Signature of Hidden Orbital-Texture in Photoemission Time-Reversal Dichroism

S. Beaulieu1*, J. Schusser2,3, S. Dong1, T. Pincelli1, M. Dendzik1,4, J. Maklar1, A. Neef1, H. Ebert5, K. Hricovini5,6, M. Wolf5, J. Braun5, L. Rettig1, J. Minár2*, R. Ernstorfer1*

1Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
2Laboratoire de Physique des Matériaux et Surfaces, CY Cergy Paris Université, 95031 Cergy-Pontoise, France
3New Technologies-Research Center, University of West Bohemia, 30614 Pilsen, Czech Republic
4Department of Applied Physics, KTH Royal Institute of Technology, Electrum 229, SE-16440, Stockholm, Kista, Sweden
5Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 11, 81377 München, Germany
6LIDYL, CEA, CNRS (UMR 9222), Université Paris-Saclay, CEA Saclay, F-91191, Gif-sur-Yvette Cedex, France

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We performed angle-resolved photoemission spectroscopy (ARPES) of bulk 2H-WSe$_2$ for different crystal orientations linked to each other by time-reversal symmetry. We introduce a new observable called time-reversal dichroism, which quantifies the modulation of the photoemission intensity upon effective time-reversal operation. We demonstrate that the hidden orbital-structure of the crystal's electronic structure leaves its imprint onto the time-reversal dichroism, due to multiple orbitals interference effects in photoemission. Our experimental results are in quantitative agreement with state-of-the-art fully relativistic calculations performed using the one-step model of photoemission. While spin-resolved ARPES probes the spin component of entangled spin-orbital texture in multiorbital systems, we demonstrate that time-reversal dichroism is sensitive to its orbital-texture counterpart.

Locking between spin and valley degrees of freedom emerges in solids possessing a combined broken inversion symmetry and strong spin-orbit coupling, leading to peculiar valley dependent spin-texture in momentum-space. This spin-valley locking leads to optical selection rules allowing for the generation of spin- and valley-polarized excited carriers [13], which can be used for all-optical selective spin injection [4,5]. In multiorbital systems, additional locking between crystal momentum and orbital angular momentum emerges as a consequence of band hybridization, leading to complex entangled spin-orbital textures, as predicted in some topological insulators (TIs) [6,7], two-dimensional electronic gases (2DEGs) [8] and transition metal dichalcogenides (TMDs). The resulting momentum-space orbital-texture can lead to orbital Hall effect (OHE) [9], orbital Rashba effect [10], and the emergence of orbital Hall insulating phases [11]. Orbitronics [12], i.e. encoding (quantum) information in the orbital angular momentum degree of freedom, can be seen as a newly emerging field, in analogy to spin- and valleytronics [13,14].

TMDC monolayers are emblematic materials with entangled spin-, orbital- and valley-degrees of freedom. In a minimal electronic structure model of TMDC monolayers [15], the valence band top at the Brillouin zone boundary (K/K') points can be described by $|K'/K\rangle \equiv \left[\left|d^V_{z^2-y^2}\right\rangle \pm i\left|d^V_{xy}\right\rangle \right\rangle \otimes \left|\uparrow/\downarrow\right\rangle + \left[\left|d^V_{x^2-y^2}\right\rangle \pm i\left|d^V_{xy}\right\rangle \right\rangle \otimes \left|\downarrow/\uparrow\right\rangle$, where the label VB1 and VB2 represented the two first spin-orbit split valence bands. While the spin texture is determined by the momentum-dependent spin state ($|\uparrow\rangle$ or $|\downarrow\rangle$), the orbital-texture is set by the valley-dependent orbital angular momentum (OAM) ($L^K_{z}/K' = \pm 2\hbar$) = $|d^V_{z^2-y^2}\rangle \pm i|d^V_{xy}\rangle$). In this case, the orbital-texture is thus governed by the valley-dependent relative phase between the in-plane transition metal d orbitals. Moreover, the $|K\rangle$ and $|K'\rangle$ valleys are related to each other via the time-reversal operator, i.e $\hat{T}|K\rangle = |K'\rangle$. In TMDC monolayers, swapping valley indexes (time-reversal) thus reverses both the spin and orbital textures. However, in bulk-TMDC of 2H polytype, the adjacent layers are rotated by 180° with respect to each other, leading to opposite and alternating local-spin polarization and orbital-texture between neighboring layers. This peculiar layered structure naturally introduces the concept of "hidden" spin- and orbital-texture, which exists within each layer, but vanishes in the bulk, i.e. when the inversion-symmetry of the crystal is restored [16]. Probing such "hidden" physical properties is experimentally challenging. While spin- and angle-resolved photoemission spectroscopy (sARPES) is now a well established surface sensitive technique to investigate hidden spin-texture [17–19], an experimental technique allowing to selectively probe its hidden orbital-texture counterpart has not been established.

