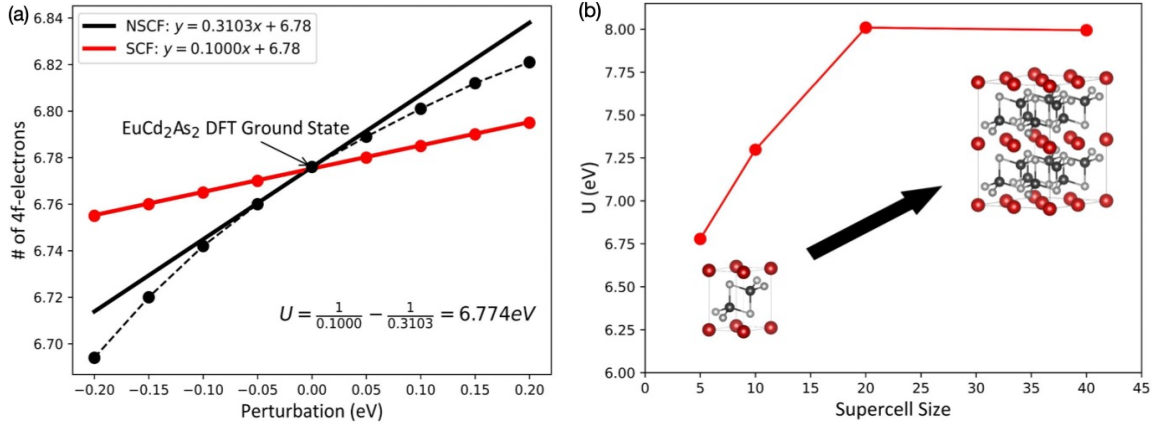


Figure 3.6: **First-principles linear-response calculations for the Hubbard U of Eu atoms in EuCd_2As_2 .** (a) Fitted charge self-consistent (solid red line) and non-self-consistent (solid black line) linear response functions for a 5-atom EuCd_2As_2 unit cell. The inverse slopes of the response functions in the linear regime can be utilized to determine the U value. (b) Convergence test of the calculated Hubbard U parameter with respect to the supercell size. The results converge to $U \sim 8$ eV in a 40-atom EuCd_2As_2 unit cell. Such a strong $U \sim 8$ eV would lead to a finite energy gap and suppression of the topological behavior in EuCd_2As_2 .

As seen in Fig. 3.6(a), the Hubbard U for a five-atom EuCd_2As_2 unit cell is calculated to be 6.77 eV. Since the U value is largely affected by charge screening, it is necessary to examine the convergence in larger DFT supercells. We performed corresponding linear-response U calculations up to a unit cell of 40 atoms, where the U value is found to converge to ~ 8 eV, as shown in Fig. 3.6(b). We also performed the calculations using different DFT ground states, including paramagnetic (PM) and AFM, and found that the resulting U values only differ by less than ~ 0.1 eV. In this regard, magnetism has only a small effect on the resulting U value of ~ 8 eV, which remains substantial in both the PM and AFM states.

Unlike the empirical values of $U \sim 3\text{--}5$ eV considered in the literatures [41, 26, 43, 35, 59], the strong Hubbard repulsion $U \sim 8$ eV discovered in our *ab initio* calculations thereby suggests a finite energy gap and only trivial band topology in EuCd_2As_2 . We also note that a meta-GGA or hybrid DFT functional would lead to an ever larger energy gap that further suppresses the topological behavior [13]. Therefore, in accord with our carrier-control transport experiments, the theoretical results also indicate that EuCd_2As_2 is likely to be a topologically trivial magnetic semiconductor.

3.5 Conclusion

Our study revealed that the carrier density dependence of the anomalous Hall conductivity in EuCd_2As_2 does not align with the expected behavior of an ideal Weyl semimetal. Instead, the scaling relationship between the AHC and longitudinal conductivity is in good agreement with the characteristics of insulating hopping transport. These observations, coupled with the substantial electronic gap revealed in the optical transmittance measurement, unambiguously establish that EuCd_2As_2 is a magnetic semiconductor instead of a Weyl semimetal. We further performed *ab initio* calculations and discovered that the underestimation of Hubbard U could play a key role in previous misidentification of the topological phase in this material system. Despite being topologically trivial, the resistivity of EuCd_2As_2 is extremely sensitive to the magnetic configuration of Eu-ordered moments, leading to a colossal magnetoresistance effect, indicative of a strong coupling between the electronic band gap and the magnetic orders. This unusual property may be useful for applications in spintronics and magneto-optoelectronics.

3.6 Appendix

3.6.1 High-field magnetoresistance

High-field magnetoresistance measurements were conducted under up to 35 T magnetic field at the National High Field Magnetic National Laboratory (NHMFL) in Tallahassee, Florida.

Figure 3.7 shows ρ_{xx} measured on a sample from 10Sn EuCd₂As₂ with magnetic field along the c axis at 1.4 K. The magnetoresistivity presents a quadratic increase as the field increases. No Shubnikov-de Haas quantum oscillations appear until 35 T.

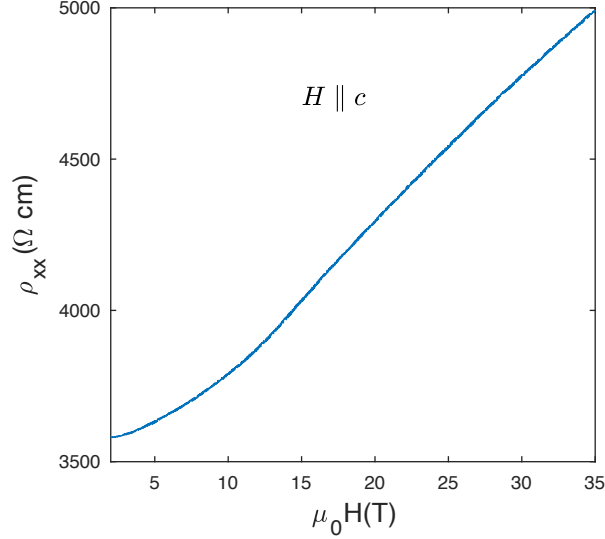


Figure 3.7: **High-field magnetoresistance.** The magnetoresistivity ρ_{xx} versus along the c axis magnetic field $\mu_0 H$ ranges from 2 to 35 T of the sample from 10Sn EuCd₂As₂.

3.6.2 Colossal magnetoresistance of samples from 15Sn and 20Sn

The magnetoresistivity ρ_{xx} as a function of the field was also conducted on samples from 15Sn and 20Sn. Figure 3.8 shows ρ_{xx} versus magnetic field at fixed temperatures between 2 and 150 K. The behaviors are qualitatively the same as those of the represented data of the sample from 10Sn shown in the main text.

3.6.3 Angle-resolved photoemission spectroscopy measurement on $\text{Eu}(\text{Cd}_{1-x}\text{In}_x)_2\text{As}_2$ ($x=5\%$)

To tune the Fermi level to the conduction band, we doped Lanthanum in EuCd₂As₂ to introduce electrons. Nominally, 5% Lanthanum was doped into Europium sites. Fig. 3.9 shows the results of ARPES measurement on 5% Indium doped crystals. Unfortunately, we did

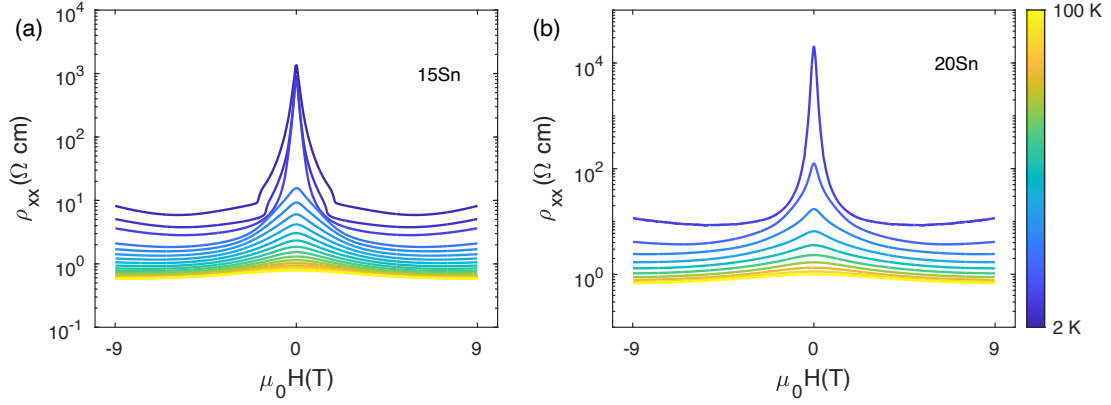


Figure 3.8: **Colossal magnetoresistance of samples from 15Sn and 20Sn.** Temperature dependence of longitudinal resistivity ρ_{xx} versus ± 9 T magnetic field along the c axis at temperatures between 2 and 150 K for samples from (a) 15Sn and (b) 20Sn.

not observe the conduction band minimum, neither through dosing K nor Rb. Even though, we observed the significant electronic band of approximately 0.65 eV in $\text{Eu}(\text{Cd}_{1-x}\text{In}_x)_2\text{As}_2$ ($x=5\%$) (the Fermi surface might be pinned by some impurity levels just below conduction band minimum), which further confirmed the gapped semiconductor nature of EuCd_2As_2 .

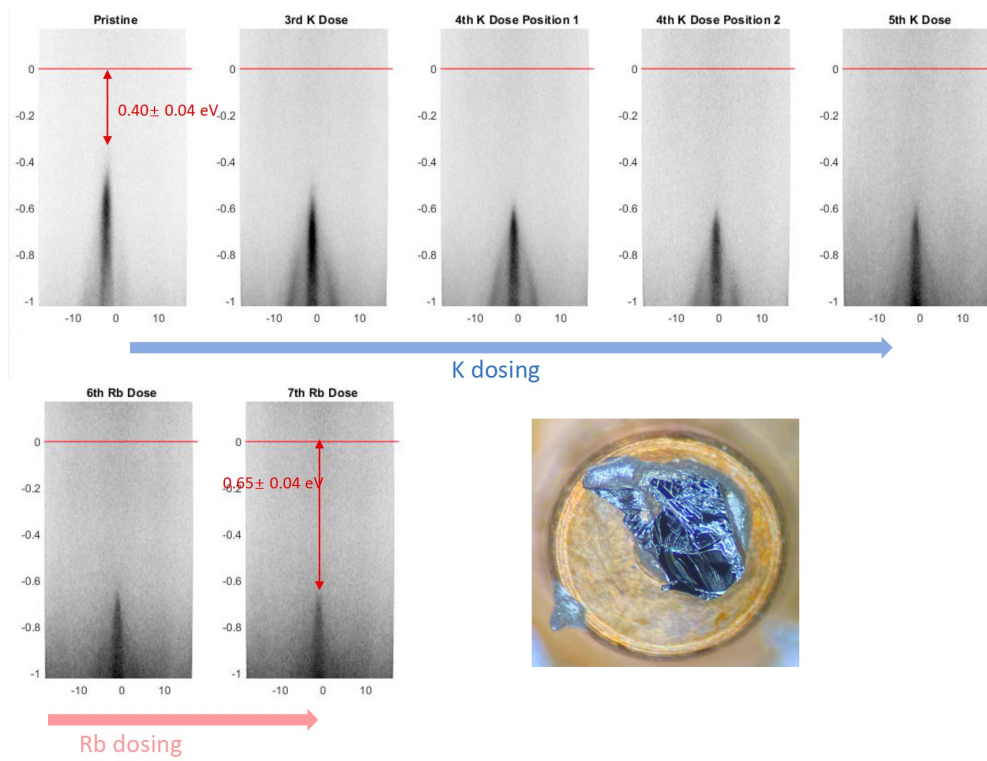


Figure 3.9: **ARPES results on $\text{Eu}(\text{Cd}_{1-x}\text{In}_x)_2\text{As}_2$ ($x=5\%$)**. Samples for ARPES measurement and the electronic band structure detected on the pristine, in-situ K dosing, and Rb dosing samples surface (credits to my collaborator, Shanmei He, from the Lawrence Berkeley laboratory).

