Surface versus bulk contributions to the giant Rashba splitting in the ferroelectric $\alpha$-GeTe(111) semiconductor.

J. Krempaský$^{1}$, H. Volfvá$^{2,3}$, S. Muff$^{1,6}$, N. Pilet$^{1}$, G. Landolt$^{1,5}$, M. Radović$^{1,8}$, M. Shi$^{1}$, D. Kriegner$^{4}$, V. Holý$^{4}$, J. Braun$^{3}$, H. Ebert$^{3}$, F. Bisti$^{1}$, V.A. Rogalev$^{1}$, V.N. Strocov$^{1}$, G. Springholz$^{7}$, J. Minár$^{12,3}$ and J. H. Dill$^{1,6}$

1Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
2New Technologies-Research Center University of West Bohemia, Plzeň, Czech Republic
3Department of Chemistry, Ludwig Maximilian University, 81377 Munich, Germany
4Department of Condensed Matter Physics, Charles University in Prague, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
5Physik-Institut, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland
6Institute of condensed matter physics, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
7Institut für Halbleiter-und Festkörperphysik, Johannes Kepler Universität, A-4040 Linz, Austria
8SwissFEL, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

In systems with broken inversion symmetry spin-orbit coupling (SOC) yields a Rashba-type spin splitting of electronic states, manifested in a k-dependent splitting of the bands. While most research had previously focused on 2D electron systems [1, 2], recently a three-dimensional (3D) form of such Rashba-effect was found in a series of bismuth tellurohalides BiTeX ($X$ =I, Br, or Cl) [3, 4, 5, 6]. Whereas these materials exhibit a very large spin-splitting they lack an important property concerning functionalisation, namely the possibility to switch or tune the spin texture. This limitation can be overcome in a new class of functional materials displaying Rashba-splitting coupled to ferroelectricity: the ferroelectric Rashba semiconductors (FERS) [7, 8]. Using spin- and angle-resolved photoemission spectroscopy (SARPES) we show that $\alpha$-GeTe(111) forms a prime member of this class, displaying a complex spin-texture for the Rashba-split surface and bulk bands arising from the intrinsic inversion symmetry breaking caused by the ferroelectric polarization of the bulk (FE). Apart from pure surface and bulk states we find surface-bulk resonant states (SBR) whose wavefunctions entangle the spinors from the bulk and surface contributions. At the Fermi level their hybridization results in unconventional spin topologies with cochiral helicities and concomitant gap opening. The $\alpha$-GeTe(111) surface states (SS) and SBR states make the semiconductor surface conducting. At the same time our SARPES data confirm that GeTe is a narrow-gap semiconductor with a well resolved Dirac point in the 3D-valence band and a giant spin-splitting $\Delta k_R \approx 0.11 \AA^{-1}$ of the bulk states. These results show that the $\alpha$-GeTe(111) surface/bulk electronic states are endowed with spin properties that are theoretically challenging to anticipate. As the helicity of the spins in Rashba bands is connected to the direction of the FE polarization, this work paves the way to all-electric non-volatile control of spin-transport properties in semiconductors.

IV-VI semiconductor compounds such as lead chalcogenides, SnTe or GeTe have been extensively studied by band-structure calculations for which relativistic effects and SOC were included [9, 10, 11]. Emphasis was primarily put on the band-edge properties and the fundamental gap [10] rather than the spin properties. However, recent theoretical work has predicted

* juraj.krempasky@psi.ch
† Gunther.Springholz@jku.at
‡ jan.minar@cup.uni-muenchen.de
§ hugo.dil@epfl.ch
that in topologically trivial $\alpha$-GeTe(111) the bulk bands are expected to be fully spin-polarized with the spin chirality directly coupled to the FE polarization \cite{7,8}. A further development of this concept into applications requires first of all an experimental verification and, deeper theoretical considerations.