We perform extreme ultraviolet (XUV) angle-resolved photoemission spectroscopy (ARPES) of bulk 2H-WSe$_2$ for crystal orientations rotated by $\alpha = 60^\circ$ with respect to each others ($R_{60^\circ}$) effectively acting as the time-reversal operator ($\hat{T}$): $R_{60^\circ}|K\rangle \equiv \hat{T}|K\rangle = |K'\rangle$. We introduce a novel observable, time-reversal dichroism ($A_T$), which probes the modulation of the photoemission intensity upon time-reversal, and which is shown to be sensitive to the orbital texture, due to multiple orbitals interference effects in photoemission. We show that time-reversal dichroism is free of any spurious contribution from experimental geometry, which typically complicates the interpretation of
FIG. 1. Modulation of the photoemission intensity upon time-reversal ($\hat{T}$): (a) Scheme of the experimental setup: a $p$-polarized fs-XUV (21.7 eV) pulse is focused onto a bulk 2H-WSe$_2$ crystal at an angle of incidence of 65° with respect to the surface normal, ejecting photoelectrons which are detected by a time-of-flight momentum microscope. (b)-(c) Scheme of the experimental geometry and the spin-orbital texture: the scattering plane (light purple plane) coincides with the crystal mirror plane ($\mathcal{M}$, green dashed line), which is along the $\Gamma$-M high symmetry direction. The spin-orbital texture is schematically represented by the orbitals and the up/down spin state at each K/K' valleys. A 60° azimuthal rotation of the crystal ($\mathcal{R}_{60^\circ}$) yields the transformation of K to K' valley (and vice-versa), and is analogue to the action of the time-reversal operator; i.e. $\mathcal{R}_{60^\circ}|K\rangle \equiv \hat{T}|K\rangle = |K'\rangle$. (d)-(e) Constant energy contours for different energies, $E - E_{VBM}$, measured for the two different crystal orientations described above ($I_{0^\circ}$ and $I_{60^\circ}$). The radius of each constant energy contour corresponds to 1.6 Å$^{-1}$.