Chapter 4

REVEALING TOPOLOGY PROPERTY OF ACd_2Pn_2 ($A =$ Eu, Sr ; $Pn = As, Sb$)

4.1 Abstract

The antiferromagnetic layered compound $EuCd_2Pn_2$ ($Pn = As, Sb$) has been regarded as a potential platform to realize magnetic Weyl semimetal in its field-induced ferromagnetic phase. However, $EuCd_2As_2$ was recently found as a trivial magnetic semiconductor, and the topological property of $EuCd_2Sb_2$ remains ambiguous. It has also been predicted that substituting As with Sb can turn $SrCd_2As_2$, the non-magnetic analog of $EuCd_2As_2$, into a Dirac semimetal. In this study, we synthesized single crystals of ACd_2Pn_2 ($A = Eu, Sr$; $Pn = As, Sb$) and conducted magneto-transport and optical measurements. The Hall effect revealed carrier density of $1.15 \times 10^{18} \text{ cm}^{-3}$ and $2.20 \times 10^{18} \text{ cm}^{-3}$, and the quantum effective mass of $0.20m_e$ and $0.26m_e$ for carriers in $SrCd_2Sb_2$ and $EuCd_2Sb_2$, respectively. Fourier transform infrared spectroscopy identified the electronic band gaps in four compounds, ACd_2Pn_2 and determined the plasma edges in ACd_2Sb_2 ($A = Eu, Sr$), which is also consistent with the measured values of carrier density and effective mass. Our results suggest that ACd_2Pn_2 are gapped semiconductors and the discrepancy between DFT calculation and experimental results is from inaccurate choice of functional.

4.2 Introduction

Topological semimetals have attracted significant attention due to their extraordinary electronic behaviors from the topology-protected electronic band structures near the Fermi level. In the past few years, the magnetic layered material $EuCd_2As_2$ was proposed to be a platform to realize several different topological phases via tuning its magnetic order [68, 78, 41, 69].

EuCd_2As_2 has the CaAl_2Si_2 -type crystal structure of space group, $P-3m1$ [No. 164], with the hexagonal Cd_2As_2 layers stacked and separated by the trigonal Eu layers. At a temperature of 9.5 K, the localized magnetic moments of Eu atoms develop a long-range magnetic order, with moments ferromagnetically coupled within layers and antiferromagnetically coupled between layers [90, 69, 58, 65]. Application of a 2 T magnetic field saturates all magnetic moments along the c axis at low temperature, stabilizing a field-induced FM state in EuCd_2As_2 . Previous *ab initio* calculations suggested that this field-induced AFM to FM transition also leads a transition from a small gap topological insulator to a Weyl semimetal with only one pair of Weyl points free from interference by other trivial energy bands [68, 78, 41].

While the earlier studies of photoemission and magneto-transport all claimed that the experimental results are consistent with the prediction of Weyl semimetal phase, more recent studies on lower carrier density samples revealed that EuCd_2As_2 is a magnetic semiconductor with an electronic gap of 0.77 eV [64, 13, 67]. One reason for such a large discrepancy is that the EuCd_2As_2 samples used in earlier studies are all hole-doped. Therefore both transport and photoemission could only probe electronic states well below the top of the valence bands and relied heavily on the comparison of the DFT calculations, which greatly underestimate the bandgap in EuCd_2As_2 . In a very recent DFT calculation, it was found that there are two possible origins the underestimation of the bandgap in EuCd_2As_2 , the choice of DFT functional and the size of onsite repulsion Hubbard potential U of Eu 4f electrons. Since DFT calculation is widely used in the prediction and design of topological materials, it is important to elucidate the origin of the underestimation of the bandgap (or overestimation of the topological region) in EuCd_2As_2 .

A promising way to address this question is a comparative study of EuCd_2Pn_2 and SrCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$). EuCd_2Sb_2 is the sister compound of EuCd_2As_2 with identical crystal structure and antiferromagnetic ground state. It was also predicted to be a Weyl semimetal in the field-induced FM phase, with five pairs of type-II Weyl crossings[71], yet the photoemission and transport experiments reported so far were also performed on heavily hole-doped samples[71, 49, 53]. SrCd_2Pn_2 is a non-magnetic analog of EuCd_2Pn_2 . It has the

same crystal structure as EuCd_2Pn_2 but without Eu ions, hence it is the ideal platform to separate the effect of 4f electrons on band structures. While most previous studies focused on its potential for thermoelectric applications[54, 29, 44, 11], a recent DFT calculation using the same functional that predicted EuCd_2As_2 to be a Weyl semimetal suggested that SrCd_2As_2 is close to a topological phase transition[14]. The calculation suggested that a negative hydrostatic pressure of 2 GPa reduces the 0.1 eV band gap, resulting in the formation of a pair of Dirac points along the Γ -A direction. It was also argued that replacing As with Sb induces a negative chemical pressure because the larger Sb ionic radius increases the nearest neighbor Cd-Pn distance. Therefore, if the prediction made by the DFT calculation is accurate, SrCd_2Sb_2 is a natural candidate to realize the Dirac semimetal phase.

In this work, we synthesized high-quality single crystals of SrCd_2As_2 , SrCd_2Sb_2 and EuCd_2Sb_2 using the flux method and conducted measurements of the electrical transport and optical properties of these samples. We found that the resistivity of SrCd_2As_2 follows a thermal activation behavior, with a bandgap of ~ 0.6 eV. The resistivity of both EuCd_2Sb_2 and SrCd_2Sb_2 shows metallic behavior, with a Hall carrier density $\sim 1 - 2 \times 10^{18} \text{cm}^{-3}$. They also exhibited pronounced Shubnikov-de Haas oscillations when an external magnetic field was applied. In the Fourier Transform Infrared spectroscopy (FTIR) measurement, we observed an electronic gap of ~ 0.86 eV, ~ 0.48 eV, and ~ 0.54 eV for SrCd_2As_2 , EuCd_2Sb_2 , and SrCd_2Sb_2 , respectively. Moreover, a plasma edge can also be observed in the optical transmittance of EuCd_2Sb_2 and SrCd_2Sb_2 , with plasma frequencies consistent with the carrier density and effective mass extracted from the transport measurements. Our study revealed that both EuCd_2Sb_2 and SrCd_2Sb_2 are doped semiconductors rather than semimetals. We also found that previous DFT calculations underestimated the band gap of all the members of EuCd_2Pn_2 and SrCd_2Pn_2 families, regardless of the presence of Eu ions. Consequently, we conclude that the choice of the functional is the main source of error in the prediction of topological properties of these materials.

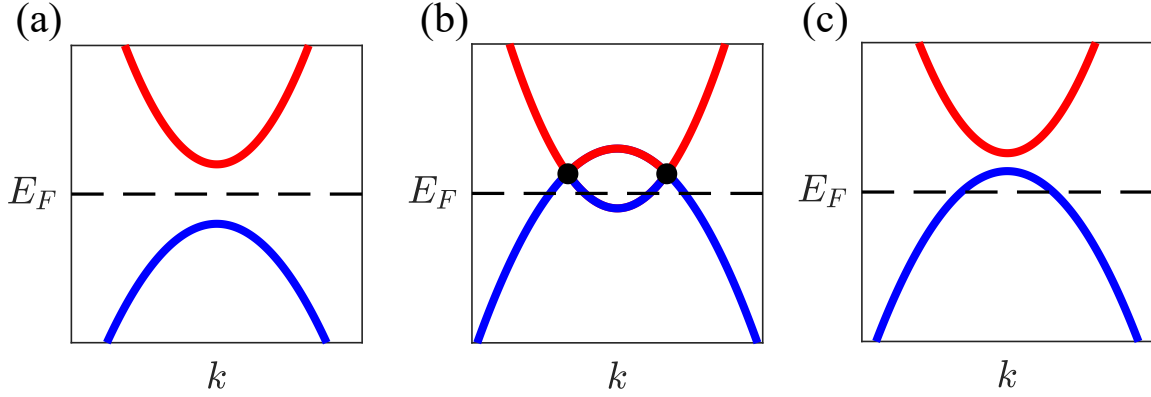


Figure 4.1: **Two scenarios of band evolution as Sb replaces As in ACd_2Pn_2 ($\text{A} = \text{Eu}, \text{Sr}$; $\text{Pn} = \text{As}, \text{Sb}$).** A schematic plot of (a) the band structure of ACd_2As_2 ($\text{A} = \text{Eu}, \text{Sr}$). (b) the first possible band structure of ACd_2Sb_2 ($\text{A} = \text{Eu}, \text{Sr}$) and (b) the second possible band structure of ACd_2Sb_2 ($\text{A} = \text{Eu}, \text{Sr}$).

4.3 Results

4.3.1 Transport and magnetic characterization

Figure 4.2(a) shows the powder x-ray diffraction of ACd_2Pn_2 ($\text{A} = \text{Sr}, \text{Eu}$; $\text{Pn} = \text{As}, \text{Sb}$) measured at room temperature. The extracted lattice constants are shown in the Appendix. All extracted lattice constants are in agreement with the previous reports. Similarly, the magnetic properties of EuCd_2Sb_2 are also consistent with previous studies [42]. Figure 4.2(b) shows the magnetization $\mathbf{M}$ as a function of the magnetic field measured at different temperatures. At the base temperature of 2 K, $\mathbf{M}$ increases linearly with c -axis magnetic field before reaching the saturation value of $\sim 7\mu_B$ per Eu atom, in agreement with the magnetic moment of a divalent Eu with half-filled $4f$ orbitals.

