Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Designing 3D topological insulators by 2D-*X*ene (X = Ge, Sn) sheet functionalization in the GaGeTe-type structures

F. Pielnhofer,* T. V. Menshchikova,* I. P. Rusinov, A. Zeugner, I. Yu. Sklyadneva, R. Heid, K.-P. Bohnen, P. Golub, A. I. Baranov, E. V. Chulkov, A. Pfitzner, M. Ruck and A. Isaeva*

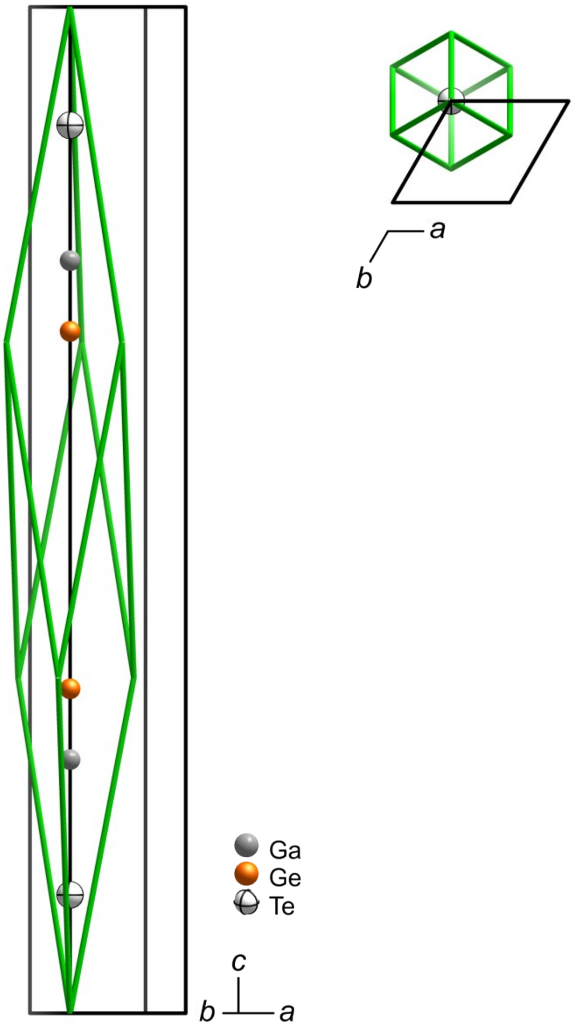
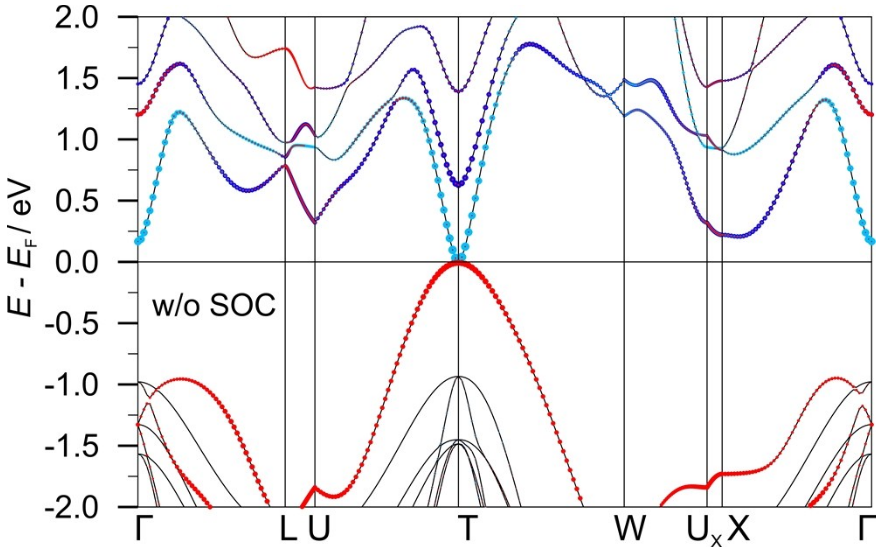


Figure S1. Crystallographic relation between the primitive (green outline) and the conventional (black outline) unit cells for GaGeTe. Atoms are shown for the primitive cell only.