The experimental apparatus features a table-top femtosecond (fs) XUV (21.7 eV, 110 meV FWHM bandwidth) beamline [22] coupled to a time-of-flight momentum microscope spectrometer (METIS 1000, SPECS GmbH), see Fig. 1(a). This detector allows for simultaneous detection of the full first Brillouin zone, over an extended binding energy range, without the need to rearrange the sample geometry [23]. More details about the experimental setup can be found elsewhere [22] [24] and in the SM. As shown in Fig. 1 (d)-(e), we recorded the 3D photoemission intensity for two different crystal orientations, rotated by 60° with respect to each other. Looking at the experimentally measured constant energy contours (CECs) for energy $E - E_{VBM} = -0.25$ eV, one can see that the photoemission intensity is strongly anisotropic around each K/K' valley, describing "croissant"-shaped patterns. This has been recently explained as originating from interference between photoelectrons emitted from the in-plane transition metal $d_{xy}$ and $d_{x^2-y^2}$ orbitals [25]. The azimuthal variation of the photoemission intensity around K/K' points, i.e. the orientation of the "croissant", changes upon rotation of the crystal by 60°. This is a signature of the modification of...
FIG. 2. Extraction of the time-reversal dichroism ($A_T$): (a)-(b) $I^{0\circ}$ and $I^{60\circ}$, the constant energy concours (CECs) for $E - E_{VBM} = -1.60$ eV, measured for two crystal orientations rotated by $60^\circ$ with respect to each other. (c) $\Delta I/I$, the raw normalized difference, i.e. $(I^{0\circ} - I^{60\circ})/(I^{0\circ} + I^{60\circ})$ between CECs shown in (a) and (b). (d)-(e) $A_{LDAD}^{0\circ}$ and $A_{LDAD}^{60\circ}$, the “left-right asymmetries”, reflect the photoemission intensity asymmetry between the $k_x < 0$ and $k_x > 0$ hemispheres, for two crystal orientations, respectively, and are calculated using Eq. 1. (f) $A_T$, the time-reversal dichroism, is calculated using Eq. 2, and represents the component of $A_{LDAD}^{0\circ}/A_{LDAD}^{60\circ}$ which is antisymmetric upon time-reversal (i.e. upon $60^\circ$ azimuthal rotation of the crystal).

the relative phase between $d_{xy}$ and $d_{x^2-y^2}$ orbitals (orbital-texture) upon time-reversal (K $\rightarrow$ K', and vice-versa). A modification of the momentum-resolved photoemission intensity upon time-reversal can also be seen for larger binding energies in Fig. 1(d)-(e). Anisotropies in the photoemission intensity emerging from multiorbital interferences are intertwined with additional modulation of the photoemission intensity coming from the matrix element dependence on the experimental geometry. In the following, we will demonstrate that proper analysis of the linear dichroism in the angular distribution for different crystal orientations allows us to completely isolate the signal emerging from the modification of the hidden orbital-texture upon time-reversal.

Dichroism in the angular distribution (both linear, LDAD, and circular, CDAD) are powerful quantities relying on the modulation of the photoemission transition dipole matrix element upon the change of the ionizing radiation polarization state. CDAD has been used to probe electronic chirality in graphene [26], helical spin-texture in topological insulator [27] and Berry curvature in TMDCs [28, 29], for example. LDAD is typically assumed to encode the non-relativistic symmetry of the ground state wavefunction [30–32], which contains information about the orbital-texture [33, 34]. However, dichroism can also have an extrinsic origin, i.e. it can emerge solely from experimental geometry symmetry breaking. Disentangling the intrinsic and extrinsic contribution to the dichroic signal is very challenging, but of fundamental importance to extract meaningful physical insight from it.

Using our multidimensional detection scheme with the $p$-polarized fs-XUV pulses incident in the $k_x$-$k_z$ plane (and along $\Gamma$-M/ M'), the normalized intensity differences between the forward ($I^\alpha(k_x, k_y, E_B)$) and backward ($I^\alpha(-k_x, k_y, E_B)$) hemisphere, i.e. the linear dichroism asymmetry in the photoelectron angular distribution ($A_{LDAD}^\alpha (k_x, k_y, E_B)$), can be extracted (see Eq. 1), without the need to rearrange the sample geometry or the light-polarization state [35, 36].

\[
A_{LDAD}^\alpha = \frac{I^\alpha(k_x, k_y, E_B) - I^\alpha(-k_x, k_y, E_B)}{I^\alpha(k_x, k_y, E_B) + I^\alpha(-k_x, k_y, E_B)}
\] (1)