Figure 4.2(c) shows the temperature dependence of in-plane resistivity $\rho(T)$ for EuCd_2As_2 and SrCd_2As_2 . The data of EuCd_2As_2 is reproduced from the data presented in the previous chapter. As discussed in the previous chapter, EuCd_2As_2 is a magnetic semiconductor with a bandgap of 0.7 eV, yet SrCd_2As_2 is even more insulating than EuCd_2As_2 . The resistivity of

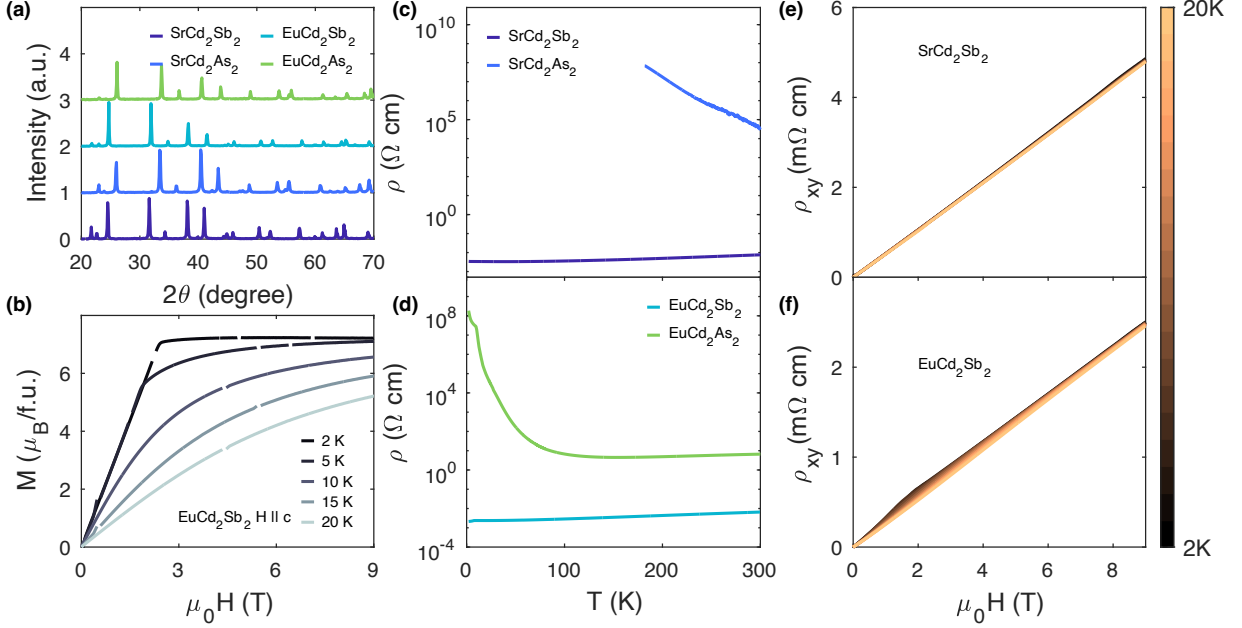


Figure 4.2: **Transport and magnetic characterizations of ACd_2Pn_2 (A = Sr, Eu; Pn = As, Sb).** (a) Powder x-ray diffraction of $SrCd_2Sb_2$, $SrCd_2As_2$, $EuCd_2Sb_2$, $EuCd_2As_2$. (b) Magnetization M versus field for $EuCd_2Sb_2$ at different temperatures. The magnetic field is applied along the c axis. The saturated magnetization is $\sim 7\mu_B$ per formula unit at the base temperature 2 K. (c) Temperature dependence of the electrical resistivity $\rho(T)$ between 2 and 300 K for $SrCd_2Sb_2$, and 180 and 300 K for $SrCd_2As_2$. (d) The temperature dependence of electrical resistivity $\rho(T)$ between 2 and 300 K for $EuCd_2Sb_2$ and $EuCd_2As_2$. Hall resistivity ρ_{xy} versus magnetic field for (e) $SrCd_2Sb_2$ and (f) $EuCd_2Sb_2$ at temperatures between 2 and 20 K.

$SrCd_2As_2$ is $\sim 10^5$ M Ω cm at room temperature and exponentially increases as temperature decreases. The resistivity below 180 K is above the limit of measurement electronics. Figure 4.2(d) shows the $\rho(T)$ for $SrCd_2Sb_2$ and $EuCd_2Sb_2$. The resistivity of both compounds decreases with temperature, showing a typical metallic behavior. In $\rho(T)$ of $EuCd_2Sb_2$, resistivity first shows an upturn while temperature approaches Néel temperature at 7.2 K, then drops as the temperature cools further down to 2 K.

Figure 4.2(e) and (f) show the Hall resistivity ρ_{xy} of $SrCd_2Sb_2$ and $EuCd_2Sb_2$ as a function of the magnetic field measured at the various temperatures between 2 and 20 K. The slope

of the ρ_{xy} is nearly temperature independent for both SrCd_2Sb_2 and EuCd_2Sb_2 . The Hall coefficient R_0 is determined from the linear fit of ρ_{xy} in the high field range. From the Hall coefficient, we extracted the hole carriers density of SrCd_2Sb_2 and EuCd_2Sb_2 at base temperature 2 K extracted from R_0 are $1.15 \times 10^{18} \text{ cm}^{-3}$ and $2.20 \times 10^{18} \text{ cm}^{-3}$, respectively.

4.3.2 Shubnikov-de Haas oscillation

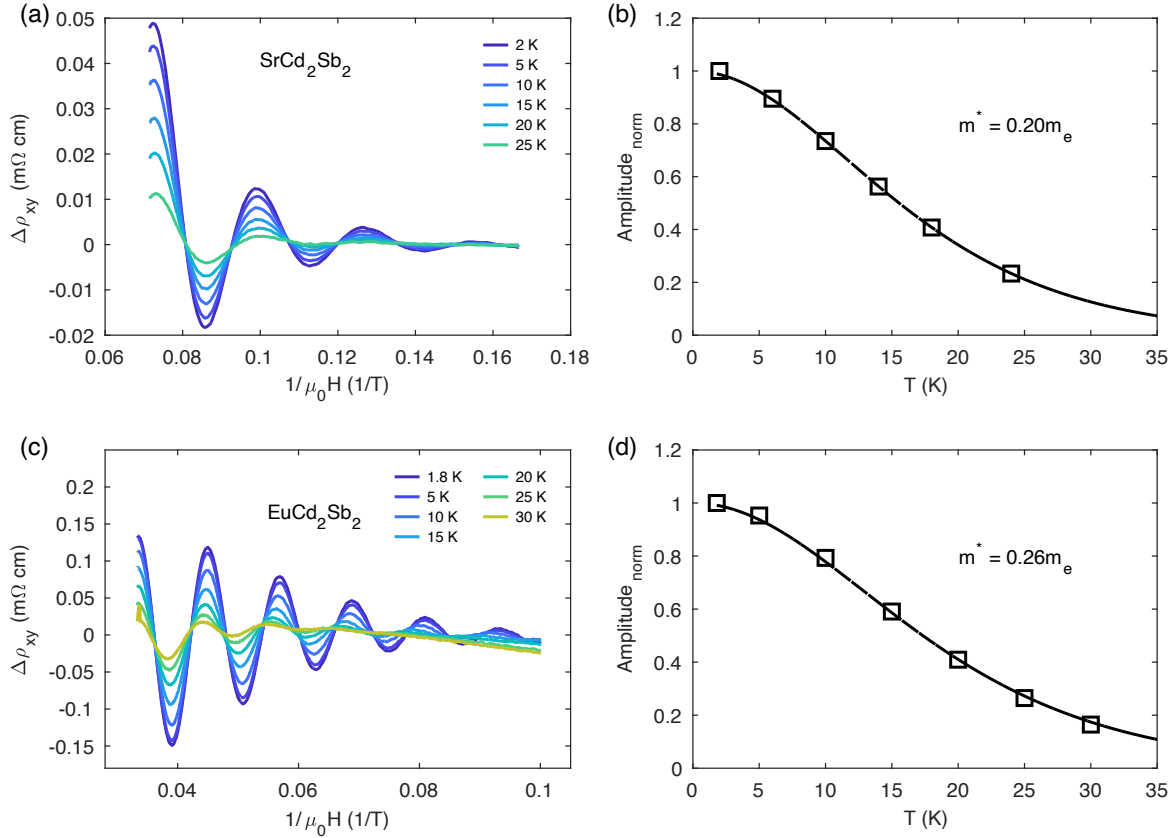


Figure 4.3: **Shubnikov-de Haas oscillation of RCd_2Sb_2 ($\text{R} = \text{Sr}, \text{Eu}$).** Oscillatory Hall resistivity, $\Delta\rho_{xy}$, versus the inverse of along c -axis magnetic field, $1/\mu_0 H$, for (a) SrCd_2Sb_2 and (b) EuCd_2Sb_2 at temperatures between 2 and 40 K, extracting from the linear background of ρ_{xy} . The fitting of the temperature dependence of oscillation amplitude for (c) SrCd_2Sb_2 and (d) EuCd_2Sb_2 using Lifshitz-Kosevich factor.

In the measurement of Hall resistivity of SrCd_2Sb_2 and EuCd_2Sb_2 , Shubnikov-de Haas (SdH) oscillations were also observed. (a) and (c) show the oscillatory part of Hall resistivity, $\Delta\rho_{xy}$, as a function of the inverse magnetic field along c -axis, $1/\mu_0 H$, at temperatures between 2 to 30 K. The magnetic field range of the extracted oscillations is between 6 to 14 T for SrCd_2Sb_2 and 10 to 31 T for EuCd_2Sb_2 . The oscillatory component $\Delta\rho_{xy}$ was extracted by subtracting a linear background of ρ_{xy} . The amplitude of $\Delta\rho_{xy}$ decays as temperature increases due to the smearing of Fermi-Dirac distribution. We fit the temperature dependence of the amplitude of oscillations to the Lifshitz-Kosevich factor,

$$R_T = \frac{\alpha T m^*}{B \sinh(\alpha T m^*/B)},$$

where $\alpha = 2\pi^2 k_B m_e / e\hbar$. The effective mass, m^* , is a ratio to the mass of the free electron, m_e . B is the average value of the magnetic field over range where oscillations were extracted. R_T is the normalized amplitude of the SdH oscillation. We determine the temperature dependence of amplitude by taking the Fast Fourier transform (FFT) analysis of SdH oscillation at each temperature. As shown in Fig. 4.3 (b) and (d), the temperature dependence of oscillation amplitude is well fitted by R_T for both SrCd_2Sb_2 and EuCd_2Sb_2 . The extracted effective masses of hole carriers are $0.2m_e$ and $0.26m_e$ for SrCd_2Sb_2 and EuCd_2Sb_2 , respectively.

4.3.3 Optical transmittance

The transmission spectra of ACd_2Pn_2 were measured using the Fourier transform infrared spectroscopy (FTIR) technique at room temperature. The incident range is between 400 and 8000 cm^{-1} , corresponding to the electronic energy range from 0.05 to 1 eV. In Fig. 4.4(a) we reproduce the EuCd_2As_2 spectrum presented in previous chapter, which remains transparent up to a wave number of 6000 cm^{-1} (equivalent to $\sim 0.74 \text{ eV}$), followed by a sharp drop in transmittance at higher wavenumbers. The transmittance of SrCd_2As_2 drops near the upper limit of the measurable range, $\sim 7000 \text{ cm}^{-1}$ (equivalent to $\sim 0.86 \text{ eV}$). These data suggest that both materials are good insulators with comparable gap size, with $\sim 0.74 \text{ eV}$ for EuCd_2As_2 and $\sim 0.86 \text{ eV}$ for SrCd_2As_2 .