(a)



(b)

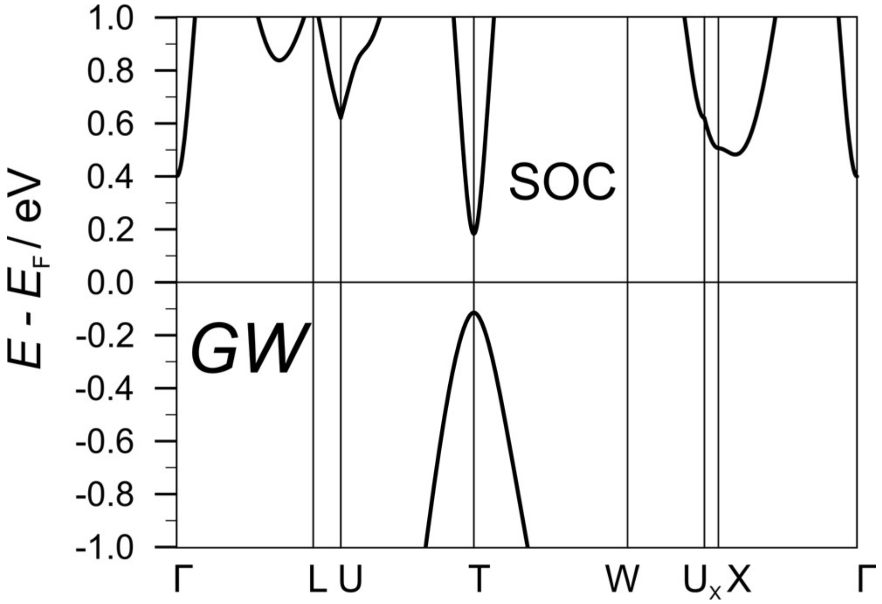


Figure S2. Bulk band structure of the primitive unit cell of GaGeTe calculated by PAW-PBE+D3 in the scalar-relativistic approach (a) and by the GW method with spin-orbit coupling (b).

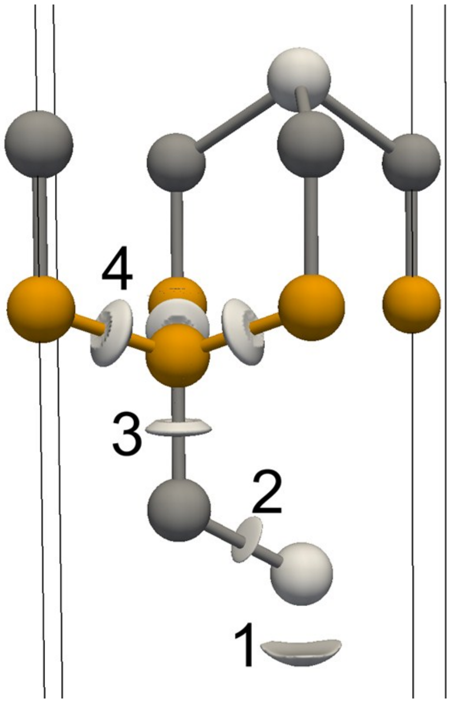


Figure S3. ELI-D localization domains for GaGeTe (a part of one unit cell is shown) computed from the electron density of a scalar-relativistic calculation: **1** – lone pair of Te (Υ= 1.33); **2** – pairwise Ga–Te covalent bond (Υ= 1.25); **3** – pairwise Ga–Ge covalent bond (Υ= 1.25); **4** – pairwise Ge–Ge covalent bond (Υ= 1.25).

Table S1. Optimized unit cell parameters and atomic coordinates for the bulk structures of *AX*Te (sp. gr. $R\bar{3}m$). The respective calculations without spin-orbit interaction taken into account did not show any significant difference.

Computational details	a, Å	c, Å	V, Å^3	Atomic coordinates			
GaGeTe							
FPLO-LDA	4.027	34.400	483.16	Ga:	1/3	2/3	0.9182
				Ge:	1/3	2/3	0.9884
				Te:	0	0	0.8812
PAW-PBE+D3 (VASP)	4.086	34.583	500.11	Ga:	1/3	2/3	0.9176
				Ge:	1/3	2/3	0.9884
				Te:	0	0	0.8806
LCAO-PP(Te)*-PBE+D2 (CRYSTAL)	4.038	34.317	484.639	Ga:	1/3	2/3	0.9180
				Ge:	1/3	2/3	0.9881
				Te:	0	0	0.8805
LCAO-AE**-PBE+D2 (CRYSTAL)	4.081	34.296	494.641	Ga:	1/3	2/3	0.9163
				Ge:	1/3	2/3	0.9875
				Te:	0	0	0.8796
GaSnTe							
PAW-PBE+D3 (VASP)	4.318	35.754	577.33	Ga:	1/3	2/3	0.9103
				Sn:	1/3	2/3	0.9839
				Te:	0	0	0.8777
LCAO-PP(Te)*-PBE+D2 (CRYSTAL)	4.296	35.372	565.477	Ga:	1/3	2/3	0.9106
				Sn:	1/3	2/3	0.9839
				Te:	0	0	0.8775
LCAO-PP(Te)*-LDA (CRYSTAL)	4.283	34.984	555.759	Ga:	1/3	2/3	0.9106
				Sn:	1/3	2/3	0.9843
				Te:	0	0	0.8778