Looking at $A_{LDAD}^{0\circ}$ and $A_{LDAD}^{60\circ}$ (Fig. 2(d)-(e)), one can notice that some features of the dichroism are invariant upon time-reversal, while others show antisymmetric behavior (sign flip). This can be understood by the fact that the contribution to the dichroism originating from experimental geometry remains unchanged upon $60^\circ$ rotation of the crystal. Moreover, depending on the energy-momentum region of the electronic structure sampled in each...
FIG. 3. Comparison between experimentally measured and theoretically calculated time-reversal dichroism ($A_T$). In the upper hemisphere of each panel, the raw photoemission intensity, and in the lower hemisphere, the time-reversal dichroism ($A_T$). (a)-(d) Experimentally measured photoemission intensity and time-reversal dichroism. (e)-(i) Calculated photoemission intensity and time-reversal dichroism. (a) and (e) $E - E_{VBM} = -0.20$ eV, (b) and (f) $E - E_{VBM} = -0.75$ eV, (c) and (g) $E - E_{VBM} = -1.60$ eV and (d) and (i) $E - E_{VBM} = -2.07$ eV. The radius of each constant energy contour corresponds to 1.6 Å⁻¹.

The idea behind the introduction of this new observable called time-reversal dichroism $A_T$ is to isolate the antisymmetric part of the $A_{LDAD}$ dichroism upon time-reversal, in order to remove any spurious contributions from experimental geometry and from bands of single-orbital character. Time-reversal dichroism is defined as,

$$A_T = \frac{A_{\alpha LDAD} - A_{\alpha' LDAD}}{2}$$  \hspace{1cm} (2)

where crystal rotation by an angle $\alpha - \alpha'$ ($R_{\alpha - \alpha'}$) is equivalent to time-reversal, i.e. $R_{\alpha - \alpha'} \equiv \hat{T}$. The resulting $A_T$ is shown in Fig. 2(f). The branches pointing along Γ-M have opposite $A_{LDAD}$ with respect to adjacent valleys and dominates the signal, while the signature of the hexagonal-shaped band surrounding the Γ-point, which is of single orbital character ($|p_z\rangle$), does not.

Indeed, a non-vanishing $A_T$ signal implies that the state-resolved dichroism changes sign upon time-reversal operation, which we interpret as a switch of the orbital texture. This novel observable is thus intrinsically free of any detrimental contribution from the experimental geometry and is related to the hidden relative phase between orbitals contributing to the photoemission signal (i.e. the hidden orbital texture).

To verify the microscopic origin of the time-reversal dichroism, we perform state-of-the-art quantitative one-step photoemission calculations based on fully relativistic density functional theory (DFT). The one-step model of photoemission is implemented in the fully relativistic Korringa-Kohn-Rostoker (KKR) method. The calculated photoemission signal is layer-resolved and includes all matrix element effects such as experimental geometry, photon energy, polarization state, and final state effects (see SM and refs. [21, 40]).

The striking similarity between experimental and theoretical results (Fig. 3) confirms that the KKR method accurately describes the ground state properties of bulk 2H-WSe$_2$ in an extended binding energy range and captures well subtleties of the photoemission process, including multiorbital interference effects. Now that the ability of the KKR method to quantitatively reproduce the experimentally measured signals is established, we will exploit the possibility to theoretically dissect the origin of the photoemission signal, in order to gain additional insights about the microscopic origin of the time-reversal dichroism.

First, we want to strengthen our assert that the time-reversal dichroism in XUV photoemission probes hidden physical quantities, i.e. quantities that are non-vanishing in each constituent layers but that are vanishing in its inversion-symmetric counterpart (bulk). To do so, we investigated the atomic-layer-resolved photocurrent and associated time-reversal dichroism. In Fig. 3(a), the photoemission intensity and associated time-reversal dichroism for signals coming from all layers (bulk) are presented. The outer (VB1) and inner (VB2) bands around each K/K’ valleys show very similar dichroism, i.e. the same positive/negative (red/blue) time-reversal dichroism patterns. While the
FIG. 4. Theoretical investigations of the microscopic origin of the time-reversal dichroism. In the upper panels, we study the atomic-layer resolved photocurrent and associated time-reversal dichroism. The signal is coming from (a) all layers (All L), (b) first Se atomic layer (Se), (c) first Se and W atomic layers (Se-W), and (d) first Se and W, and second Se atomic layers (Se-W-Se). In the lower panels, we investigate the role of spin-orbit coupling on the photocurrent and associated time-reversal dichroism, by going from the fully relativistic to the non-relativistic limit, upon modulating the speed of light in the calculations. (e) For ‘standard’ speed of light (fully relativistic), which we defined as $1/c^2 = 1$. (f)-(i) For enhanced speed of light, $1/c^2 = 0.5$, $1/c^2 = 0.25$, and $1/c^2 = 10^{-3}$ (non-relativistic limit), respectively. All the constant energy contours are taken at $E - E_{VBM} = -0.75$ eV, and their radii correspond to $1.6 \text{ Å}$. 