Figure 4.4(b) shows the transmission spectrum of SrCd_2Sb_2 and EuCd_2Sb_2 . Unlike SrCd_2As_2 and EuCd_2As_2 , the transmittance measured at low frequencies is nearly zero, then it begins to increase as the wavenumber of the incident light increases above $\sim 2000\text{-}2500\text{ cm}^{-1}$. At higher wavenumber, it reaches a maximum and drops sharply at $\sim 4000\text{ cm}^{-1}$ and $\sim 4500\text{ cm}^{-1}$ for EuCd_2Sb_2 and SrCd_2Sb_2 . Such behavior is consistent with a doped semiconductor. The low-frequency suppression of transmittance is due to the Drude response of doped carriers. The materials become transparent above plasma frequency, until reaching the frequency that corresponds to the bandgap energy. From these data we determined that the size of the bandgap is 0.48 eV for EuCd_2Sb_2 and 0.54 eV for SrCd_2Sb_2 .

The plasma frequency, w_p , is related to the carrier density n and the effective mass of carriers m^* :

$$w_p^2 = \frac{ne^2}{\epsilon_0\epsilon_{\text{opt}}m^*}.$$

Here, ϵ_0 is the vacuum permittivity and ϵ_{opt} is the relative background permittivity of the samples

The effective mass, m^* , and carrier density, n , are determined from magneto-transport measurements. The relative permittivity of EuCd_2Sb_2 and SrCd_2Sb_2 is unknown. Nevertheless, using the typical values of relative permittivity, we obtained a plasma frequency that is consistent with experimental data.

4.4 Conclusion

Our study revealed an insulating nature of the non-magnetic analog of EuCd_2As_2 - SrCd_2As_2 . Substituting As with Sb in RCd_2As_2 ($\text{R} = \text{Eu}, \text{Sr}$) results in metallic temperature dependence in the resistivity of RCd_2Sb_2 . However, the FTIR measurements metallic transport behavior is due to the doped carrier, and the materials do possess an electronic band gap. The very similar size of the bandgap between the Eu and Sr compounds suggest that the Eu 4f electrons is not the origin of the underestimation of the bandgap. Our results suggest that the choice of DFT functional plays a crucial role in the correct prediction of topological phase.

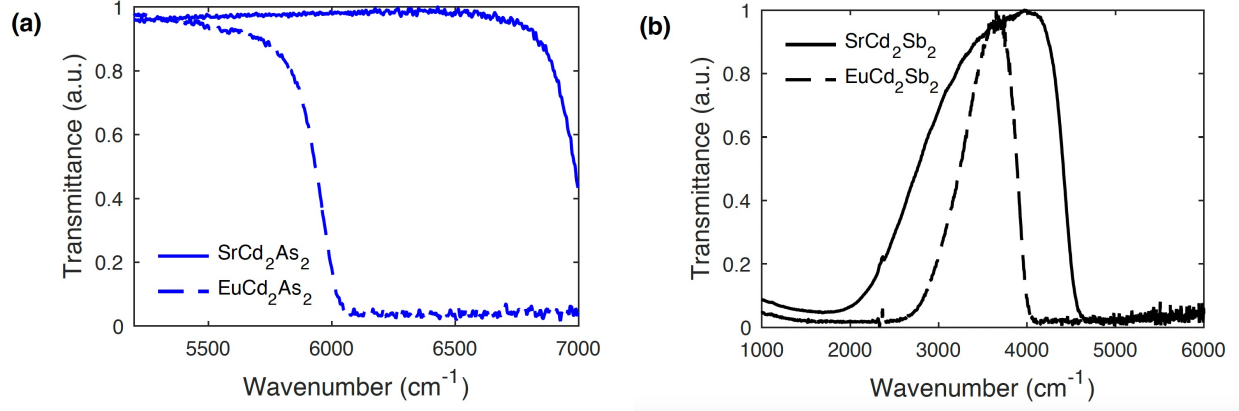


Figure 4.4: **Transmittance of RCd_2Pn_2 ($\text{R} = \text{Eu}, \text{Sr}$; $\text{Pn} = \text{As}, \text{Sb}$) at room temperature.** (a) Transmittance spectrum of (a) RCd_2As_2 ($\text{R} = \text{Eu}, \text{Sr}$) and (b) RCd_2Sb_2 ($\text{R} = \text{Eu}, \text{Sr}$).

4.5 Appendix

4.5.1 Crystal lattice constants

The extracted lattice constants from the Rietveld analysis of powder x-ray diffraction of ACd_2Pn_2 ($\text{A} = \text{Sr}, \text{Eu}$; $\text{Pn} = \text{As}, \text{Sb}$) at room temperature.

Crystal	a (Å)	c (Å)
EuCd_2Sb_2	4.7019	7.7208
EuCd_2As_2	4.4463	7.3390
SrCd_2Sb_2	4.7180	7.8300
SrCd_2As_2	4.4629	7.4264

Table 4.1: **Crystal lattice constants of ACd_2Pn_2 .** The lattice constants are obtained from the Rietveld analysis of the powder X-ray diffraction at room temperature.

Chapter 5

THE INTERPLAY BETWEEN MAGNETISM AND ELECTRONIC STRUCTURE IN EuCd_2Sb_2

5.1 Abstract

In the previous two chapters, we presented our findings that contrary to theoretical predictions, ACd_2Pn_2 ($A = \text{Eu, Sr}$; $\text{Pn} = \text{As, Sb}$) are gapped semiconductors rather than topological semimetals. This significant discrepancy between density functional theory (DFT) calculations and experimental results arises from the use of an inappropriate functional in calculation. In this chapter, we will demonstrate the strong interplay between magnetic ordering and the electronic band structure of EuCd_2Pn_2 , highlighting its potential for spintronics applications.

5.2 Introduction

Although we have determined that EuCd_2As_2 is a trivial magnetic semiconductor, it exhibits an intriguing colossal magnetoresistance at low temperatures. This phenomenon is usually a result of the strong interplay between the magnetism and the electronic structure, where the resistance is strongly modulated by the change of electronic structure induced by the change of magnetic configurations. Indeed, it was observed that there is a reduction of the bandgap of EuCd_2As_2 by 100 meV when the magnetic moments are fully saturated by the external magnetic fields.

In contrast to the highly insulating EuCd_2As_2 , EuCd_2Sb_2 is a doped magnetic semiconductor that shows pronounce SdH oscillations. This offers a possibility to monitor the change of electronic structure by comparing the oscillation frequency with the field-induced magnetization. In this chapter, we present a comparative study of the angle dependence

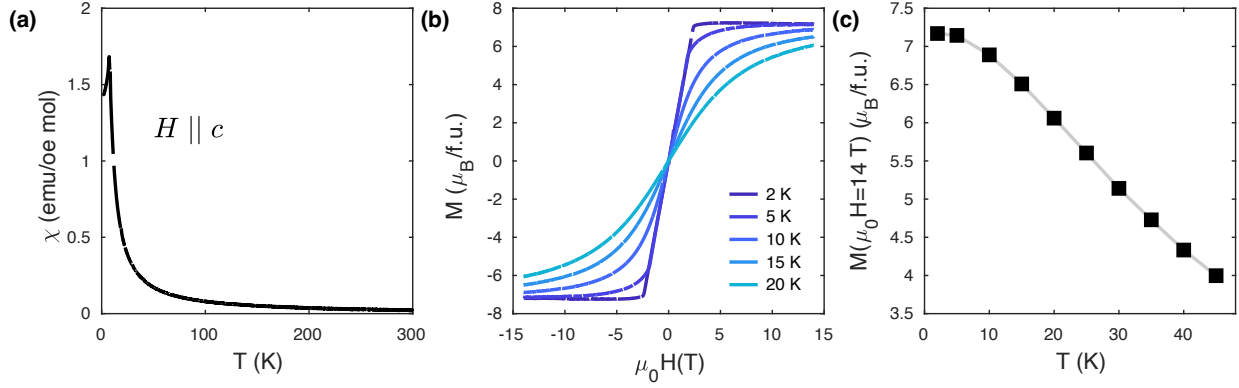


Figure 5.1: **Magnetic characterization of EuCd_2Sb_2 .** (a) Temperature dependence of magnetic susceptibility χ with 0.1 T magnetic field applied along the c axis. (b) Magnetization as a function of along c -axis magnetic field at different temperatures below 20 K. The saturated magnetization is $\sim 7\mu_B$ per formula unit at the base temperature 2 K. (c) Temperature dependence of magnetization at 14 T.

of SdH oscillations of both EuCd_2Sb_2 and SrCd_2Sb_2 and show that the magnetism indeed strongly modifies the shape of the Fermi surface. We also present the angle dependence of the anomalous Hall conductivity, which is consistent with the modulation of energy bands due to the magnetization rotation.

5.3 Results

5.3.1 Magnetic characterizations

We first present the the magnetic property of EuCd_2Sb_2 . As shown in Fig. 5.1 (a), the temperature dependence of magnetic susceptibility χ under along c axis external magnetic field follows the Curie-Weiss temperature dependence, with a kink at 7.2 K indicating the onset of AFM order. Fig. 5.1 (b) shows the magnetization $\mathbf{M}$ as a function of the field measured at different temperatures. At the base temperature of 2 K, $\mathbf{M}$ increases linearly before reaching the saturated value of $\pm 7\mu_B$ per Eu atom, in agreement with the magnetic moment of a divalent Eu with half-filled $4f$ orbitals. Fig. 5.1 (c) shows the saturated $\mathbf{M}$

at different temperatures. As temperature increases from 2 K to 45 K, the magnetization under magnetic field 14 T decreases from $7\mu_B$ to $4\mu_B$.

