Spin Hall effect in 2D metallic delafossite PtCoO$_2$ and vicinity topology

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The two-dimensional (2D) metal PtCoO$_2$ is renowned for the lowest room temperature resistivity among all oxides, close to that of the top two materials Ag and Cu$^{1,2}$. In addition, we theoretically predict a strong intrinsic spin Hall effect$^{34}$. This originates from six strongly-tilted Dirac cones that we find in the electronic structure near the Fermi surface, where a gap is opened by large spin-orbit coupling (SOC). This is underpinned by rich topological properties; in particular, the phenomenology of a mirror Chern metal$^5$ is realized not exactly, but very accurately, on account of an approximate crystalline symmetry. We expect that such ‘vicinity topology’ to be a feature of relevance well beyond this material. Our Wilson loop analysis indicates further elaborate features such as fragile topology$^{6–8}$. These findings highlight PtCoO$_2$ as a promising material for spintronic applications as well as a platform to study the interplay of symmetry and topology.

PtCoO$_2$ crystallizes in the delafossite structure in which, as shown in Fig. 1a, Pt and Co respectively form triangular lattices and are stacked alternately$^7$. Their formal valences and configuration are Pt$^{1+}$ with 5$d^6$ and Co$^{3+}$ with 3$d^6$. Within this ionic-bonding picture, Co forms a band insulating state due to the crystal field splitting, while Pt is characterized by metallic $d_{3z^2−r^2}$ electrons.

The conductivity is exceptionally high for an oxide, and the electronic transport is strongly 2D$^{6,10}$. The Fermi surface is a single cylinder with hexagonal deformation (Fig. 1b), and the sharpness seen in the angle resolved photoemission spectroscopy (ARPES) bands indicates that electron correlation is nearly-free Pt-derived $d_{3z^2−r^2}$ electrons on a triangular lattice sandwiched by insulating layers of CoO$_2$.$^{10,12}$ However, as we show here, PtCoO$_2$ is far from being captured by this picture, but has a rich orbital and topological structure. We clarify this by constructing a two-dimensional nine-band tight-binding model on a triangular lattice, which consists of Pt 5$d$, 6$s$ and 6$p$ orbitals obtained as maximally-localized Wannier functions for the first-principles band structure.

Figure 1b displays the numerically calculated orbital shape along the Fermi surface, and we already find unexpected rich features. The orbital is not a simple $d_{3z^2−r^2}$, but lies within the $xy$-plane, e.g. $d_{3z^2−r^2}$-like, and aligns perpendicular to the sides of the hexagon. This orbital-momentum locking cannot emerge in the naive single-orbital triangular lattice picture and may explain characteristic behaviors of the material such as reduced impurity scattering$^{13}$.

Another remarkable feature is the existence of Dirac cones just below the Fermi level. This becomes apparent when we switch off the SOC. The band structure with and without SOC is shown in Fig. 1c, where we find strongly tilted 2D Dirac cones near the six corners of the hexagonal Fermi surface (encircled in Fig. 1bc and enlarged in 1d). Without SOC, these Dirac cones are robust because of the crystalline symmetry: A perturbation preserving the crystalline symmetry can shift the position of the crossing along the Γ–M line, but cannot remove it without merging the six copies at the Γ point. The tilt is large enough that the cone is flipped, such that the electron pockets are absorbed into the larger Fermi surface, placing it in the type II Dirac fermion category$^{14}$. The SOC of Pt is so strong ($\sim 0.55$ eV for $H_{SO} = \lambda L \cdot S$) that an energy gap of $\sim 0.43$ eV opens at the Dirac nodes as shown in Fig. 1e, which is consistent with recent ARPES observations$^{15}$. While the large gap washes out the conical energy dispersion, features of the Dirac nodes are inherited in band topology and transport properties as we detail below.