$A_T$ signal coming from the topmost selenium (Se) atomic layer (Fig. 4(b)) is strongly different from the one of the full calculation (Fig. 4(a)), including the photocurrent from the first tungsten (W) layer (Fig. 4(c)) is already enough to almost perfectly reproduce all features of the full calculation, which is in good agreement with the predicted W $d_{xy}$ and $d_{x^2-y^2}$ orbitals nature of the valence band at K/K’ points. These calculations unambiguously confirm that time-reversal dichroism probes hidden physical quantities, which are modulated upon time-reversal.

Second, we want to fully disentangle the signatures of spin- and orbital-textures on time-reversal dichroism. To do so, we have investigated the photoemission intensity and associated time-reversal dichroism in both the fully relativistic and non-relativistic limit (vanishing spin-orbit coupling (SOC)). Indeed, SOC is at the origin of the hidden spin-polarization of the two topmost valence bands at K/K’, and thus of the emergence of the peculiar spin-texture in 2H-TMDCs. In the limit where SOC vanishes (non-relativistic limit), the two oppositely spin-polarized topmost valence bands at K/K’ are merging together, leading to the annihilation of the spin-polarization, but to a conservation of the orbital-texture. Because the dominant relativistic corrections scale with $1/c^2$, where $c$ is the speed of light, a straightforward theoretical approach to go from the fully relativistic to the non-relativistic limit, and thus to modify the strength of SOC, is to modulate the speed of light. In Fig. 4(e), one can see that in the fully relativistic case, the topmost valence band at K/K’ are spin-orbit-split, and have similar time-reversal dichroism patterns, already suggesting its sensitivity to orbital-texture. Strikingly, the non-relativistic time-reversal dichroism from the degenerate band at K/K’ is identical to the dichroism of the associated topmost valence band in the fully relativistic case. This observation is a smoking-gun evidence that the time-reversal dichroism is a powerful probe of the hidden orbital-texture, which exists even in the absence of spin-orbit coupling and thus of spin-texture.

Last, we want to briefly discuss the main conceptual differences between the newly introduced time-reversal dichroism and well-established circular dichroism (CD-ARPES), which has recently been shown to be sensitive to the local Berry curvature [28, 29], a quantity intimately related to the local orbital angular momentum. Indeed, both Berry
curvature and orbital-texture originate from the hybridization of orbitals. Hybridization results in a valley-dependent relative phase between participating orbitals, which can also be understood as a valley-dependent imbalance of the occupation of angular momentum states. In CD-ARPES, circularly polarized photons with well-defined spin angular momentum thus preferentially photoemit electrons for given valleys, associated with a given imbalance of angular momentum states, resulting in a non-vanishing valley-integrated dichroic signal [29]. On the other hand, time-reversal dichroism, which here relies on the use of linearly polarized photons, results in a vanishing valley-integrated dichroism, but in clear momentum-resolved dichroism within each valley, which switch sign, i.e. is antisymmetric, upon time-reversal. This originates from the orbital’s relative-phase sensitivity due to the interferometric nature of photoemission, explaining the sensitivity of time-reversal dichroism to the (hidden) orbital texture.