5.3.2 Temperature dependence of Shubnikov-de Haas oscillation

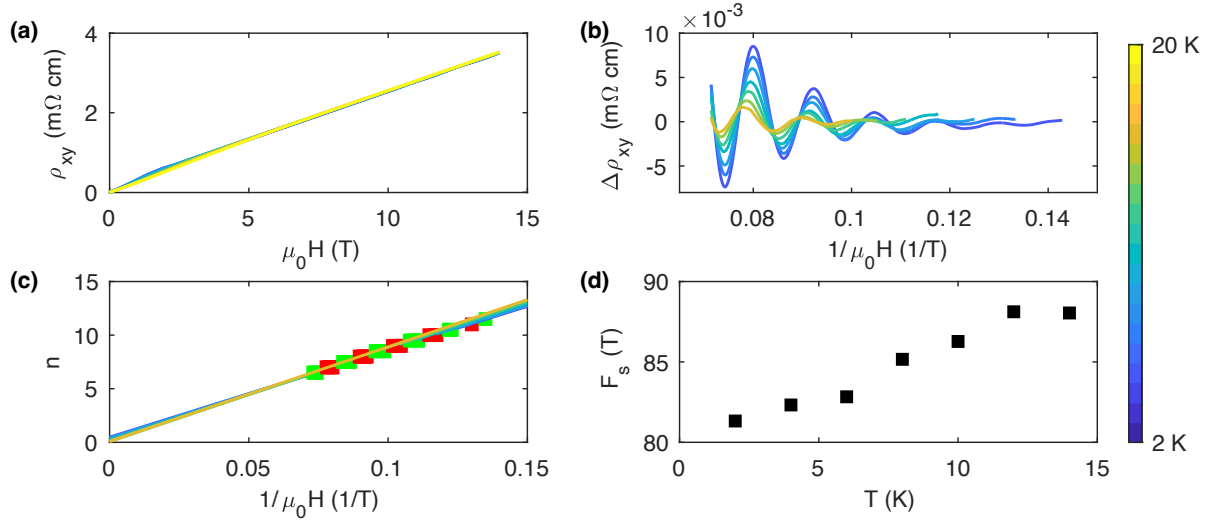


Figure 5.2: **Temperature dependence of Shubnikov-de Haas oscillation of EuCd₂Sb₂.** (a) Hall resistivity, $\Delta\rho_{xy}$, as a function of magnetic field at temperatures between 2 and 20 K. (b) Oscillatory Hall resistivity, $\Delta\rho_{xy}$, as a function of inverse field, $1/\mu_0 H$, at temperatures between 2 and 14 K, extracting from the linear background of ρ_{xy} . (c) Landau level index against the inverse magnetic field. The integer Landau level indices are assigned to $\Delta\rho_{xy}$ peaks, while half-integer Landau level indices are assigned to $\Delta\rho_{xy}$ valleys. The solid lines are linear fits of Landau indices at temperatures between 2 and 14 K. All peaks and valleys fall in the linear fits. (d) Temperature dependence of oscillation frequencies extracted from the slopes of linear fits of Landau level indices.

We then move to the magneto-transport study of EuCd₂Sb₂. Fig. 5.3 (a) shows the Hall resistivity, ρ_{xy} , as a function of c -axis magnetic field at temperatures from 2 K to 20 K. The slope of Hall resistivity has negligible change at the temperature below 20 K. With the magnetic field $\mu_0 H$ above 7 T, the SdH oscillations are observed. In Fig. 5.3 (b), the oscillatory part of the resistivity, $\Delta\rho_{xy}$, is plotted against the inverse of the magnetic field, $1/\mu_0 H$. The oscillatory part is extracted by subtracting a linear background of ρ_{xy} . As shown

in Fig. 5.3 (c), the positions of peaks and valleys of $\Delta\rho_{xy}$ are extracted and plotted against the Landau index n with the peaks assigned to the integer index and valleys assigned to the half-integer index. The peaks and valleys of each temperature are then fitted in a straight line. The slope yields the oscillation frequency at each temperature. Fig. 5.3 (b) shows the temperature dependence of the oscillation frequency F_s . Notably, as the temperature ramps, the oscillation frequency increases from 80 T to 90 T. For the SdH oscillation, the amplitude of SdH oscillations decays with temperature due to the smearing of the Fermi-Dirac distribution, but the frequency is usually a constant as a function of temperature. A significant change in oscillation frequency versus temperature is not expected. Compared with the temperature dependence of the saturated magnetization moments under a 14 T magnetic field, we found the change in oscillation frequency versus temperature is associated with the magnetization. The electronic band structure of EuCd_2Sb_2 is strongly correlated with the magnetization.

5.3.3 Magnetic field angle dependence of Shubnikov-de Haas oscillation frequency

To further understand the interplay between magnetism and electronic band structure in EuCd_2Sb_2 , we conducted a magnetic field angle dependence of magnetoresistance measurement that the applied magnetic field rotates from perpendicular ($\theta = 0^\circ$) to parallel ($\theta = 90^\circ$) with sample plane. To elucidate the effect of magnetism solely, the angle-dependent measurement is also conducted on non-magnetic analog SrCd_2Sb_2 . The magnetic field is along the c axis and up to 31 T for EuCd_2Sb_2 , 14 T for SrCd_2Sb_2 . As Fig. 5.3 (a) and (d) show, the SdH oscillations appear on ρ_{xx} at different magnetic field angles for both EuCd_2Sb_2 and SrCd_2Sb_2 . The oscillatory parts were then extracted by subtracting the second polynomial background of ρ_{xx} and plotted with an offset shown in Fig. 5.3 (b) and (e). Then the oscillation frequencies were obtained from the linear fitting of peaks and valleys of oscillatory resistivity. Fig. 5.3 (c) and (f) show the angle dependence of oscillation frequency for EuCd_2Sb_2 and SrCd_2Sb_2 , respectively. For typical three-dimensional materials, the Fermi

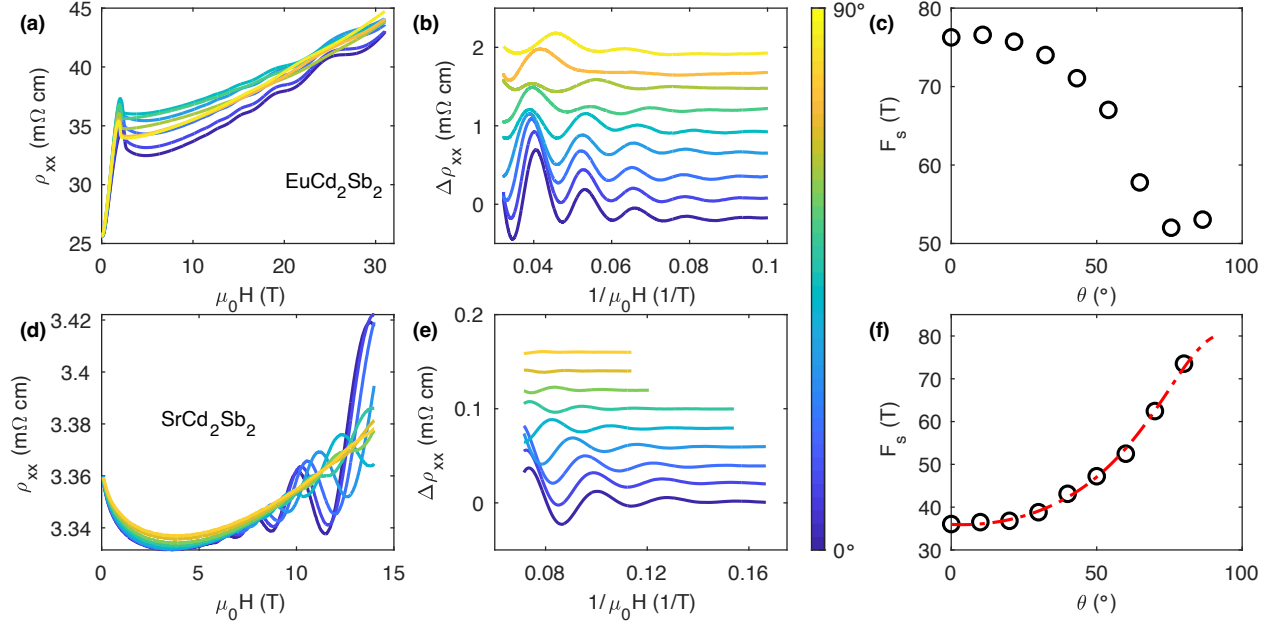


Figure 5.3: **Magnetic field angle dependence of Shubnikov-de Haas oscillation of EuCd₂Sb₂ and SrCd₂Sb₂.** (a) and (d) Magneto-resistivity, ρ_{xx} , under a magnetic field of 31 T and 14 T rotating from $\mu_0 H \parallel c$ axis (0°) to $\mu_0 H \parallel ab$ plane (90°) for EuCd₂Sb₂ and SrCd₂Sb₂, respectively. (b) and (e) Oscillatory part of magneto-resistivity, $\Delta\rho_{xx}$, under different magnetic field angles for EuCd₂Sb₂ and SrCd₂Sb₂, respectively. $\Delta\rho_{xx}$ are offset for clarity. (c) and (f) Angle dependence of oscillation frequency F_s by tracking the peak and valley position in $1/B$ and fitting the linear slope. The red dot line in (f) denotes the fitting to the equation of the angle dependence of, F_s , of a three-dimensional Fermi pocket.

pocket is ellipsoid, and the angle dependence of frequency can be fitted in the formula

$$F_S^{3D} = \frac{F_c F_{a/b}}{[(F_c \sin\theta)^2 + (F_{a/b} \sin\theta)^2]^{1/2}}, \quad (5.1)$$

where F_c and $F_{a/b}$ indicate the oscillation frequencies when the magnetic field is in-plane (90°) and out-of-plane (0°), respectively. For SrCd₂Sb₂, the oscillation frequency increases as the magnetic field angle rotates from 38 T to 74 T. The angle dependence of frequency can be well fitted into Equ. 5.1; While for EuCd₂Sb₂, as the angle increases, the SdH oscillation frequency decreases from 78 T to 50 T, which deviates to the behavior of typical three-dimensional semimetals. Furthermore, according to the Onsager equation, the cross-

sectional area of the Fermi pocket, A , can be estimated from the oscillation frequencies and the Fermi wave vectors k can be estimated from the cross-sectional area.

5.3.4 Magnetic field angle dependence of anomalous Hall effect

Except for the anomalous magnetic field angle dependence of quantum oscillation frequency, we observed the anomalous magnetic field angle dependence of the anomalous Hall effect in EuCd_2Sb_2 . Fig. 5.4 (a) shows the Hall resistivity as a function of the magnetic field at different angles. As the magnetic field rotates toward the sample plane, the effective magnetic field perpendicular to the sample plane $\mu_0 H \cos\theta$ diminishes and the ordinary Hall resistivity approaches zero. The magnetic field is perpendicular to the current direction once in the sample plane. Fig. 5.4 (b) shows the anomalous Hall resistivity, ρ_{xy}^A , as the magnetic field rotating from out-of-plane to in-plane by subtracting the linear background of ρ_{xy} . The ρ_{xy}^A is fully saturated at 14 T and $\rho_{xy}(14T)$ is plotted against rotating angle θ in Fig. 5.4 (c).

