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Orbital Chemistry of High Valence Band Convergence and Low-Dimensional Topology in PbTe

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Supporting Information

S.1 Additional Tight-Binding Thought Experiments for Valence Band Convergence

Here, we give the result of thought experiments showing how the tight-binding (TB) valence band (VB) structure evolves upon varying parameters describing the anion-site in PbTe and upon varying $V_{sp\sigma}$ and A with SOC. Note that Te serves as a proxy for the anion-site in general in PbX (X = S, Se, Te) compounds.

As discussed in the main text, the SOC interactions tend to break the convergence of the Δ and W VB extrema with respect to the L and Σ bands, so it is instructive to repeat the thought experiment from Fig. 4 of the main text with SOC interactions included in the calculation. The results are shown in Fig. 51. The W, Σ , and Δ VBMs all increase as the $V_{sp\sigma}$ interaction parameter decreases (Fig. 51a-c), but at $V_{sp\sigma}^*$, the W band is ~ 0.2 eV below the L VBM. Also, instead of the Δ VBM being greater in energy than the L point at this value, it is virtually converged at only ~ 0.04 eV below the L VBM. Analogous behavior is seen when A is increased to A^{*} (Fig. S1d-f).



Figure S1: Evolution of PbTe TB band structure with SOC when $V_{sp\sigma}$ is equal to (a) 0.9 eV, (b) 0.8 eV, and (c) 0.7 eV and with the energy difference between the Te-p and Pb-s onsite energies set to (d) 5.5 eV, (e) 7.5 eV, and (f) 9.4 eV. As $V_{sp\sigma}$ decreases from (a)-(c), the CBM at L increases in energy relative to the VBM at L, the Σ , Δ , and W VBMs increases in energy relative to the L VBM. The same trend is seen as A increases (d)-(f). The δ values are calculated based on the calculated maximum along Σ and not the exact Σ' -point.

In the main text, we discuss that the energy of the VB edge along Σ and Δ depend on the anion s-p interactions, which are quantified by the parameter, $V_{sp\sigma,Te}$. As seen in Fig. S2 as the strength of $V_{sp\sigma,Te}$ increases, both the Δ and Σ VB extrema increase in energy relative to the L and W bands, which have no dependence on $V_{sp\sigma,Te}$ and remain at a constant absolute energy.



Figure S2: TB electron band calculations (without SOC) as $V_{sp\sigma,Te}$ parameter increases from 0.3 eV to 0.5 eV. (a) When $V_{sp\sigma} = 0.3$ eV, the Σ , L, and Δ bands are all below the L VBM. The L VBM is 0.10 eV above the Σ VBM. (b) As $V_{sp\sigma,Te}$ is increased to 0.4 eV, the Σ and Δ VBs both increase relative to L such that the Σ and L maxima are exactly converged and the Δ VB is ~ 0.1 eV below. (c) When $V_{sp\sigma,Te}$ increases to 0.5 eV, the Σ and Δ VB extrema are greater in energy than the L VBM.

The difference in on-site energy between the anion-s and anion-p orbitals (s-p splitting) also impacts the convergence behavior of the VBs. Like $V_{sp\sigma,Te}$, the s-p splitting only contributes to the energy of the Σ and Δ bands, but not the L and W bands. Fig. S3 depicts how the TB bands evolve as the difference in the Te-p and Te-s on-site energies, $E_{p,Te} - E_{s,Te}$, decreases. In this virtual thought experiment, the trend is analogous to that when $V_{sp\sigma,Te}$ decreases. That is as s-p splitting decreases, the L and W maxima remain constant, while the Δ and Σ VBMs increase in energy.



Figure S3: PbTe electron band structure calculated using the TB model (without SOC) as $E_{p,Te} - E_{s,Te}$ decreases. (a) When $E_{p,Te} - E_{s,Te} = 10.5$ eV, the VBM is at L, and the Σ maximum is 0.1 eV lower in energy. The Δ maximum is ~ 0.3 eV below the VBM. (b) As $E_{p,Te} - E_{s,Te}$ decreases to 7.0 eV, both the Δ and Σ bands increase relative to the L and W bands. The Σ band maximum is 0.09 eV below the L band, while the Δ band is ~ 0.2 eV below. (c) When $E_{p,Te} - E_{s,Te} = 3.5$ eV, the Σ and L VBM's are equivalent in energy, and the Δ band is ~ 0.1 eV below the VBM. The relative energy of the W band is unchanged when $E_{p,Te} - E_{s,Te}$ is decreased.

Finally, we study the VB structure as the strength of the anion p-p interactions (quantified

by $V_{pp,Te} = V_{pp\sigma,Te} - V_{pp\pi,Te}$ increases (Fig. S4). Unlike the anion s-p parameters, the anion p-p parameters impact the energy of the W and L bands in addition to the Δ and Σ bands. As predicted from the analytical approximations of convergence in the main text, the Σ , W, and Δ bands increases in energy relative to the L band as $V_{pp,Te}$ increases. In fact, when $V_{pp,Te} \sim 1.6 \text{ eV}$, they are all effectively converged within $\sim 0.1 \text{ eV}$.



Figure S4: Tight-binding electronic structure for PbTe as $V_{pp,Te}$ increases. (a) When $V_{pp,Te} = 1.0$ eV, the VBM is at L. The Σ maximum is 0.1 eV below the L VBM, and the Δ and W band are ~ 0.3 eV below the L band. (b) When $V_{pp,Te}$ increases to 1.3 eV, the W, Σ , and Δ VB's all increase relative to L. The Σ , W, and Δ bands ~ 0.03 eV, 0.1 eV, and 0.03 eV below the L VBM, respectively. (c) As $V_{pp,Te}$ is further increased to 1.6 eV the W, Σ , and Δ bands are all slightly higher in energy than the L band. The Σ and W bands are ~ 0.05 eV higher, and the Δ band is ~ 0.1 eV above L.

S.2 PbTe Bands Calculated via Density Functional Theory

The electronic band structure for PbTe calculated using Density Functional Theory (DFT) with the Perdew-Burke-Ernzerhof $(PBE)^{[]}$ functional can be seen in Fig. S5. The methods for this calculation can be found elsewhere.²



Figure S5: Band structure of PbTe calculated using DFT-PBE without SOC.

References

- [1] X. Xu and W. A. Goddard, J. Chem. Phys., 2004, **121**, 4068–4082.
- [2] M. K. Brod, M. Y. Toriyama and G. J. Snyder, Chem. Mater., 2020, 32, 9771–9779.