In conclusion, we have introduced a novel and fully general observable in angle-resolved photoemission spectroscopy called time-reversal dichroism, which probes the modulation of the photoemission intensity upon crystal rotation mimicking time-reversal. We have demonstrated that the hidden orbital texture of prototypical bulk 2H-WSe$_2$ leaves its imprint onto the time-reversal dichroism through the multiorbital interference process in photoemission. This observable is free of contributions from experimental geometry, which are typically present in (linear or circular) dichroism in ARPES. Similar to the role of spin-resolved ARPES to experimentally elucidate complex momentum-space spin-texture, we envision that time-reversal dichroism in ARPES could emerge as the new standard observable to probe peculiar momentum-space orbital-texture in complex multiorbital materials. Moreover, extension of the approach to time-resolved time-reversal dichroism experiments is straightforward and will give access to the orbital-texture of excited states and changes of orbital texture in out-of-equilibrium states, on ultrafast timescales.

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Supplementary Material:
Signature of Hidden Orbital-Texture in Photoemission Time-Reversal Dichroism

S1. DETAILS ABOUT THE EXPERIMENTAL SETUP

The experimental apparatus features a table-top femtosecond XUV beamline coupled to a photoemission end-station. Briefly, a home-built optical parametric chirped-pulse amplifier (OPCPA) delivering 15 W (800 nm, 30 fs) at 500 kHz repetition rate [37] is used to drive high-order harmonic generation (HHG) by tightly focusing the second harmonic of the laser pulses (400 nm) onto a thin and dense Argon gas jet. The nonperturbative nonlinear interaction between the laser pulses and the Argon atoms leads to the generation of a comb of odd harmonics of the driving laser, extending up to the 11th order. A single harmonic (7th order, 21.7 eV) is isolated by reflection on a focusing multilayer XUV mirror and propagation through a 400 nm thick Sn metallic filter. A photon flux of up to $2 \times 10^{11}$ photons/s at the sample position is obtained (110 meV FWHM). The bulk 2H-WSe$_2$ samples (HQ Graphene) were cleaved at room temperature and base pressure of $5 \times 10^{-11}$ mbar, and handled by a 6-axis manipulator (SPECS GmbH). The photoemission data are acquired using a time-of-flight momentum microscope (METIS1000, SPECS GmbH). This detector allows for simultaneous detection of the full surface Brillouin zone, over an extended binding energy range, without the need to rearrange the sample geometry [23]. Concerning the data post-processing, we use a recently developed open-source workflow [38] to efficiently convert the raw single-event-based datasets into binned calibrated data hypervolumes of the desired dimension (here 120x120x120, corresponding to 0.038 Å$^{-1}$ and 67 meV bin sizes), including axes calibration and artifact corrections (including symmetry distortion corrections [39]). The resulting 3D photoemission intensity data have the coordinates $I(k_x, k_y, E_B)$.

S2. DETAILS ABOUT THE KKR CALCULATIONS

As mentioned in the manuscript, our photoemission calculations are based on fully relativistic density functional theory (DFT). The one-step model of photoemission is implemented in the fully relativistic Korringa-Kohn-Rostoker (KKR) method of the Munich band structure software package, based on Green’s function and multiple scattering spin-density matrix formalism [41]. The SPR-KKR scheme solves the Dirac equation, hence all the relativistic effects are fully included. The local density approximation (LDA) has been chosen as an exchange-correlation functional. The bulk potential converged in atomic spheres approximation geometry. The bulk 2H-WSe$_2$ crystallizes in a $P6_3/mmc$ structure with a lattice constant of 3.280 Å. We employed the same empty sphere placement as described in [42]. To obtain a good fit to the experimental data, it was needed to modify the Wigner-Seitz radius of individual atomic types to the following ratio: W = 1.24, Se = 1 and the vacuum type = 1.04. We found a good agreement between the ground state potential which we obtained with the ASA and a full potential calculations as implemented in SPR-KKR. We used $l_{max}=3$ to obtain the self-consistent field. After the self-consistency was reached, the one-step model of photoemission was used to calculate the photoemission intensities, using the same geometries as in the experiments. The photoemission signal includes all the matrix element effects such as experimental geometry, photon energy, polarization state, and final state effects.