InSnTe							
PAW-PBE+D3 (VASP)	4.482	37.113	645.64	In:	1/3	2/3	0.9106
				Sn:	1/3	2/3	0.9862
				Te:	0	0	0.8752
LCAO-PP(Te)*-PBE+D2 (CRYSTAL)	4.465	37.321	644.345	In:	1/3	2/3	0.9100
				Sn:	1/3	2/3	0.9855
				Te:	0	0	0.8743
LCAO-PP(Te)*-LDA (CRYSTAL)	4.450	36.766	630.375	In:	1/3	2/3	0.9100
				Sn:	1/3	2/3	0.9857
				Te:	0	0	0.8751

* pseudo-potential for Te; ** all-electron basis set (see Methods for details).

Table S2. The product of the parity eigenvalues δ_i at the high symmetrical points $\Gamma_{i=(n1n2n3)}$ of the primitive rhombohedral cell of GaGeTe (the points are marked in Fig. 2a). Both FPLO[1],[2] and VASP codes provided identical results.

Γ	T	X1	X2	X2	L1	L2	L3
+	–	+	+	+	+	+	+

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[1] Rasche, B.; Isaeva, A.; Ruck, M.; Borisenko, S.; Zabolotnyy, V.; Büchner, B.; Koepernik, K; Ortix, C.; Richter, M. Van Den Brink, J. Stacked Topological Insulator Built from Bismuth-Based Graphene Sheet Analogues. *Nat. Mater.* **2013**, *12*, 422–425.

[2] Koepernik, K.; Eschrig, H. Full-Potential Nonorthogonal Local-Orbital Minimum-Basis Band-Structure Scheme. *Phys. Rev. B* **1999**, *59*, 1743.

Table S3. Averaged QTAIM effective charges for *AX*Te. Experimental GaGeTe crystal structure was taken for PAW and (L)APW calculations and the optimized GaGeTe structure was taken for the LCAO-AE-PBE+D2 ones. As illustrated by the example of (L)APW calculations, inclusion of SOC does not affect the results significantly. Structures of hypothetical *A*SnTe structures were taken from PAW–PBE+D3 optimisation.

Atom	PAW(ABINIT)	LCAO-AE-PBE+D2 (CRYSTAL)	(L)APW sc-rel	(L)APW sc-rel+SOC
GaGeTe				
Ga	+0.50	+0.63	+0.44	+0.44
Ge	–0.06	–0.12	–0.05	–0.05
Te	–0.37	–0.51	–0.40	–0.39
GaSnTe				
Ga	+0.44	–	–	–
Sn	0	–	–	–
Te	–0.44	–	–	–
InSnTe				
In	+0.49	–	–	+0.49
Sn	0	–	–	–0.03
Te	–0.49	–	–	–0.46

Table S4. Selected delocalization indices and corresponding interatomic distances for the experimental GaGeTe crystal structure from the results of PAW and (L)APW calculations and the model InSnTe structure from PAW–PBE+D3 optimisation. Certain delocalization indices have not been evaluated from (L)APW calculations due to the high computational demands.

Atoms (A–B)	Interatomic distance, *d*(A–B), Å	Calculated delocalization index $\delta_{(A,B)}$		
		PAW (ABINIT)	(L)APW sc-rel	(L)APW sc-rel + SOC
GaGeTe				
Ga–Ge (nearest neighbors)	2.442	0.730	0.724	0.722
Ge–Ge (nearest neighbors)	2.457	0.797	0.792	0.791
Ga–Te	2.657	0.694	0.701	0.699
Ga···Ga	4.048	0.016	–	–
Ge···Ge (2NN)	4.048	0.046	–	–
Ge···Ge (3NN)	4.736	0.005	–	–
Ga···Ge (2NN)	3.963	0.045	0.046	0.046
Ge···Te	4.381	0.066	0.066	0.065
Te···Te	4.048	0.101	–	–
Te···Te	4.131	0.082	0.083	0.084
InSnTe				
In–Sn (nearest neighbors)	2.806	0.704	–	0.689
Sn–Sn (nearest neighbors)	2.784	0.796	–	0.798
In–Te	2.902	0.671	–	0.672
Sn···Sn (2NN)	4.482	–	–	0.047
In···Sn (2NN)	4.624	0.044	–	0.042
Sn···Te	4.864	0.060	–	0.061
Te···Te	4.044	0.108	–	–
Te···Te	4.482	0.071	–	–

Table S5. Numerical analysis of ELI-D topology for GaGeTe (based on scalar-relativistic results).