Figure 1: **Basic properties of $\alpha$-GeTe(111) and experimental geometry.** (a) Brillouine zone; (b) RHEED and (c) LEED pattern of the bulk and surface, respectively; (d) Te-terminated semi-infinite surface structural model with highlighted distorted rhombohedral cell. Orange arrow shows the displacement of the Ge-atom responsible for the polar FE ordering. (e) Experimental geometry with schematic drawing of our SARPES experiment. (f) Spin-resolved initial state Bloch spectral functions calculated for bulk Brillouine zone along $ZU$ and $ZA$ directions. (inset) $\vec{B}_{x,y}$ quiver plot along the green arrow. Calculated spin-integrated (g) and spin-resolved (h) BSF from a semi-infinite surface. (i) Logarithmic false color map of ISM determinant demonstrating bulk, surface and SBR character of calculated ARPES spectral intensities \cite{16,15}. The green arrow indicates the $k_y$ momentum span where bulk Rashba splitting is best observed.

Experiments were performed on 200 nm thick $\alpha$-GeTe(111) monocrystalline films grown by molecular beam epitaxy on BaF$_2$(111) substrates \cite{12,13}, with a Te-terminated surface prepared in situ [see Methods and Supplemental Information (SI) I.II.1]. Fig. 1(b-d) show the surface structural model together with results of the sample characterization by in-situ low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED). The lack of surface reconstruction in LEED and the presence of Kikuchi lines in RHEED indicate superior quality $\alpha$-GeTe(111) surface with spontaneous FE moments \cite{14}. Below $T_C = 700$ K there is a spontaneous paraelectric to FE phase transition in which the cubic rock-salt phase changes to a polar rhombohedral structure, forming a FE-phase induced by elongation of the unit cell along the (111) direction (see the orange arrow in Fig. 1d). A concomitant shift in the Te-sublattice is inducing an almost perfect collective FE-order, up to $\approx 92\%$ oriented along the (111) direction perpendicular to the sample surface (SI II.2). The resulting symmetry breaking inside the $\alpha$-GeTe(111) triple-layers is responsible for the bulk Rashba-splitting. Of importance
for the surface-sensitive UV-SARPES on unpoled samples is that the spontaneous polarization of FE domains persist in the sub-surface region, as this ensures a net spin polarization also for the bulk states (SI II.3).

Due to the small probing depth of ARPES, measured energy-, angle- and spin-resolved spectra can hardly be compared directly with a calculated band-structure because photoemission intensities do not relate directly to dispersions of bare bands. The task to describe the surface electronic structure differs from that in the bulk in several ways. Due to the broken crystal symmetry the bulk spin-resolved band-structure calculations is different compared to a semi-infinite surface [Fig. 1(f-g)], mainly due to the presence of surface states (SS). The star-like feature in a constant energy map (CEM) from bulk initial states orient along ΓK, whereas surface-like initial states orient along ΓM. Furthermore, for certain binding energies and momenta, the canted spin of the bulk states is opposite to what is predicted for surface states with rather tangential helicity. Thus, mixing the spectral weights from surface and bulk states inevitably result in a competition of spin textures between bulk and surface states which in our case facilitate their discrimination in a spin-resolved experiment.

Since ARPES data critically depend on photoemission final states, to build a bridge between SARPES and theoretical band-structure calculations we use so-called one-step photoemission model (1SM, see Methods). In this most rigorous interpretation besides bulk states also surface evanescent (SS) and surface-bulk-resonance (SBR) states are considered. To better understand their spectral weights, we employ the 1SM determinant criterion [15, 16] in Fig. 1(i) in order to qualitatively discern their contributions in the measured valence states. Within the determinant logarithmic scale small values correspond to surface states with the maximum of their wavefunctions between the first atomic layer and the surface potential. States which embed in the bulk continuum have values close to one and are shown by black shades. On the other hand the SBR states, being partially reflected from bulk states, are given as red shades. The SS/SBR and SBR/bulk transitions appear gradually, but as a whole the SBR is the primary spectral weight dispersing across the gap, forming metallic states at $E_F$, and degenerating with bulk Rashba bands at lower binding energies ($E_B$).