Before moving to topology, let us summarize the relevant crystalline symmetries. The first symmetry is the invariance under vertical mirror $\sigma_x : x \rightarrow −x$ (and its two symmetric partners obtained by $C_3$ rotation). This protects the six Dirac nodes in the absence of SOC as discussed above. The second is inversion symmetry $I : r \rightarrow −r$. In combination with the time-reversal symmetry (TRS), this makes the bands Kramers degenerate. The third, which plays an important role in the following topological discussion, is only approximate, defined by the basal mirror $\sigma_b : z \rightarrow −z$. While this symmetry is absent in the stacked delafossite structure as a whole, it is respected in a single Pt and its adjacent oxygen layers, which determines the electronic structure of the 2D metallic Pt electrons and oxygen crystal fields (see Fig. 1f). While we consider a two-dimensional model here, we note that orbital functions have three-dimensional structures and the basal-mirror symmetry $\sigma_b$ imposes a constraint on their hybridization. For instance, as we depict in Fig. 1g, a $d_z$ orbital (odd in $z$) electron cannot tunnel to a $d_{3z^2−r^2}$ orbital (even in $z$). As the mirror operation acts as $i\sigma_z$ for spins, SOC $\lambda L \cdot S$ preserves the mirror symmetry $\sigma_b$.

Now, let us discuss how the present material fits inside the theory of band topology classification$^{5–8,16–22}$. An important role is played by the hybrid Wannier function, a real-space wave function constructed from Bloch states localized in one direction but retaining plane wave character in other direc-
Fig. 1. Electronic structure. a, Crystal structure of PtCoO₂. b, Hexagonally warped Fermi surface (red curve) and the corresponding orbital eigenfunction (green). c, Band structure along high symmetry lines. Solid and dashed lines show the band dispersions with and without spin-orbit coupling, respectively. The spin-orbit coupling is $\lambda = 0.55$ eV. d, e, 3D picture of the tilted Dirac cone before and after adding the spin-orbit coupling. Their locations are indicated by circles in b, c. f, Pt layer with adjacent O atoms. g, Schematic picture of a typical hopping process forbidden in a basal-mirror symmetric structure.

The motion of the Wannier center in crystals can be visualized using the non-Abelian Wilson loop, defined as (P: path ordered product)

$$W[l] = P \exp \left[ -i \int_{l} d\mathbf{k} \cdot \mathcal{A}(\mathbf{k}) \right],$$

(1)

$$\mathcal{P}_{\mu}^{n}(\mathbf{k}) = -i(km)[\partial_{\mu}]kn,$$

(2)

where $|kn\rangle$ is the cell-periodic Bloch wave function of the $n$-th band. $m, n$ run over the (arbitrary) subset that constitutes the hybrid Wannier function of interest, and here, we select each Kramers pair as the subset. The eigenvalues of $\mathcal{W}[l]$ are expressed as $e^{2\pi nX(\mathbf{k})}/a$ for a loop $l$ wrapping the Brillouin zone and parametrized by $\mathbf{k}$ as in Fig. 2b (a: unit cell length). We can investigate the band topology using the Wannier-center positions $\pm X(\mathbf{k}) \in (-a/2, a/2)$ of the Kramers pair. The red and blue lines in Fig. 2a display schematically their motions as a function of momentum $\mathbf{k}$. A non-trivial topology is indicated if the Wannier centers move to a different unit cell as $\mathbf{k}$ is increased by $2\pi$. One can intuitively understand this as a Hall effect. When a dc-electric field is applied to the crystal in the $y$-direction, the momentum is replaced by $\mathbf{k} \rightarrow -i\mathbf{E}\mathbf{t}$ within the Peierls approximation ($E$: field strength, $t$: time). This leads to a Hall current $J_{M}$ as the Wannier-centers move perpendicular to the electric field. In contrast to the usual Hall effect, this Hall current is charge neutral because the two states in the Kramers pair move in opposite directions.