S3. BAND STRUCTURE: COMPARISON BETWEEN EXPERIMENT AND KKR CALCULATION

As explained in the previous subsection, after the optimization of the Wigner-Seitz radius of individual atomic types, we reached a very good agreement with the experimentally measured electronic band structure of bulk 2H-WSe$_2$. To qualitatively show the agreement between experimentally measured band structure, we have plotted the experimentally measured photoemission intensity along Γ-K and Γ-M high symmetry directions, as well as the corresponding calculated photoemission intensity using the one-step model of photoemission (SPR-KKR). The data are shown in Fig. S5.
S4. KKR Simulations: From the Fully Relativistic to the Non-Relativistic Limit

As described in detail in the manuscript, in TMDCs, the combined broken inversion symmetry within each layer and the large spin-orbit coupling lead to peculiar momentum-space spin-orbital textures. In order to disentangle the effect of spin from orbital degrees of freedom, it would be particularly interesting to have a theoretical way to manipulate the spin-orbit coupling (SOC), and investigate the sensitivity of the time-reversal dichroism ($\hat{A}_T$) to its strength.

For vanishing spin-orbit coupling, the two top-most valence bands, which typically exhibit strong and opposite spin-polarized character around the K/K’ points, are expected to merge together. This new degeneracy at the Brillouin zone boundary is thus expected to annihilate the spin-polarized character of these bands. However, these two normally spin-split bands have the same orbital-texture within each given valley. Thus, the orbital-texture is expected to be invariant with respect to a modification of the SOC strength, so is expected to be the time-reversal dichroism ($\hat{A}_T$).

Within the KKR framework, there are several ways to manipulate the SOC. Since SOC is of relativistic origin, and since dominant relativistic corrections scale with $1/c^2$, where $c$ is the speed of light, one straightforward approach to theoretically mimic the non-relativistic limit is to increase the speed of light.

In Fig. S6, we show the calculated band structure along K-Γ-K’ high symmetry direction, for different speeds of light.

In Fig. S6 we show the calculated band structure along K-Γ-K’ high symmetry direction, for different speeds of
light. The same data have been used to extract the time-reversal dichroism presented in Fig. 4 of the main paper. One can clearly notice that when the speed of light is increased (going from (a) to (d)), the spin-orbit-split band (e.g. valence band top at the K/K' points) are merging together.

**FIG. S7. Fully relativistic and non-relativistic time-reversal dichroism:** For all panels, the upper hemisphere is the photoemission intensity for a given crystal orientation, where the scattering plane coincides with the crystal mirror plane (along Γ-M). The lower hemisphere is the extracted time-reversal dichroism ($\hat{A}_\perp$). For panels (a)-(c), we use ‘standard’ speed of light ($1/c^2=1$), which corresponds to the fully relativistic case. For panels (d)-(f), we use enhanced speed of light ($1/c^2=10^{-3}$), which corresponds to the non-relativistic limit. The energies relative to the valence band maximum are (a),(d) $E - E_{VBM}=-0.35$ eV, (b),(e) $E - E_{VBM}=-0.75$ eV and (c),(f) $E - E_{VBM}=-1.60$ eV.