What is the origin of the metallic states at $E_F$? We note that SBR materialize as a superposition of bulk and surface spectral weight contributions, readily identified in corresponding theoretical CEMs in Fig. 1(f-g). We note that by mixing SS with bulk states the SS typically lose their well-defined surface character at $E_F$ by forming a SBR. Our results suggest that hybridization between the SS and bulk states is in-fact ”mediated” by SBR. Recently such hybridization mechanism was also confirmed in Sb$_2$Te$_3$ topological insulators [17]. An important observation is that the SBR fill the gap from the valence band maximum (VBM) all the way up to $E_F$, with progressively increased bulk-like spectral weight toward the VBM [Fig. 2(b)]. The in-gap states reaching $E_F$ display rather 2D than 3D character in $k_z$, as seen in the band-map section I in Fig. 2(a). The metallic states filling the gap couple more to surface than bulk states for two reasons. First, consistently with the 1SM predictions in Fig. 1(i), the spectral weight at $E_F$ for momenta $k_F < 0.3 \, \text{Å}^{-1}$ belongs to the SBR states and not to pure surface states. This corroborates their momentum distribution dispersing toward the pure surface states near $k_F \approx 0.4 \, \text{Å}^{-1}$, as seen by the momentum distribution curves (MDC) in Fig. 2(e) and Fig. 3b. Second, the SBR states filling the gap clearly detach from the main 3D-valence band dispersive trend inside the band-map section II.
Figure 2: ARPES $k_z$ dispersion and comparison with semi-infinite surface calculations. (a) UV-ARPES data taken along the ZΓZ direction for selected photon energies point out the Z-point around 22 eV with the Dirac point (DP) located around -0.25 eV $E_B$. The dashed lines highlight the dispersion of the DP along with the top of the valence band, indicating a bulk gap of few tens meV. Yellow arrows indicate the 2D-like dispersion of the SBR inside the gap (section I), in contrast to the 3D-like dispersion of the bulk-like band in section II. (b) CEMs for selected $E_B$ inside the gap measured at $h\nu$ of 22 eV and 475 eV in (c). (d) ARPES 1SM calculation calculated for $h\nu$ of 22 eV along $\Gamma\bar{M}\Gamma$ showing the influence of matrix-element effects on the spectral weight, which expose the surface states in the band-map section III. (e) MDCs showing the 2D-like dispersion of SBR states at $E_F$. (f) Comparison of the semi-infinite and 10-layer slab calculations and corresponding second-derivative ARPES data in panel (g) highlights the SBR buildup in the valence band [yellow dashed lines in (f) and white dots in (g)].

To further understand our ARPES data it is useful to compare them with the semi-infinite and finite slab of 10-layers. As seen in Fig. 2(f), it is evident that the SBR-states pile up as a superposition of bulk-projected states giving rise to enhanced spectral intensity. Such SBR spectral intensity buildup is highlighted with dashed lines and is dominant in the valence band ARPES. It refers to SBR states with strong coupling to the bulk continuum. Consequently, in agreement with the 1SM calculations, whole portions of pure bulk-VB states, denoted with red and blue lines, are overlaid in ARPES with the SBR states making their identification difficult by means of ground state bulk band-structure calculations [7, 10]. On the other hand the comparison between the 1SM ARPES calculation for $h\nu=22$ eV in Fig. 2(d) with the corresponding experimental data in panel (a) is rather convincing.

We discuss next our spin-resolved measurements near $E_F$. Spin-resolved populations of spin-up and spin-down electrons were measured along the $\tau$ direction perpendicular to the scattering plane [Fig. 1(e)]. We use a well-established quantitative 3D-vectorial analysis [18] for
Figure 3: Energy dispersions measured by ARPES and SARPES near $E_F$. (a,b) (top) Valence band ARPES data with populations of spin-up and spin-down electrons near $E_F$, as a function of electron momentum along $\Gamma K \Gamma$ and $M \Gamma M$ (mid panels) with corresponding spin polarizations $P_x$ and $P_y$ at $E_F$ (bottom panels). (c) Expected spin-resolved Fermi surface map (FSM) compared with experimental data in (d). Spin-resolved theoretical predictions from semi-infinite surface in Fig. 1(h) (gray arrows), are overlaid with smoothed $\vec{P}_{xy}$ data from a,b (light-green arrows). Dark-green arrows mark the results from the 3D vectorial spin analysis based on simultaneously fitted MDC peaks [thin lines in (d), see SI V]. The difference in spin-texture between the simplified model sketched in panel (c) and the experimental result is due to spin hybridization of the SBR wavefunctions indicated by dashed arrows in panel (e) (see text).