The present material PtCoO₂ turns out to be trivial within the 2D classification scheme of band topology, which is due to the weak violation of basal mirror symmetry $\sigma_h$ (We discuss the 3D classification in Supplementary A in which we show that an intersection of the CoO₂ bands above the Fermi level makes the Fermi surface band $Z_2$ non-trivial). However, this does not mean that the physical properties of the material are trivial. On the contrary, we show that this material realizes the physics of the mirror Chern metal, i.e., the bands and edge states are approximately quantified by the mirror Chern number. In order to clarify this, let us decompose the Hamiltonian into $H_{\text{tot}} = H_{M} + H_{\text{FB}}$ to consider the basal mirror-symmetric part $H_{M}$ first, and then discuss the perturbative effect of the anti-symmetric part $H_{\text{FB}}$ later. The motion of the two Wannier centers $\pm X(\mathbf{k})$ associated with each Kramers pair of bands are plotted in Fig. 2c, where red-blue and gray symbols are the results for $H_{M}$ and $H_{\text{tot}}$, respectively. We see that the trajectories for $H_{M}$ wrap the unit cell several times, and the winding number can be associated with mirror Chern numbers. Since mirror symmetry $\sigma_h$ is present for $H_{M}$, we can split the Kramers-degenerate bands into two mirror sectors $M_{\pm} = \{ |\mu_{\pm} \rangle; \sigma_{h}|\mu_{\pm} \rangle = \pm i|\mu_{\pm} \rangle \}$, where each band has its own Chern number $C(M_{\pm})$. While the total Chern number $C(M_{+}) + C(M_{-})$ vanishes due to TRS, the difference, the mirror Chern number $C_{M} = (C(M_{+}) - C(M_{-}))/2$ is a topological quantity coinciding with the wrapping of the Wannier center resulting in $C_{M} = +4, +2, -6, -2, +2$ for bands descending from the Fermi energy. The effect of the mirror-breaking term $H_{\text{FB}}$ turns out to be small as the gray and red-blue symbols appear to be on top of each other. However, as shown in Fig. 2e, small gaps open at crossing points of the Wannier centers except for those at $k_{x} = 0, \pi$ that are protected by Kramers degeneracy. As a consequence of the approximate mirror symmetry, pronounced helical edge states appear in the spectrum (Fig. 2d). The number of edge states appearing between the bands is given by the difference of the mirror Chern numbers. This clearly shows that the present system is characterized by the mirror Chern number, although the mirror is only an approximate symmetry and edge states have small gaps (see Fig. 2f). This leads to a concept of vicinity topology in which the phenomenology of a topological material such as exotic quantum transport or edge properties may become

- **Fig. 1.** Electronic structure. a, Crystal structure of PtCoO₂. b, Hexagonally warped Fermi surface (red curve) and the corresponding orbital eigenfunction (green). c, Band structure along high symmetry lines. Solid and dashed lines show the band dispersions with and without spin-orbit coupling, respectively. The spin-orbit coupling is $\lambda = 0.55$ eV. d, e, 3D picture of the tilted Dirac cone before and after adding the spin-orbit coupling. Their locations are indicated by circles in b, c. f, Pt layer with adjacent O atoms. g, Schematic picture of a typical hopping process forbidden in a basal-mirror symmetric structure.
realized even when the associated symmetry is not present in the whole structure.

As a physical consequence of the vicinity topology, we predict that an intrinsic spin Hall effect, underpinned by the mirror Chern number takes place in PtCoO$_2$. Indeed, we find large spin Hall conductivity $\sigma_{xy}^2$ (per layer) as shown in Fig. 3a, which is calculated with the Kubo formula:

$$\sigma_{xy}^2 = \frac{e}{\hbar} \sum_{k \in k} \Omega^2(k) f_{FD}(\varepsilon_{kn} - \mu),$$

$$\Omega^2(k) = \sum_{m \neq n} 2 \Im \langle \langle km | j_\parallel | kn \rangle \langle km | v_\parallel | kn \rangle \rangle. \tag{4}$$

Here $v$ is the velocity operator, $j_\parallel = (1/2) \langle \hbar \sigma_i/2, v_\parallel \rangle$ is the spin current operator, and $f_{FD}$ is the Fermi-Dirac function. It is convenient to use a hole picture starting from a fully-occupied Fermi-surface band. The fully occupied state (setting $\mu - 1$ eV) has no Hall response, and as we lower the chemical potential $\mu$, the spin Hall conductivity drastically increases. Figure 3b shows the momentum-resolved spin Hall conductivity, where the dominant contribution in (3) comes from the green region. This spin Hall effect can be traced back to the non-zero mirror Chern number in terms of vicinity topology, as the associated mirror Hall current is well spin polarized; see the spin component of (approximate) mirror eigenstates along the Fermi surface, shown in Supplementary Fig. 4.