In addition to the Fig. 4 of the manuscript, which shows the effect of the spin-orbit splitting (going progressively from fully relativistic to the non-relativistic limit) on the time-reversal dichroism for a given binding energy, here we want to present extended data with two different effective speed of light: $1/c^2=1$ (fully relativistic) and $1/c^2=10^{-3}$ (non-relativistic limit), for different selected binding energies. Fig. S7 (a) and (d) shows that the dichroism slightly below the valence band top ($E_B=-0.35$ eV) is almost unaffected when going from the fully relativistic to the non-relativistic limit. Indeed, while the absolute amplitude of the time-reversal dichroism is slightly enhanced in the non-relativistic limit, the alternating positive and negative signal emerging from the croissant shaped photoemission intensity around K/K' valleys is invariant upon modification of the SOC strength. Fig. S7 (b) and (e) shows constant energy contours (CECs) for larger binding energy ($E_B=-0.75$ eV). In the fully relativistic case (b), one can see that the photoemission intensity features two concentric trigonally warped ‘circles’ around each K/K’ valleys, which can be associated with the two spin-orbit-split valence bands. The dichroism of both bands is very similar, around each valley, because they have the same hidden orbital-texture. When going to the non-relativistic case (e), the inner ‘circle’ disappear, since the splitting between these bands is of relativistic origin (SOC). Moreover, one can notice that the dichroism of the outer trigonally warped ‘circle’ (VB1), does not qualitatively change when going to the non-relativistic case. We can thus conclude that the time-reversal linear dichroism ($A_\perp$) is a quantity which is of non-relativistic origin.

### S5. ORBITAL-RESOLVED TIME-REVERSAL DICHROISM FROM KKR CALCULATIONS

One other knob that is available within our KKR framework is to turn-off some initial- and final-state channels. We will use this knob to strengthen our conclusions about the microscopic origin of the time-reversal dichroism.
FIG. S8. Orbital-resolved time-reversal dichroism from KKR calculations: Role of initial states: For all panels, the upper hemisphere is the photoemission intensity for a given crystal orientation, where the scattering plane coincides with the crystal mirror plane (along Γ-M), for a constant energy of $E - E_{VBM} = -0.75$ eV. The lower hemisphere is the associated time-reversal dichroism ($\hat{A_T}$). (a) For full calculation. (b) For disabled $p$-type initial states. (c) For disabled $d$-type initial states.

We first investigated the role of initial-state channels in the emergence of time-reversal dichroism. In Fig. S8(b), we show the photoemission intensity and associated time-reversal dichroism for the full calculation, i.e. where all orbital-types are ‘enabled’. In Fig. S8(b) and (c), we show the photoemission intensity and associated time-reversal dichroism when $p$-type and $d$-type initial orbitals have been disabled in the calculation, respectively. While turning off the contribution of $p$-type orbitals leave the time-reversal dichroism most unchanged (compared to full calculation), turning off the contribution of $d$-type orbitals leads to a completely different time-reversal dichroism signal. These observations confirm our conclusion that the time-reversal dichroism, for this binding energy, emerges as a consequence of interference between $d_{xy}$ and $d_{x^2-y^2}$ orbitals in the photoemission process, as well as the modification of the interferometric pattern upon time-reversal.

Corresponding authors:
beaulieu@fhi-berlin.mpg.de
jminar@ntc.zcu.cz
ernstorfer@fhi-berlin.mpg.de

FIG. S9. Orbital-resolved time-reversal dichroism from KKR calculations: Role of final states: For all panels, the upper hemisphere is the photoemission intensity for a given crystal orientation, where the scattering plane coincides with the crystal mirror plane (along Γ-M), for an constant energy of $E - E_{VBM} = -0.75$ eV. The lower hemisphere is the associated time-reversal dichroism ($\hat{A_T}$). (a) For full calculation. (b) For disabled $d$-type final states. (c) For disabled $f$-type final states.

Similarly to the above-described procedure, we also investigated the role of final-state channels in the emergence of time-reversal dichroism. As one can see in Fig. S9, turning off the contribution of $d$-type final states leave the time-reversal dichroism mostly unchanged (compared to full calculation), while turning off the contribution of $f$-type final states leads to a completely different time-reversal dichroism signal. These observations further confirm our conclusion that the time-reversal dichroism, for this binding energy, emerges as a consequence of interference between $d_{xy}$ and $d_{x^2-y^2}$ orbitals in the photoemission process.
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