Simultaneous peak fitting of spin-integrated MDCs and spin polarizations. The polarization curves are modeled until the best fit is reached by simultaneously fitting the MDC intensity and the polarizations $P_x$, $P_y$ and $P_z$ (SI III). Of importance are the MDC-peaks 1-2-3 labeled in Fig. 3(a,b), the visibility of which is comprehensively described within the simultaneous fitting.
The resulting spin-texture at $E_F$ is seen in Fig. 3(c). Thick arrows compare the 3D-fits with the in-plane polarization predictions ($\overrightarrow{P}_{x,y}$) from the semi-infinite surface (quiver plot in gray color). As a whole the SARPES data at $E_F$ suggest that the SBR metallic states filling the gap have unconventional spin texture with parallel spin orientations different from the simple Rashba model. Our conjecture is that such spin topology in the momentum distribution can be reconciled via SOC-induced hybridization of the SBR-states. Highlighted in orange are regions where the bulk and surface contributions to the SBR wavefunctions hybridize. The resulting gap opening in momentum distribution, sketched in Fig. 3(e), is inducing a small spectral weight shift which realize the cochiral spin texture (SI III). Similar interband gap opening and spin reorientation has been observed in 2D Rashba systems [19, 20]. As a matter of fact, the in-gap states inside the band-map section I in Fig. 2(d) display rather 2D than 3D character.

To further examine our ARPES data we note that our experimental geometry predicts in 1SM calculations a suppression of spectral weight in $\Gamma M\Gamma$ below the DP for positive momenta. In fact, on the experimental side the bulk contributions to the SBR function wash out; uncovering the surface states inside the non-dispersive band-map section III [Fig.2 (a)]. This photoemission-transition matrix-element effect provides a direct evidence that the bulk and surface states indeed overlap in the initial states. As seen in Figure 2, a side effect of the vanished spectral weight intensity is that the CEMs appear with pronounced 3-fold rather than 6-fold symmetry [21, 21].

---

**Figure 4:** Rasbha splitting and out-of-plane spin polarization of bulk bands. (a) ARPES constant energy map (CEM) measured in the Z-point ($h\nu = 475$ eV) at -0.4 eV $E_B$. Spin-resolved MDCs are measured along $\Gamma M\Gamma$ (vertical) and $K\Gamma K$ (horizontal) measured in equivalent Z-point at $h\nu = 22$ eV. The spectral weight of bulk Rashba states for positive momenta vanishes as seen in Fig. 3(a), exposing the surface states (SS) denoted with violet arrows. The SS helicity (violet arrows) is opposite to pure Rashba bulk states (arrows with red and blue hues). Yellow frames highlight momenta where the 1SM predicts pure bulk states (yellow arrows in Fig. 1(f,i)). The measured in-plane $\overrightarrow{P}_{x,y}$ polarization for both bulk bands aligns with canted spins consistently with the bulk Rashba initial states, showing a giant spin-splitting $\Delta k_R \approx 0.11 \text{ Å}^{-1}$. Along $K\Gamma K$ the semi-infinite surface quiver is displayed in gray arrows. It is compared to measured (light-green quiver) and 3D-fitted (dark-green) spin textures. (b) Hexagonal warping in the out-of-plane spin polarization $P_z$ measured along the paths (A) and (B). (inset) Corresponding 1SM $P_z$ calculation.
We now look at the influence of the opposite helicity of SS and SBR states on the measured spin texture. It turns out that an ideal locus of \( k \)-space momenta for measuring pure bulk-Rashba properties is around \(-0.5 \) eV \( E_B \) in \( \Gamma \mathbf{M} \mathbf{M} \). The black shades in the photoemission determinant along the green arrow in Fig. 1(i) predict bulk states with distinct canted helicity for in-plane \( \overrightarrow{P}_{x,y} \) polarization \([P_x \approx 2P_y \), as seen in the inset in Fig. 1(f)]. The same canted helicity is perfectly reflected in the measured polarization in Fig. 4(a). Such experimental confirmation traces back the magnitude and direction of the spin polarization vector to the states from which these electrons originate. This is non-trivial, since especially for systems with large SOC, the total angular momentum is relevant for photoemission process rather than only the spin quantum number \([22]\). Since the degree of spin polarization can depend strongly on the \( h \nu \) \([22]\), the same states were probed with different photon energies (SI III). Because the same canted spin arrangement was confirmed in all cases, we conclude that the measured spin signals trace back to initial state bulk Rashba spinors, making this the first experimental confirmation of the spin texture of a FERS.