It is interesting to compare this value with the fcc Pt known for a large intrinsic spin Hall effect. The spin Hall conductivity of PtCoO$_2$ shown above translates into $\sim 450(\hbar/e) (\Omega cm)^{-1}$ for the bulk, while the measured value for fcc Pt is $\sim 330(\hbar/e) (\Omega cm)^{-1}$. The calculated spin Hall coefficient in PtCoO$_2$ is not sensitive to temperature and is ex-
pected to persist to room temperature. This is because the Fermi surface band is well separated from the lower occupied bands and the inter-band cancellation in the integral (3) is weak.

For spintronic applications, it is important for the material to have a long spin relaxation time so that the spin current is well preserved\cite{27}. With the extremely long mean free path, the present material is already advantageous in this perspective\cite{15}. However, the richness of the orbital structure and the crystalline symmetry makes it even more attractive. Since the present system is inversion symmetric, spin relaxation from spin precession due to Rashba or Dresselhaus term, known as the D’yakonov-Perel mechanism\cite{27,28} is absent. Thus, spin relaxation mainly occurs through the Elliott-Yafet mechanism\cite{27,29,30}, i.e., accompanied by impurity and phonon scattering. As detailed in Supplementary D, the effective mirror symmetry protects the mirror Hall current against mirror-preserving scattering processes, and makes the spin relaxation time even longer.

As a future perspective, we point out that PtCoO$_2$ may serve as an experimental testbed for crystalline stable and metastable (or fragile) topologies\cite{6–8}. As opposed to stable topology, metastable topology entails topological notions of individual bands that do not necessarily persist when many bands are considered. The mirror symmetric parent $H_M$ has an additional $C_{2z} = i\sigma_h$ symmetry by virtue of inversion symmetry. While the mirror Chern number, protected by $\sigma_h$, is a stable topological indicator, the combined anti-unitary $C_2 T$ symmetry protects a metastable topological indicator also observable in the flow of Wannier centers. $C_2 T$ protects the Wannier center crossings at 0 and $\pm \pi$ within each isolated Kramers pair of bands\cite{78,31}, leading to a metastable Z classification of the flow of Wannier centers\cite{2} (see Supplementary B and C for details). What’s interesting about PtCoO$_2$ is that the two topological indicators can be separately broken, for example at the top surface. If we have a Pt layer surface, $\sigma_h$ is strongly broken since the oxygen is missing on one side, while $C_{2z}$ is only weakly broken due to the Co layer coupling as in the bulk. Thus, surface sensitive probes such as a scanning tunneling microscope may be able to access a state where only metastable topology is realized, making it possible study various theoretical proposals\cite{6–8}.

To summarize, we revealed here the rich orbital and topological physics behind PtCoO$_2$, and its interplay with the crystalline symmetry, including approximate ones. The retrieved mirror Chern numbers importantly pave the way for experimental and theoretical investigations into "vicinity topologies" that arise due to approximate symmetries, falling outside the scope of recent classification procedures\cite{19–21} but connecting to their physics (edge states, transport etc.) in an effective manner. The Wilson loop analysis intimately fits within this analysis as it can be utilized unbiasedly, signaling topologies by protecting crossings that can be slightly gapped in case of approximate symmetries.