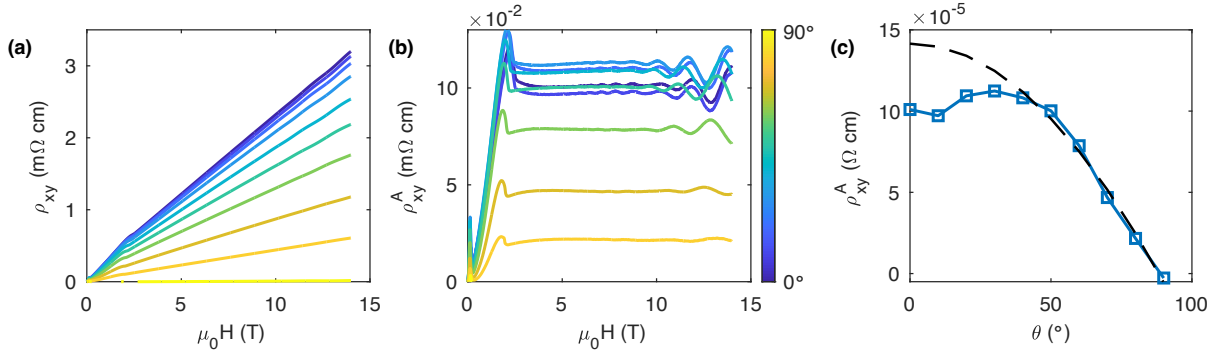


Figure 5.4: **Magnetic field angle dependence of anomalous Hall effect of EuCd_2Sb_2 .** (a) Hall resistivity, ρ_{xy} , as a function of magnetic field up to 14 T as the field angle rotating from $\mu_0 H \parallel c$ axis (0°) to $\mu_0 H \parallel ab$ plane (90°). (b) Anomalous Hall resistivity, $\Delta\rho_{xy}^A$, under different magnetic field angles, obtained by subtracting the linear background of ρ_{xy} . (c) Angle dependence of $\Delta\rho_{xy}^A$. The dashed line indicates the perpendicular effective magnetic field as a function of angle.

5.4 Conclusion

Despite being topologically trivial, the resistivity of EuCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$) is extremely sensitive to the magnetic configuration of Eu-ordered moments. EuCd_2As_2 has a colossal magnetoresistance effect that the resistivity drops a few orders of magnitude as the magnetic field increases. EuCd_2Sb_2 exhibits a significant temperature dependence and magnetic field angle dependence of oscillation frequency. All of these behaviors indicate a strong coupling between magnetism and electronic band structure in EuCd_2Pn_2 . This unusual property makes EuCd_2Pn_2 great candidates in spintronics applications.

Chapter 6

SUMMARY AND OUTLOOK

In this dissertation, I presented our studies on one of the leading Weyl semimetal candidates, EuCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$) in different aspects including single crystal synthesis, materials characterization, magneto-transport measurement, and photoemission measurement.

Our study of EuCd_2As_2 revealed that the carrier density dependence of the anomalous Hall conductivity (AHC) in EuCd_2As_2 does not align with the expected behavior of an ideal Weyl semimetal. Instead, the scaling relationship between the AHC and the longitudinal conductivity is in good agreement with the characteristics of insulating hopping transport. These observations, coupled with the substantial electronic gap revealed in the optical transmittance measurement, establish that EuCd_2As_2 is a magnetic semiconductor with an electronic gap of 0.77 eV instead of a Weyl semimetal.

Moreover, to investigate the origin of the significant discrepancy between DFT calculation and experimental results, we conducted magneto-transport and optical studies on EuCd_2Sb_2 and non-magnetic analog SrCd_2Pn_2 ($\text{Pn} = \text{As}, \text{Sb}$), which revealed ACd_2Pn_2 are all doped semiconductors and the discrepancy between DFT calculation and experimental result is from the inaccurate choice of functional in DFT calculation.

Despite being topologically trivial, the resistivity of EuCd_2Pn_2 is extremely sensitive to the magnetic configuration of Eu-ordered moments, leading to a colossal magnetoresistance effect in EuCd_2As_2 and a magnetic moments dependence and anomalous magnetic field angle dependence of SdH oscillation frequency in EuCd_2Sb_2 . The electronic band structure of EuCd_2Pn_2 is strongly coupling with the magnetic orders.

In conclusion, the research presented in this thesis 1) revealed that EuCd_2As_2 , proposed

as one of the leading candidates for realizing a Weyl semimetal, is a doped semiconductor rather than a semimetal; 2) identified that the underestimation of the electronic band gap of EuCd_2Pn_2 in previous DFT calculations arises from the inappropriate choice of functional approximation. Future prediction and design of ideal Weyl semimetals should carefully consider the choice of functional in DFT calculation; 3) found that the strong coupling between the electronic band gap and the magnetic order in EuCd_2Pn_2 , indicating a great potential for future spintronic applications; 4) developed an experimental toolkit for identifying the topological phase in p-type materials for the future study of topological semimetals.

Bibliography

- [1] Zhijun Wang QuanSheng Wu Matthias Troyer-Xi Dai B. Andrei Bernevig Alexey A. Soluyanov, Dominik Gresch. Type-ii weyl semimetals. *Nature*, 527:495–498, Nov 2015.
- [2] Tsuneya Ando. Physics of Graphene: Zero-Mode Anomalies and Roles of Symmetry. *Progress of Theoretical Physics Supplement*, 176:203–226, 06 2008.
- [3] N. P. Armitage, E. J. Mele, and Ashvin Vishwanath. Weyl and Dirac semimetals in three-dimensional solids. *Rev. Mod. Phys.*, 90:015001, Jan 2018.
- [4] Leon Balents. Weyl electrons kiss. *Physics*, 4(36), May 2011.
- [5] Michael Victor Berry. Quantal phase factors accompanying adiabatic changes. *Proc. R. Soc. London, Ser. A*, 392, March 1984.
- [6] P. E. Blöchl. Projector augmented-wave method. *Phys. Rev. B*, 50:17953–17979, Dec 1994.
- [7] A. A. Burkov. Anomalous Hall effect in Weyl metals. *Phys. Rev. Lett.*, 113:187202, Oct 2014.
- [8] A. A. Burkov. Giant planar hall effect in topological metals. *Phys. Rev. B*, 96:041110, Jul 2017.
- [9] Haiwen Liu Jian Wang Zhi-Min Liao Da-Peng Yu Cai-Zhen Li, Li-Xian Wang. Giant negative magnetoresistance induced by the chiral anomaly in individual Cd_3As_2 nanowires. *Nature Communications*, 6(10137):1490–1493, December 2015.

- [10] Xiangyu Cao, Jie-Xiang Yu, Pengliang Leng, Changjiang Yi, Xiaoyang Chen, Yunkun Yang, Shanshan Liu, Lingyao Kong, Zihan Li, Xiang Dong, Youguo Shi, Manuel Bibes, Rui Peng, Jiadong Zang, and Faxian Xiu. Giant nonlinear anomalous Hall effect induced by spin-dependent band structure evolution. *Phys. Rev. Res.*, 4:023100, May 2022.
- [11] Bijuan Chen, Zheng Deng, Wenmin Li, Moran Gao, Zhi Li, Guoqiang Zhao, Shuang Yu, Xiancheng Wang, Qingqing Liu, and Changqing Jin. $(\text{Sr}_{1-x}\text{Na}_x)(\text{Cd}_{1-x}\text{Mn}_x)_2\text{As}_2$: A new charge and spin doping decoupled diluted magnetic semiconductors with CaAl_2Si_2 -type structure. *Journal of Applied Physics*, 120(8):083902, 08 2016.
- [12] Matteo Cococcioni and Stefano de Gironcoli. Linear response approach to the calculation of the effective interaction parameters in the LDA+U method. *Phys. Rev. B*, 71:035105, Jan 2005.
- [13] Giuseppe Cuono, Raghottam M. Sattigeri, Carmine Autieri, and Tomasz Dietl. Ab initio overestimation of the topological region in Eu-based compounds. *Phys. Rev. B*, 108:075150, Aug 2023.
- [14] Jonathan M. DeStefano and Lin-Lin Wang. Pressure effect on band inversion in AECd_2As_2 ($\text{AE} = \text{Ca}, \text{Sr}, \text{Ba}$). *Phys. Rev. B*, 103:115207, Mar 2021.
- [15] Paul Adrien Maurice Dirac and Ralph Howard Fowler. The quantum theory of the electron. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 117(778):610–624, 1928.
- [16] Zhong Fang, Naoto Nagaosa, Kei S. Takahashi, Atsushi Asamitsu, Roland Mathieu, Takeshi Ogasawara, Hiroyuki Yamada, Masashi Kawasaki, Yoshinori Tokura, and Kiyoyuki Terakura. The anomalous hall effect and magnetic monopoles in momentum space. *Science*, 302(5642):92–95, 2003.

- [17] J. Furthmüller G. Kresse. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science*, 6:15–50, 1996.
- [18] Elena Gati, Sergey L. Bud’ko, Lin-Lin Wang, Adrian Valadkhani, Ritu Gupta, Brinda Kuthanazhi, Li Xiang, John M. Wilde, Aashish Sapkota, Zurab Guguchia, Rustem Khasanov, Roser Valentí, and Paul C. Canfield. Pressure-induced ferromagnetism in the topological semimetal EuCd_2As_2 . *Phys. Rev. B*, 104:155124, Oct 2021.
- [19] Weyl H. Gravitation and the electron. *Proc Natl Acad Sci U S A.*, 15:323–334, Apr 1929.
- [20] F. D. M. Haldane. Attachment of surface ”fermi arcs” to the bulk fermi surface: ”fermi-level plumbing” in topological metals, 2014.
- [21] M. Z. Hasan and C. L. Kane. Colloquium: Topological insulators. *Rev. Mod. Phys.*, 82:3045–3067, Nov 2010.
- [22] L. P. He, X. C. Hong, J. K. Dong, J. Pan, Z. Zhang, J. Zhang, and S. Y. Li. Quantum transport evidence for the three-dimensional dirac semimetal phase in cd_3as_2 . *Phys. Rev. Lett.*, 113:246402, Dec 2014.
- [23] Conyers Herring. Accidental degeneracy in the energy bands of crystals. *Phys. Rev.*, 52:365–373, Aug 1937.
- [24] Pavan Hosur, S. A. Parameswaran, and Ashvin Vishwanath. Charge transport in weyl semimetals. *Phys. Rev. Lett.*, 108:046602, Jan 2012.
- [25] Jin Hu, Su-Yang Xu, Ni Ni, and Zhiqiang Mao. Transport of topological semimetals. *Annual Review of Materials Research*, 49(Volume 49, 2019):207–252, 2019.