Finally we comment on the out-of-plane polarization. The band anisotropy between \( \Gamma \mathbf{M} \) and \( \mathbf{K} \) induce rather strong hexagonal warping effect responsible for the out-of-plane \( P_z \) spin polarization component \([7, 23, 24]\). SARPES data in data seen in Fig. 4(b) confirm the hexagonal warping measured in two equivalent \( \overrightarrow{\Gamma \mathbf{M}} \) directions denoted (A) and (B). As seen in the inset 1SM calculations, the measured warping is in excellent agreement with measured data.

In a broader perspective, the unveiled \( \alpha \)-GeTe(111) bulk spin structure has far reaching consequences both for fundamental physics and applications. Based on our results \( \alpha \)-GeTe(111) is the prime candidate in spin-orbit-driven Rashba physics in 3D \( k \)-space. Resolving the spin structure at \( E_F \) and inside the narrow gap is relevant in terms of potential device-oriented applications. Namely, GeTe appears to have always \( p \)-type metallic transport properties due to Ge-vacancies which lead naturally to a large density of holes in the valence band states \([23]\). Nevertheless it manifests macroscopic, robust and reversible ferroelectricity promising for technological applications. Our findings confirm that a bulk Rashba effect and ferroelectricity coexist and are coupled. We emphasize that the giant spin-splitting \( \Delta k_R \approx 0.11 \) \( \mathring{A} \) is formed by bands which interconnect the Rashba-split conduction- and valence band continuum. We anticipate that the \( \alpha \)-GeTe(111) Rashba physics is likely to extend to \( \text{Ge}_{1-x}\text{Mn}_x\text{Te} \) multiferroic Rashba semiconductors because the rhombohedral distortion persists up to \( x = 0.25 \) \([14]\). Thus the quest for semiconductors with combined functional properties might extend to systems where magnetism, ferroelectricity and Rashba physics would offer unique property combinations for potential device applications.

Methods

Sample preparation method.

Experiments were performed on 200 nm thick \( \alpha \)-GeTe(111) films grown by molecular beam epitaxy on BaF\(_2\)(111) substrates \([12, 13]\). A protective amorphous Te-cap used to avoid surface oxidation and degradation was removed in the ultrahigh vacuum chamber by annealing the thin film for 30 min at 250°C. The surface quality checked by LEED shows the 1×1 diffraction pattern of the \( \alpha \)-GeTe(111) surface seen in Fig. 1c.

ARPES and spin-resolved ARPES

The VUV-ARPES/SARPES experiments were performed at the COPHEE end-station of the SIS beamline \([26]\), Swiss Light Source (SLS), using \( p \)-polarized photons in the energy range 20–25 eV, and an Omicron EA 125 hemispherical energy analyzer equipped with two orthogonally mounted classic Mott detectors. The whole set-up allows the simultaneous measurements of all three spatial components of the spin-polarization vector for each point of the band structure. The geometry of the experimental set-up is schematically shown in Fig. 1e. The spin-resolved MDCs were measured by rotating the sample azimuth...
\( \phi \) such that \( \overline{M\Gamma M} \) or \( \overline{K\Gamma K} \) were aligned perpendicular to the scattering plane. Direct and immediate visualization of the spin splitting as a function of electron momentum was measured by exploiting the manipulator tilt angular degrees of freedom [see \( \tau \) in Fig. 1(e)]. The spin-integrated Fermi surfaces were measured with the channeltron detectors of the SARPES set-up by on-the-fly sweeping the manipulator tilt angle (\( \tau \)) for selected polar angles \( \theta \) as seen in the experimental setup in Fig. 1(e). The angular and resolution-broadened energy range in spin-resolved mode were 1.5° and 60 meV, respectively. In spin-integrated mode the resolutions were set to 0.5° and 20 meV. To enhance the bulk sensitivity compared to VUV-ARPES, experiments were also performed in the soft-X-ray energy range at the ADRESS beamline [27]. The experimental results in the main text were reproduced on three samples with individual annealing preparation over different experimental runs. All data were taken at 20 K.