METHODS

First-principles band calculation

We perform a first principles band calculation for PtCoO$_2$ adopting the lattice structure obtained in Ref. 10, and using the full potential linearized augmented plane wave method with the PBE-GGA exchange-correlation functional\cite{32} as implemented in the WIEN2K package\cite{33}. The scalar relativistic approximation is adopted for the relativistic effects of valence electrons. The value of $KK_{\text{max}}$ is set to 8, and 1,000 $k$-points are taken for the self-consistent calculation. From this band calculation, we obtain maximally localized Wannier orbitals, which consists of Pt $s$, $p \times 3$, $d \times 5$ orbitals, using Wannier90\cite{34–36} and Wien2Wannier\cite{37} packages.

The spin-orbit coupling, dropped in the scalar relativistic approximation, is explicitly added to the obtained tight-binding model as an on-site term. The strength of the spin-orbit coupling $\lambda$ is determined in such a way as to reproduce the energy level splitting at the $\Gamma$ point in the fully-relativistic band calculation. Our estimation $\lambda \sim 0.55$ eV agrees quite well with the theoretical values for the Pt atom calculated in more sophisticated frameworks\cite{38,39}.

Wilson loop eigenvalues

To carry out the computation of the Wilson loop operator (1), we consider an equidistant $k$-mesh $\{k_i\}_{i=1}^L$ on the path $l$ ($L$ is set to 150) and an operator $U_l = \langle k, m|k, n\rangle$, which converges to $\exp[i\mathbf{A}(k_i) \cdot d\mathbf{k}]$ in the continuous limit $L \to \infty$. The Wilson loop operator $W[l]$ is obtained as a matrix product $\left(\prod_{i=1}^L U_i\right)^\dagger$.

Edge states

The band dispersion shown in Fig. 2d is obtained in a slab geometry, i.e., we consider Pt sites at $R = (m - n/2, \sqrt{3}n/2)$ (in unit of $a$), where the translational invariance is present for one direction, $n \in \mathbb{Z}$, while the array of atoms is terminated in the other direction, $m = 1, \ldots, M$ ($M$ is set to 40).

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Appendix A: Three dimensional classification

In the present work, in order to capture in-plane transport properties, we have focused on the two-dimensional tight-binding model composed of Pt electrons only. However, there are also the bands derived from the CoO$_2$ layers in reality, and they weakly hybridize with the Pt bands via the inter-layer hopping. While it should not change the 2D transport properties, topological classification of bands may change when Pt-layer bands intersect CoO$_2$-layer bands. Indeed, the Pt Fermi-surface band intersects the Co-derived bands and has a different topological characterization in the three-dimensional classification. To verify this, we additionally take account of 3$d$ orbital of Co atoms and 2$p$ orbital of O atoms (at two distinct positions), and construct a twenty-band 3D tight-binding model.

We show the band structure in Supplementary Fig. 1, where we colored the band by the weights of the additional atoms (blue for Co and red for O). As in the ionic-bond picture, the Co 3$d$ bands split into lower three ($a_{1g}$ and $e_{g}^\pi$) and upper two ($e_{g}^{\sigma}$) bands due to the crystal field, which results in formation of a band insulator. We note that the size of this splitting may be underestimated since the local-density approximation for the density functional fails to capture the correlated nature of 3$d$ electrons. Notably, the Fermi-surface band has intersections with the Co $e_{g}^{\sigma}$ bands, and undergoes the band inversion at the M point leading to an interchange of the inversion eigenvalues. As a result, the Fermi-surface band has a nontrivial strong index in terms of the three-dimensional classification of the topological insulators, which ensures that the helical edge states appear in between the Fermi-surface band and the Co $e_{g}^{\sigma}$ bands.

Although this reflects the topological richness of the present system, we emphasize that the two-dimensional characterization along with the approximate mirror symmetry given in the main text should be essential for the (in-plane) transport properties, since the corresponding edge states are responsible for the spin Hall response.