- [26] Guiyuan Hua, Simin Nie, Zhida Song, Rui Yu, Gang Xu, and Kailun Yao. Dirac semimetal in type-IV magnetic space groups. *Phys. Rev. B*, 98:201116, Nov 2018.
- [27] Hai-Zhou Lu Huachen Zhang Hongchao Liu-Rong Ma Zhiyong Fan-Shun-Qing Shen Hui Li, Hongtao He and Jiannong Wang. Negative magnetoresistance in dirac semimetal Cd_3As_2 . *Nat Commun*, 7(10301), 2016.
- [28] A.M. Kosevich I.M. Lifshitz. Theory of magnetic susceptibility in metals at low temperature. *JETP*, 29(4):730, 07 1956.
- [29] Min Jin, Liangtao Zheng, Cheng Sun, Long Jiang, Xiang Meng, Qing Chen, and Wen Li. Manipulation of hole and band for thermoelectric enhancements in SrCd_2Sb_2 Zintl compound. *Chemical Engineering Journal*, 420:130530, 2021.
- [30] Na Hyun Jo, Brinda Kuthanazhi, Yun Wu, Erik Timmons, Tae-Hoon Kim, Lin Zhou, Lin-Lin Wang, Benjamin G. Ueland, Andriy Palasyuk, Dominic H. Ryan, Robert J. McQueeney, Kyungchan Lee, Benjamin Schrunk, Anton A. Burkov, Ruslan Prozorov, Sergey L. Bud'ko, Adam Kaminski, and Paul C. Canfield. Manipulating magnetism in the topological semimetal EuCd_2As_2 . *Phys. Rev. B*, 101:140402, Apr 2020.
- [31] Heon-Jung Kim, Ki-Seok Kim, J.-F. Wang, M. Sasaki, N. Satoh, A. Ohnishi, M. Kitaura, M. Yang, and L. Li. Dirac versus weyl fermions in topological insulators: Adler-bell-jackiw anomaly in transport phenomena. *Phys. Rev. Lett.*, 111:246603, Dec 2013.
- [32] K. v. Klitzing, G. Dorda, and M. Pepper. New method for high-accuracy determination of the fine-structure constant based on quantized hall resistance. *Phys. Rev. Lett.*, 45:494–497, Aug 1980.
- [33] G. Kresse and J. Furthmüller. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B*, 54:11169–11186, Oct 1996.

- [34] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B*, 59:1758–1775, Jan 1999.
- [35] Jyoti Krishna, T. Nautiyal, and T. Maitra. First-principles study of electronic structure, transport, and optical properties of EuCd_2As_2 . *Phys. Rev. B*, 98:125110, Sep 2018.
- [36] D. S. Lambert and D. D. O'Regan. Use of DFT + U + J with linear response parameters to predict non-magnetic oxide band gaps with hybrid-functional accuracy. *Phys. Rev. Res.*, 5:013160, Mar 2023.
- [37] R. B. Laughlin. Quantized hall conductivity in two dimensions. *Phys. Rev. B*, 23:5632–5633, May 1981.
- [38] D. F. Liu, A. J. Liang, E. K. Liu, Q. N. Xu, Y. W. Li, C. Chen, D. Pei, W. J. Shi, S. K. Mo, P. Dudin, T. Kim, C. Cacho, G. Li, Y. Sun, L. X. Yang, Z. K. Liu, S. S. P. Parkin, C. Felser, and Y. L. Chen. Magnetic Weyl semimetal phase in a kagomé crystal. *Science*, 365(6459):1282–1285, 2019.
- [39] Haiwen Liu, Hua Jiang, Ziqiang Wang, Robert Joynt, and X. C. Xie. Discrete scale invariance in topological semimetals. *arXiv: Materials Science*, 2018.
- [40] B. Q. Lv, T. Qian, and H. Ding. Experimental perspective on three-dimensional topological semimetals. *Rev. Mod. Phys.*, 93:025002, Apr 2021.
- [41] J.-Z. Ma, S. M. Nie, C. J. Yi, J. Jandke, T. Shang, M. Y. Yao, M. Naamneh, L. Q. Yan, Y. Sun, A. Chikina, V. N. Strocov, M. Medarde, M. Song, Y.-M. Xiong, G. Xu, W. Wulfhekel, J. Mesot, M. Reticcioli, C. Franchini, C. Mudry, M. Müller, Y. G. Shi, T. Qian, H. Ding, and M. Shi. Spin fluctuation induced weyl semimetal state in the paramagnetic phase of EuCd_2As_2 . *Science Advances*, 5(7):eaaw4718, 2019.

- [42] J.-Z. Ma, S. M. Nie, C. J. Yi, J. Jandke, T. Shang, M. Y. Yao, M. Naamneh, L. Q. Yan, Y. Sun, A. Chikina, V. N. Strocov, M. Medarde, M. Song, Y.-M. Xiong, G. Xu, W. Wulfhekel, J. Mesot, M. Reticcioli, C. Franchini, C. Mudry, M. Müller, Y. G. Shi, T. Qian, H. Ding, and M. Shi. Spin fluctuation induced weyl semimetal state in the paramagnetic phase of EuCd_2As_2 . *Science Advances*, 5(7):eaaw4718, 2019.
- [43] Junzhang Ma, Han Wang, Simin Nie, Changjiang Yi, Yuanfeng Xu, Hang Li, Jasmin Jandke, Wulf Wulfhekel, Yaobo Huang, Damien West, Pierre Richard, Alla Chikina, Vladimir N. Strocov, Joël Mesot, Hongming Weng, Shengbai Zhang, Youguo Shi, Tian Qian, Ming Shi, and Hong Ding. Emergence of nontrivial low-energy Dirac fermions in antiferromagnetic EuCd_2As_2 . *Advanced Materials*, 32(14):1907565, 2020.
- [44] Mumtaz Manzoor, Debidatta Behera, Ramesh Sharma, Muhammad Waqas Iqbal, S.K. Mukherjee, R. Khenata, S. Bin-Omran, Thamraa Alshahrani, E. El Shiekh, and T. Ouahrani. Structural, electronic, optical, and thermoelectric studies on Zintl SrCd_2Pn_2 ($\text{Pn}=\text{P}/\text{As}$) compounds for solar cell applications: A first principle approach. *Journal of Solid State Chemistry*, 326:124188, 2023.
- [45] Roger S. K. Mong, Andrew M. Essin, and Joel E. Moore. Antiferromagnetic topological insulators. *Phys. Rev. B*, 81:245209, Jun 2010.
- [46] Noam Morali, Rajib Batabyal, Pranab Kumar Nag, Enke Liu, Qiunan Xu, Yan Sun, Binghai Yan, Claudia Felser, Nurit Avraham, and Haim Beidenkopf. Fermi-arc diversity on surface terminations of the magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$. *Science*, 365(6459):1286–1291, 2019.
- [47] H. Murakawa, M. S. Bahramy, M. Tokunaga, Y. Kohama, C. Bell, Y. Kaneko, N. Nagaosa, H. Y. Hwang, and Y. Tokura. Detection of berry’s phase in a bulk rashba semiconductor. *Science*, 342(6165):1490–1493, 2013.

- [48] Naoto Nagaosa, Jairo Sinova, Shigeki Onoda, A. H. MacDonald, and N. P. Ong. Anomalous Hall effect. *Rev. Mod. Phys.*, 82:1539–1592, May 2010.
- [49] Ayano Nakamura, Shinichi Nishihaya, Hiroaki Ishizuka, Markus Kriener, Mizuki Ohno, Yuto Watanabe, Masashi Kawasaki, and Masaki Uchida. Berry curvature derived negative magnetoelectricity observed in type-II magnetic weyl semimetal films. *Phys. Rev. B*, 109:L121108, Mar 2024.
- [50] S. Nandy, Gargee Sharma, A. Taraphder, and Sumanta Tewari. Chiral anomaly as the origin of the planar hall effect in weyl semimetals. *Phys. Rev. Lett.*, 119:176804, Oct 2017.
- [51] Simin Nie, Tatsuki Hashimoto, and Fritz B. Prinz. Magnetic Weyl semimetal in $\text{K}_2\text{Mn}_3(\text{AsO}_4)_3$ with the minimum number of Weyl points. *Phys. Rev. Lett.*, 128:176401, Apr 2022.
- [52] H.B. Nielsen and Masao Ninomiya. The adler-bell-jackiw anomaly and weyl fermions in a crystal. *Physics Letters B*, 130(6):389–396, 1983.
- [53] Mizuki Ohno, Susumu Minami, Yusuke Nakazawa, Shin Sato, Markus Kriener, Ryotaro Arita, Masashi Kawasaki, and Masaki Uchida. Maximizing intrinsic anomalous Hall effect by controlling the Fermi level in simple Weyl semimetal films. *Phys. Rev. B*, 105:L201101, May 2022.
- [54] Tribhuwan Pandey and Abhishek K. Singh. High thermopower and ultra low thermal conductivity in Cd-based Zintl phase compounds. *Phys. Chem. Chem. Phys.*, 17:16917–16926, 2015.
- [55] S. A. Parameswaran, T. Grover, D. A. Abanin, D. A. Pesin, and A. Vishwanath. Probing the chiral anomaly with nonlocal transport in three-dimensional topological semimetals. *Phys. Rev. X*, 4:031035, Sep 2014.

- [56] Udhara S. Kaluarachchi Paul C. Canfield, Tai Kong and Na Hyun Jo. Use of frit-disc crucibles for routine and exploratory solution growth of single crystalline samples. *Philosophical Magazine*, 96(1):84–92, 2016.
- [57] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.*, 78:1396–1396, Feb 1997.
- [58] M. C. Rahn, J.-R. Soh, S. Francoual, L. S. I. Veiga, J. Stremper, J. Mardegan, D. Y. Yan, Y. F. Guo, Y. G. Shi, and A. T. Boothroyd. Coupling of magnetic order and charge transport in the candidate dirac semimetal EuCd_2As_2 . *Phys. Rev. B*, 97:214422, Jun 2018.
- [59] M. C. Rahn, J.-R. Soh, S. Francoual, L. S. I. Veiga, J. Stremper, J. Mardegan, D. Y. Yan, Y. F. Guo, Y. G. Shi, and A. T. Boothroyd. Coupling of magnetic order and charge transport in the candidate dirac semimetal EuCd_2As_2 . *Phys. Rev. B*, 97:214422, Jun 2018.
- [60] A P Ramirez. Colossal magnetoresistance. *Journal of Physics: Condensed Matter*, 9(39):8171, Sep 1997.
- [61] Juan Rodríguez-Carvajal. Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Condensed Matter*, 192(1):55–69, 1993.
- [62] Subhajit Roychowdhury, Mengyu Yao, Kartik Samanta, Seokjin Bae, Dong Chen, Sailong Ju, Arjun Raghavan, Nitesh Kumar, Procopios Constantinou, Satya N. Guin, Nicholas Clark Plumb, Marisa Romanelli, Horst Borrmann, Maia G. Vergniory, Vladimir N. Strocov, Vidya Madhavan, Chandra Shekhar, and Claudia Felser. Anomalous Hall conductivity and Nernst effect of the ideal Weyl semimetallic ferromagnet EuCd_2As_2 . *Advanced Science*, 10(13):2207121, 2023.