First principle calculations

The ab-initio calculations are based on density functional theory (DFT) as implemented within the multiple scattering theory (SPRKKR) [28, 29]. SOC has been naturally included by use of a fully relativistic four-component scheme. As a first step of our investigations we performed self-consistent calculations (SCF) for 3D bulk as well as 2D semi-infinite surface of \( \alpha \)-GeTe(111) within the screened KKR formalism [29]. The corresponding ground state band structures are presented in terms of Bloch spectral functions (BSF). The converged SCF potentials served as an input quantities for our spectroscopic investigations. The ARPES calculations were performed in the framework of the fully relativistic one-step model of photoemission [16, 30] in its spin-density matrix formulation [31], which accounts properly for the complete spin-polarization vector, in particular for Rashba systems like GeTe. Together with a realistic model for the surface barrier potential, one-step calculations based on a semi-infinite half-space configuration were decisive to substantiate the \( \alpha \)-GeTe(111) surface-generated spectral features on both qualitative and quantitative levels.

Acknowledgments

Constructive discussions with S. Picozzi, R. Calarco and R. Bertacco are gratefully acknowledged. This work was supported by the Swiss National Science Foundation Project No. PP00P2_1447421. We acknowledge the financial support from German funding agencies DFG (SPP1666) and the German ministry BMBF (05K13WMA) is also gratefully acknowledged (H.V., H.E., J.B. and J.M.). J.M. acknowledges the CENTEM project, Reg.No. CZ.1.05/2.1.00/03.0088, co-funded by the ERDF as part of the Ministry of Education, Youth and Sports OP RDI program. D.K. and V.H. acknowledge the financial support of Czech Science Foundation (project 14-08124S)

References

[1] Dil, J. H. Spin and angle resolved photoemission on non-magnetic low-dimensional systems. J. Phys.: Condens. Matter 21, 403001 (2009).
[2] Okuda, T. & Kimura, A. Spin- and angle-resolved photoemission of strongly spin–orbit coupled systems. Journal of the Physical Society of Japan 82 (2013).
[3] Ishizaka, K. et al. Giant Rashba-type spin splitting in bulk BiTeI. Nat. Materials 10, 521–526 (2011).
[4] Landolt, G. et al. Disentanglement of surface and bulk Rashba spin splittings in noncentrosymmetric BiTeI. Phys. Rev. Lett. 109 (2012).
[5] Landolt, G. et al. Bulk and surface Rashba splitting in single termination BiTeCl. New J. Phys. 15 (2013).
[6] Crepaldi, A. et al. Giant Ambipolar Rashba Effect in the Semiconductor BiTeI. Phys. Rev. Lett. 109, 096803 (2012).
[7] Di Sante, D., Barone, P., Bertacco, R. & Picozzi, S. Electric Control of the Giant Rashba Effect in Bulk GeTe. *Advanced Materials* **25**, 509–513 (2013).

[8] Picozzi, S. Ferroelectric Rashba Semiconductors as a novel class of multifunctional materials. *Frontiers in Physics* **2** (2014).

[9] Herman, F., Kortum, R., Ortenburger, I. & P. Van Dyke, J. RELATIVISTIC BAND STRUCTURE OF GeTe, SnTe, PbTe, PbSe, AND PbS. *Journal de Physique Colloques* **29**, 62–77 (1968).

[10] Ley, L. & Cardona, M. (eds.) *Photoemission in Solids II* (Springer-Verlag Berlin Heidelberg, 1979).

[11] Yu, P. & Cardona, M. *Fundamentals of semiconductors, Physics and Materials Properties* (Springer-Verlag Berlin Heidelberg, 2010).