Appendix B: $\mathbb{Z}_2$ Fu-Kane-Mele class and $\mathbb{Z}$ mirror Chern class

PtCoO$_2$ belongs to space group (SG) $\bar{R}3m$ (#166) that is a symmorphic space group obtained from the combination of the rhombohedral Bravais lattice with point group $D_{3d} = \{E, 2C_3, 3C'_3, I, 2IC_3, 3IC'_3\}$. Due to TRS ($T$) and inversion symmetry ($I$) every band is at least doubly degenerate, i.e. they form Kramers pairs, over the whole Brillouin zone. We show in Supplementary Fig. 2a the band structure of the 9-band tight-binding model of PtCoO$_2$, where we label the bands (Kramers pairs) from below as $\{B_1, B_2, B_3, B_4, B_5, B_6, B_7, B_8, B_9\}$. We observe that every two successive bands are disconnected by a gap such that the topology of each band can be characterized separately. Importantly for the topological characterization of the bands we

Supplementary Figure 1. Band structure of the twenty-band tight-binding model with spin-orbit coupling along high-symmetry lines (of the 2D Brillouin zone). Weight of Co (O) electrons is represented by blue (red).
define that two bands are separated by a gap if we can find an energy gap between the bands at every \( k \) of the Brillouin zone independently of the dispersion relation of the gap. In the following we refer to the gap between the two successive bands \( \mathcal{B}_i \) and \( \mathcal{B}_{i+1} \) as \( \Delta_{i,i+1} \). We note that the Fermi level crosses the band \( \mathcal{B}_5 \) and hence crosses the gap \( \Delta_{35} \) and \( \Delta_{56} \).

We show the edge spectrum of the 9-band tight-binding model of PtCoO\(_2\) obtained on a slab geometry, in Fig. 2d and Supplementary Fig. 2b for below and above the Fermi level, respectively. We deduce the presence of edge states within the gaps \( \{\Delta_{12}, \Delta_{34}, \Delta_{45}, \Delta_{67}, \Delta_{89}\} \), and no edge states within the gaps \( \{\Delta_{23}, \Delta_{56}, \Delta_{78}\} \). In the following we determine their topological origin which turns out to be intrinsically related to the crystalline symmetries PtCoO\(_2\).

Centrosymmetry allows for a straightforward computation of the Fu-Kane-Mele \( \mathbb{Z}_2 \) invariant of every band in terms of the inversion eigenvalues at the time-reversal invariant momenta\(^\text{17} \), see Supplementary Fig. 2c. Supplementary Figure 2c shows that two bands above the Fermi level have nontrivial Fu-Kane-Mele topology (\( \mathcal{B}_6 \) and \( \mathcal{B}_7 \)), while the Fu-Kane-Mele invariants of all the other bands are trivial. We therefore conclude that the edge states within the gap \( \Delta_{67} \) and \( \Delta_{56} \) host the helical edge states of a topological insulator which are protected by TRS only. The many other edge states observed in Fig. 2d and Supplementary Fig. 2b, especially at the Fermi level, must have a different explanation.

It turns out that the bands of PtCoO\(_2\) around the Fermi level only slightly break basal-mirror symmetry \( \sigma_b \) (=\( IC_2 \)) such that they bear features reminiscent of the higher symmetric space group SG191 whose point group is \( D_{3h} = D_{3d} \times \{\sigma_b\} \). By globally imposing \( \sigma_b \) symmetry the mirror Chern number\(^3 \) of every band is well defined by its presence. For this we simply compute the Chern number within eachmirror symmetry sector, i.e. \( C^+_i(\sigma_b) \) from even (odd) eigenstates under \( \sigma_b \). Practically it is most easily done by writing the Bloch Hamiltonian in the form \( \mathcal{H} = \mathcal{H}_r \oplus \mathcal{H}_l \), i.e. splitting the two mirror sectors, and then to compute the Chern number from a single block; the Chern number of the other block is then simply given through time reversal, i.e. \( C^-_i(\sigma_b) = - C^+_i \). Remarkably we find a nonzero mirror Chern number in each band, namely \( C^+_1(\mathcal{B}_1) = +2 \), \( C^+_2(\mathcal{B}_2) = -2 \), \( C^+_3(\mathcal{B}_3) = -6 \), \( C^+_4(\mathcal{B}_4) = +2 \), \( C^+_5(\mathcal{B}_5) = +4 \), \( C^+_6(\mathcal{B}_6) = -3 \), \( C^+_7(\mathcal{B}_7) = +3 \), \( C^+_8(\mathcal{B}_8) = -2 \), \( C^+_9(\mathcal{B}_9) = +2 \), see Supplementary Fig. 3. We note that this agrees with the \( \mathbb{Z} \) classification by K-theory of two-dimensional mirror symmetric topological insulators of the class AII\(^40 \).