- [63] D. Santos-Cottin, I. Mohelský, J. Wyzula, F. Le Mardelé, I. Kapon, S. Nasrallah, N. Barišić, I. Živković, J. R. Soh, F. Guo, K. Rigaux, M. Puppín, J. H. Dil, B. Gudac, Z. Rukelj, M. Novak, A. B. Kuzmenko, C. C. Homes, Tomasz Dietl, M. Orlita, and Ana Akrap. EuCd_2As_2 : A magnetic semiconductor. *Phys. Rev. Lett.*, 131:186704, Nov 2023.
- [64] D. Santos-Cottin, I. Mohelský, J. Wyzula, F. Le Mardelé, I. Kapon, S. Nasrallah, N. Barišić, I. Živković, J. R. Soh, F. Guo, K. Rigaux, M. Puppín, J. H. Dil, B. Gudac, Z. Rukelj, M. Novak, A. B. Kuzmenko, C. C. Homes, Tomasz Dietl, M. Orlita, and Ana Akrap. EuCd_2As_2 : A magnetic semiconductor. *Phys. Rev. Lett.*, 131:186704, Nov 2023.
- [65] Inga Schellenberg, Ulrike Pfannenschmidt, Matthias Eul, Schwickert, Christian, Pöttgen, and Rainer. A ^{121}Sb and ^{151}Eu mössbauer spectroscopic investigation of EuCd_2X_2 ($\text{X} = \text{P}, \text{As}, \text{Sb}$) and YbCd_2Sb_2 . *Zeitschrift für anorganische und allgemeine Chemie*, 637(12):1863–1870.
- [66] Inga Schellenberg, Ulrike Pfannenschmidt, Matthias Eul, Schwickert, Christian, Pöttgen, and Rainer. A ^{121}Sb and ^{151}Eu mössbauer spectroscopic investigation of EuCd_2X_2 ($\text{X} = \text{P}, \text{As}, \text{Sb}$) and YbCd_2Sb_2 . *Zeitschrift für anorganische und allgemeine Chemie*, 637(12):1863–1870.
- [67] Yue Shi, Zhaoyu Liu, Logan A. Burnett, Seokhyeong Lee, Chaowei Hu, Qianni Jiang, Jiaqi Cai, Xiaodong Xu, Mo Li, Cheng-Chien Chen, and Jiun-Haw Chu. Absence of Weyl nodes in EuCd_2As_2 revealed by the carrier density dependence of the anomalous Hall effect. *Phys. Rev. B*, 109:125202, Mar 2024.
- [68] J.-R. Soh, F. de Juan, M. G. Vergniory, N. B. M. Schröter, M. C. Rahn, D. Y. Yan, J. Jiang, M. Bristow, P. Reiss, J. N. Blandy, Y. F. Guo, Y. G. Shi, T. K. Kim, A. McCollam, S. H. Simon, Y. Chen, A. I. Coldea, and A. T. Boothroyd. Ideal Weyl semimetal induced by magnetic exchange. *Phys. Rev. B*, 100:201102, Nov 2019.

- [69] J.-R. Soh, C. Donnerer, K. M. Hughes, E. Schierle, E. Weschke, D. Prabhakaran, and A. T. Boothroyd. Magnetic and electronic structure of the layered rare-earth pnictide EuCd_2Sb_2 . *Phys. Rev. B*, 98:064419, Aug 2018.
- [70] Wang Z Wu Q Troyer M Dai X Bernevig BA Soluyanov AA, Gresch D. Type-ii weyl semimetals. *Nature*, 527:495, Nov 2015.
- [71] Hao Su, Benchao Gong, Wujun Shi, Haifeng Yang, Hongyuan Wang, Wei Xia, Zhenhai Yu, Peng-Jie Guo, Jinhua Wang, Linchao Ding, Liangcai Xu, Xiaokang Li, Xia Wang, Zhiqiang Zou, Na Yu, Zengwei Zhu, Yulin Chen, Zhongkai Liu, Kai Liu, Gang Li, and Yanfeng Guo. Magnetic exchange induced Weyl state in a semimetal EuCd_2Sb_2 . *APL Materials*, 8(1):011109, 01 2020.
- [72] K. M. Taddei, L. Yin, L. D. Sanjeewa, Y. Li, J. Xing, C. dela Cruz, D. Phelan, A. S. Sefat, and D. S. Parker. Single pair of weyl nodes in the spin-canted structure of EuCd_2As_2 . *Phys. Rev. B*, 105:L140401, Apr 2022.
- [73] D. J. Thouless, M. Kohmoto, M. P. Nightingale, and M. den Nijs. Quantized hall conductance in a two-dimensional periodic potential. *Phys. Rev. Lett.*, 49:405–408, Aug 1982.
- [74] M. Udagawa and E. J. Bergholtz. Field-selective anomaly and chiral mode reversal in type-ii weyl materials. *Phys. Rev. Lett.*, 117:086401, Aug 2016.
- [75] Xiangang Wan, Ari M. Turner, Ashvin Vishwanath, and Sergey Y. Savrasov. Topological semimetal and fermi-arc surface states in the electronic structure of pyrochlore iridates. *Phys. Rev. B*, 83:205101, May 2011.
- [76] Guangqiang Wang, Guoqing Chang, Huibin Zhou, Wenlong Ma, Hsin Lin, M. Zahid Hasan, Su-Yang Xu, and Shuang Jia. Field-induced metal-insulator transition in $\beta\text{-EuP}_3$. *Chinese Physics Letters*, 37(10):107501, oct 2020.

- [77] H. P. Wang, D. S. Wu, Y. G. Shi, and N. L. Wang. Anisotropic transport and optical spectroscopy study on antiferromagnetic triangular lattice EuCd_2As_2 : An interplay between magnetism and charge transport properties. *Phys. Rev. B*, 94:045112, Jul 2016.
- [78] Lin-Lin Wang, Na Hyun Jo, Brinda Kuthanazhi, Yun Wu, Robert J. McQueeney, Adam Kaminski, and Paul C. Canfield. Single pair of Weyl fermions in the half-metallic semimetal EuCd_2As_2 . *Phys. Rev. B*, 99:245147, Jun 2019.
- [79] Yang Wang, Cong Li, Taimin Miao, Shuai Zhang, Yong Li, Liqin Zhou, Meng Yang, Chaohui Yin, Yongqing Cai, Chunyao Song, Hailan Luo, Hao Chen, Hanqing Mao, Lin Zhao, Hanbin Deng, Yingkai Sun, Changjiang Zhu, Fengfeng Zhang, Feng Yang, Zhimin Wang, Shenjin Zhang, Qinjun Peng, Shuheng Pan, Youguo Shi, Hongming Weng, Tao Xiang, Zuyan Xu, and X. J. Zhou. Giant and reversible electronic structure evolution in a magnetic topological material EuCd_2As_2 . *Phys. Rev. B*, 106:085134, Aug 2022.
- [80] Yuxiang Wang, Jianwen Ma, Jian Yuan, Wenbin Wu, Yong Zhang, Yicheng Mou, Jiaming Gu, Peihong Cheng, Wu Shi, Xiang Yuan, Jinglei Zhang, Yanfeng Guo, and Cheng Zhang. Absence of metallicity and bias-dependent resistivity in low-carrier-density EuCd_2As_2 , 2023.
- [81] Li Y Liu Y Wang J Liu J Dai JY Wang Y-Li L Yan J Mandrus D Xie XC Wang J Wang H, Liu H. Discovery of log-periodic oscillations in ultraquantum topological materials. *Sci Adv.*, 4(11), 2018.
- [82] Jun Xiong, Satya K. Kushwaha, Tian Liang, Jason W. Krizan, Max Hirschberger, Wudi Wang, R. J. Cava, and N. P. Ong. Evidence for the chiral anomaly in the dirac semimetal Na_3Bi . *Science*, 350(6259):413–416, 2015.

- [83] Gang Xu, Hongming Weng, Zhijun Wang, Xi Dai, and Zhong Fang. Chern semimetal and the quantized anomalous hall effect in HgCr_2Se_4 . *Phys. Rev. Lett.*, 107:186806, Oct 2011.
- [84] Y. Xu, L. Das, J. Z. Ma, C. J. Yi, S. M. Nie, Y. G. Shi, A. Tiwari, S. S. Tsirkin, T. Neupert, M. Medarde, M. Shi, J. Chang, and T. Shang. Unconventional transverse transport above and below the magnetic transition temperature in Weyl semimetal EuCd_2As_2 . *Phys. Rev. Lett.*, 126:076602, Feb 2021.
- [85] Binghai Yan and Claudia Felser. Topological materials: Weyl semimetals. *Annual Review of Condensed Matter Physics*, 8(1):337–354, 2017.
- [86] Kai-Yu Yang, Yuan-Ming Lu, and Ying Ran. Quantum Hall effects in a Weyl semimetal: Possible application in pyrochlore iridates. *Phys. Rev. B*, 84:075129, Aug 2011.
- [87] Shuo-Ying Yang, Yaojia Wang, Brenden R. Ortiz, Defa Liu, Jacob Gayles, Elena Derunova, Rafael Gonzalez-Hernandez, Libor Šmejkal, Yulin Chen, Stuart S. P. Parkin, Stephen D. Wilson, Eric S. Toberer, Tyrel McQueen, and Mazhar N. Ali. Giant, unconventional anomalous Hall effect in the metallic frustrated magnet candidate, KV_3Sb_5 . *Science Advances*, 6(31):eabb6003, 2020.
- [88] Ortiz BR Liu D Gayles J Derunova E Gonzalez-Hernandez R Šmejkal L Chen Y Parkin SSP Wilson SD Toberer ES McQueen T Ali MN Yang SY, Wang Y. Giant, unconventional anomalous hall effect in the metallic frustrated magnet candidate, KV_3Sb_5 . *Sci Adv.*, 31(6), Jul 2020.
- [89] Zhi-Ming Yu, Yugui Yao, and Shengyuan A. Yang. Predicted unusual magnetoresponse in type-ii weyl semimetals. *Phys. Rev. Lett.*, 117:077202, Aug 2016.

- [90] Hui Zhang, Liang Fang, Mei-Bo Tang, Hao-Hong Chen, Xin-Xin Yang, Xiangxin Guo, Jing-Tai Zhao, and Yuri Grin. Synthesis and properties of CaCd_2Sb_2 and EuCd_2Sb_2 . *Intermetallics*, 18(1):193–198, 2010.
- [91] Wang W Liu Y Chen ZG Lu S Liang S Cao J Yuan X Tang L Li Q Zhou C Gu T Wu Y Zou J Xiu F Zhang C, Zhang E. Room-temperature chiral charge pumping in dirac semimetals. *Nat Commun.*, 9(13741), 2017.
- [92] Wei Xia Ningning Wang Xiaodong Lv Xiaolei Liu Hao Su Zhongyang Li Desheng Wu Wei Wu Ziyi Liu Jinggeng Zhao Mingtao Li Shujia Li Xin Li Zhaohui Dong Chunyin Zhou Lili Zhang Xia Wang Na Yu Zhiqiang Zou Jianlin Luo Jinguang Cheng Lin Wang Zhicheng Zhong Yanfeng Guo Zhenhai Yu, Xuejiao Chen. Pressure-induced ideal Weyl semimetal state in the layered antiferromagnet EuCd_2As_2 , 2022.
- [93] Tiwari R.P. Zyuzin, A.A. Intrinsic anomalous hall effect in type-ii weyl semimetals. *Jetp Lett.*, 103:717–722, April 2016.