[12] Lechner, R. T. *et al.* Phase separation and exchange biasing in the ferromagnetic IV-VI semiconductor Ge$_{1-x}$Mn$_x$Te. *Applied Physics Letters* **97**, – (2010).

[13] Hassan, M. *et al.* Molecular beam epitaxy of single phase gemnte with high ferromagnetic transition temperature. *Journal of Crystal Growth* **323**, 363 – 367 (2011). Proceedings of the 16th International Conference on Molecular Beam Epitaxy (ICMBE).

[14] Przybylińska, H. *et al.* Magnetic-Field-Induced Ferroelectric Polarization Reversal in the Multiferroic Ge$_{1-x}$Mn$_x$Te Semiconductor. *Phys. Rev. Lett.* **112**, 047202 (2014).

[15] Echenique, P. M. & Pendry, J. B. The existence and detection of rydberg states at surfaces. *J. Phys. C: Solid State Phys.* **11**, 2065–2075 (1978).

[16] Braun, J. & Donath, M. Theory of photoemission from surfaces. *J. Phys.: Condens. Matter* **16**, 2539–2555 (2004).

[17] Seibel, C. *et al.* Connection of a Topological Surface State with the Bulk Continuum in Sb$_2$Te$_3$(0001). *Phys. Rev. Lett.* **114**, 066802 (2015).

[18] Meier, F., Dil, J. H. & Osterwalder, J. Measuring spin polarization vectors in angle-resolved photoemission spectroscopy. *New J. Phys.* **11**, 125008 (2009).

[19] Bentmann, H., Abdelouahed, S., Mulazzi, M., Henk, J. & Reinert, F. Direct Observation of Interband Spin-Orbit Coupling in a Two-Dimensional Electron System. *Phys. Rev. Lett.* **108**, 196801 (2012).

[20] Slomski, B. *et al.* Interband spin-orbit coupling between anti-parallel spin states in Pb quantum well states. *New J. Phys.* **15**, 125031 (2013).

[21] A 3-fold rather than 6-fold symmetry in CEMs is expected due to rhombohedral distortion along the (111) axis which for GeTe give rise to a structure with 3-fold rather than 6-fold coordination.

[22] Heinzmann, U. & Dil, J. H. Spin–orbit-induced photoelectron spin polarization in angle-resolved photoemission from both atomic and condensed matter targets. *Journal of Physics: Condensed Matter* **24**, 173001 (2012).

[23] Fu, L. Hexagonal Warping Effects in the Surface States of the Topological Insulator Bi$_2$Te$_3$. *Phys. Rev. Lett.* **103**, 266801 (2009).

[24] Eremeev, S. V. *et al.* Atom-specific spin mapping and buried topological states in a homologous series of topological insulators. *Nat Commun* **3**, 103 (2012).
[25] Edwards, A. H. et al. Electronic structure of intrinsic defects in crystalline germanium telluride. *Phys. Rev. B* **73**, 045210 (2006).

[26] Hoesch, M. et al. Spin-polarized Fermi surface mapping. *J. Electron Spectrosc. Relat. Phenom.* **124**, 263 (2002).

[27] Strocov, V. N. et al. High-resolution soft X-ray beamline ADRESS at the Swiss Light Source for resonant inelastic X-ray scattering and angle-resolved photoelectron spectroscopies. *Journal of Synchrotron Radiation* **17**, 631–643 (2010).

[28] Ebert, H. et al. (2014) Munich SPR-KKR package, version 7.2, [http://olymp.cup.uni-muenchen.de: /ak/ebert/SPRKKR](http://olymp.cup.uni-muenchen.de: /ak/ebert/SPRKKR).

[29] Ebert, H., Ködderitzsch, D. & Minár, J. Calculating condensed matter properties using the KKR-Green’s function method–recent developments and applications. *Rep. Prog. Phys.* **74** (2011).

[30] Ebert, H. *Electronic Structure and Physical Properties of Solids, Lecture Notes in Physics*, vol. 535 (Springer-Verlag Berlin Heidelberg, 2000).

[31] Braun, J. et al. Exceptional behavior of d-like surface resonances on W(110): the one-step model in its density matrix formulation. *New Journal of Physics* **16**, 015005 (2014).