It is now straightforward to deduce the edge states making use of the bulk-boundary correspondence for the Chern class\(^41 \) within a single mirror sector, i.e the number of edge states is reflected in the difference in Chern number between gapped sets of bands. From the bulk mirror Chern numbers obtained above, we deduce the existence of two chiral edge branches crossing the gap \( \Delta_{12} \), no edge states within the gap \( \Delta_{23} \), six chiral edge branches crossing the \( \Delta_{34} \), four chiral edge branches within \( \Delta_{45} \), no edge states within the gap \( \Delta_{56} \), three chiral edge branches within \( \Delta_{67} \), no edge states within the gap \( \Delta_{78} \), and two chiral edge branches within \( \Delta_{89} \). This seems to match perfectly with the edge spectrum of Fig. 2d and Supplementary Fig. 2b, albeit sometimes hard to see due to the narrow band gaps. Since the total mirror Chern number for the bands \( 1, 2, \ldots, 5 \) is zero—the Chern class is additive in the vector bundle sense, i.e. \( C^+_1(\mathcal{B}_1 \oplus \mathcal{B}_3 \oplus \mathcal{B}_5) = C^+_1(\mathcal{B}_1) + C^+_3(\mathcal{B}_3) + C^+_5(\mathcal{B}_5) = 2 + (-6) + 4 = 0 \)—we do not expect edge states within the gap \( \Delta_{56} \), in agreement with Fig. 2d. The gap \( \Delta_{56} \) hosts chiral edge states that cross the Fermi level, as a consequence of the bulk mirror Chern numbers \( C^+_1(\mathcal{B}_1 \oplus \mathcal{B}_3 \oplus \mathcal{B}_5) = -4 \) and \( C^+_5(\mathcal{B}_3 \oplus \mathcal{B}_5) = +4 \).

We conclude that, in addition to the two bands with nonzero Fu-Kane-Mele invariant, the edge states of PtCoO\(_2\) are reminiscent of the nontrivial topology of the \( \sigma_b \)-symmetric parent model. Once again, we emphasize that this is because of the weak breaking
of the basal mirror, giving the possibility to observe vicinity topologies as a results of approximate symmetries. Indeed, the robustness of the edge states at the Fermi level originates from the almost perfect $\sigma_h$ symmetry of the bands in the vicinity of the Fermi level, see Supplementary Fig. 4.

Appendix C: Metastable (fragile) topology in PtCoO$_2$

We here want to briefly consider the connection to the recently coined concepts of metastable (fragile) topologies. It has been shown that hexagonal lattices naturally hosts nontrivial topology enforced by the crystal symmetries and TRS$^7$, which can be related to the separation of elementary band representations by energy gaps$^{20,42}$. The existence of separable elementary band representations for a given space group depends the Wyckoff quantisation of Wilson loop windings. Indeed, the combined anti-unitary $C\pi$ Kramers pair over the Brillouin zone is then readily given through the Wilson loop matrix of any Kramers pair of bands is $\mathcal{W}(\pi) \in \text{SO}(2)$. The classification of Wilson loop windings of a Kramers pair over the Brillouin zone is then readily given through $\pi_4(\text{SO}(2)) = \mathbb{Z}$. Therefore, when $\sigma_h$ and $I$ are broken, while $C_2$ is preserved, the Wilson loop windings of type of Fig. 2c will remain, as a consequence of the fact that Wilson crossings at 0 and $\pm \pi$ are protected by $C_2T$. This feature is stable for any Kramers pair of bands that is separated by an energy gap above and below from the other bands. However the fact that $\pi_4(\text{SO}(n)) = \mathbb{Z}_2$ when $n > 2$ readily tells us that it cannot pertain to thermodynamical (stable) properties of the system and rather characterises its metastable (fragile) properties. We thus conclude that these notions may find a suitable testbed in PtCoO$_2$.