Attribution of ELI-D feature	Basin population q/e–	Bond polarity index, p
Ge core	27.74	
Ga core	27.69	
Te core	45.75	
Te lone pair (LP)	3.07	
Ga–Te disynaptic basin	1.73	0.35 (0.56 e Ga, 1.17 e Te)
Ge–Ge disynaptic basin	2.10	0
Ge–Ga disynaptic basin	2.30	0

Note: The corresponding ELIBON (ELI-based oxidation numbers[3]; analogous to QTAIM formal atomic charges) constitute:

Ge –0.04; Ga +2.16; Te –2.01.

Upon integration of ELI-D data, bond basin populations were equally distributed between the Ge and Ga atoms according to low values of bond polarity index. Due to the high polarity index, the basin population for the Ga–Te was completely ascribed to the Te atoms.

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[3] Veremchuk, I.; Mori, T.; Prots, Yu.; Schnelle, W.; Leithe-Jasper, A.; Kohout, M.; Grin, Yu. Synthesis, chemical bonding and physical properties of *RE*RhB4 (*RE* = Y, Dy–Lu). *J. Solid State Chem*. **2008**, *181*, 1983–1991.

Table S6. States treated as valence in the calculations.

Method	Ga, Ge	Te	In	Sn
(L)APW	3*p*, 3*d*, 4*s*, 4*p*	4*p*, 4*d*, 5*s*, 5*p*	4*d*, 5*s*, 5*p*	4*p*, 4*d*, 5*s*, 5*p*
PAW (Abinit)	3*d*, 4*s*, 4*p*	5*s*, 5*p*	4*d*, 5*s*, 5*p*	4*d*, 5*s*, 5*p*

Nomenclature Discussion

The recently introduced notions “germanane” and “stanene” (by analogy with the nomenclature for 2D carbon materials) should not be confused with the long-known germane (GeH_4) and stannane (SnH_4), molecular equivalents to silane, SiH_4. The notions “germanene” and “germanane” are being used interchangeably for two-atom-thick germanium sheets with almost the same degree of buckling (0.86 Å for the former[4] and 0.79 Å for the latter[5]). The same appears to hold for “stanene” and “stanine”. According to the IUPAC-nomenclature for hydrocarbons, the suffix “-ane” would imply a hydrogen-saturated sheet with sp^3-hybridized germanium atoms, whereas the choice of “-ene” denomination would suggest sp^2-hybridisation of the atoms that generally should have resulted in (almost) planar layers. Following the Zintl concept the germanium/tin fragment in β-$CaGe_2$ / $BaSn_2$, that is negatively charged and thus sp^3-hybridized, corresponds to “germanane”/ “stanane” in these terms. On the other hand, β-$CaGe_2$ is most conventionally called calcium germanide if the relative electronegativity of the constituents is taken into account. In an attempt to unite both classifications used for systematic naming of 2D and 3D materials, for instance, β-$CaGe_2$ could also be coined “calcium germananide”. This approach applied to GaGeTe in order to highlight the relation to 2D materials would yield gallium-germanane-telluride; hence its Ge structural fragment can be called “germanane-like”. As can be seen from this discussion, a term that would fulfil requirements of both 2D and 3D nomenclatures is hard to conceive, so we forewent using any and just highlighted in the main text that a germanene-like (or stanene-like) fragment is functionalized in the bulk GaGeTe (InSnTe) by covalent bonding.

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[4] Zhang, L.; Bampoulis, P.; Rudenko, A. N.; Yao, Q.; van Houselt, A.; Poelsema, B.; Katsnelson, M. I.; Zandvliet, H. J. W. Structural and Electronic Properties of Germanene on MoS_2. *Phys. Rev. Lett.* **2016**, *116*, 256804.

[5] Jiang, S.; Bianco, E.; Goldberger, J. E. The Structure and Amorphization of Germanane. *J. Mater. Chem. C* **2014**, *2*, 3185–3188.