Appendix D: Spin polarization of the mirror eigenstate and the Elliott-Yafet mechanism for spin relaxation

In the Elliott-Yafet mechanism, the spin flipping process occurs even in nonmagnetic scattering because spin is no longer conserved in the presence of the SOC. The breaking of the spin conservation is especially crucial when the SOC is strong as in the present system. However, since the spin flip also alters the mirror eigenvalue, such processes are strongly suppressed when the mirror symmetry $\sigma_h$ is present.

To understand this in a more quantitative manner, let us see how much the spin and mirror conservation are broken in the Fermi surface of the present system. We denote the Kramers-degenerate eigenstates on the Fermi surface as $|\tilde{\theta}\rangle$, where $\tilde{\theta}$ is the
Supplementary Figure 4. Weight of spin and orbital component for the effective spin-up wave function on the Fermi surface $|\theta\uparrow\rangle$, parametrized by the angle in momentum space $\theta$. $\theta = 0$ is set to the $\Gamma$–M direction. Red (blue) indicates spin-up (down) component. Note the logarithmic scale in the zoomed plot in the right panel.

Angle in momentum space and $\sigma = \uparrow, \downarrow$ is defined to satisfy $\langle \theta\uparrow | \sigma_z | \theta\downarrow \rangle = 0$. While these eigenstates are usual spin-polarized states when the SOC is absent, they are represented as

\[
|\theta\uparrow\rangle = \sum_m [a_{\theta m}|m\rangle \otimes |\uparrow\rangle + b_{\theta m}|m\rangle \otimes |\downarrow\rangle], \tag{S1}
\]

\[
|\theta\downarrow\rangle = \sum_m [a^*_{\theta m}|m\rangle \otimes |\downarrow\rangle - b^*_{\theta m}|m\rangle \otimes |\uparrow\rangle], \tag{S2}
\]

with nonzero spin mixing $\sum_m |b_{\theta m}|^2$ due to the broken spin conservation with finite SOC. Here $m$ labels the orbitals and $|\uparrow\rangle, |\downarrow\rangle$ is the spin basis. This mixing leads to spin flip even in nonmagnetic scattering, whose amplitude is characterized by a factor $|\langle \theta\uparrow | W | \theta\downarrow \rangle|^2$ in the golden rule calculation ($W$: scattering matrix).

The amplitudes $|a_{\theta m}|^2$, $|b_{\theta m}|^2$ are plotted in Supplementary Fig. 4 for $|\theta\uparrow\rangle$. While the spin mixing of $\sum_m |b_{\theta m}|^2 \sim 0.03$ is as large as typical heavy elements (e.g., $\sim 0.01$ for In, $\sim 0.05$ for Pb, and $\sim 0.1$ for Hg\textsuperscript{45}), the Fermi surface also has a rich orbital structure. This may be advantageous since the spin flip amplitude also depends how the scattering matrix $W$ mixes the orbital degree of freedom. In particular, when $W$ is mirror symmetric (such as in-plane defects of Pt atoms), mirror (and spin) flip should be strongly prevented thanks to the approximate mirror symmetry $\sigma_h$. The mirror flipping amplitude is associated with the breaking of the mirror conservation, which is, as clearly shown in Supplementary Fig. 4, remarkably small $\sim 10^{-4}$. Namely, mirror-symmetric channels are much less effective on the spin relaxation, and only mirror-breaking channels (such as oxygen vacancies) contribute to the spin relaxation. Hence, the spin diffusion length in the present system is expected to be long in spite of a strong SOC.