Supporting information for

Combining Alloy Scattering of Phonons and Resonant Electronic Levels to Reach a High Thermoelectric Figure of Merit in PbTeSe and PbTeS alloys.

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In this supplement, additional figures present the results of various band structure calculations mentioned in the main text. Figures S1 and S2 compare the effects of the different approximations taken. Figure S3 underlines the fact that, if the lattice constants of the PbTeSe and PbTeS alloys is not allowed to change as it does experimentally, the Tl resonant level remains unaffected by S/Te or Se/Te substitution. This is the basis for the conclusion in the main text that the composition-dependent behavior of Tl is due to lattice constant changes, or chemical pressure. Figure S4 illustrates the quality of the fit of the Tl resonant level to a square root of energy function, as done in the main text; it justifies the use of free-electron-like bands with a parabolic dispersion in the method of the 4 coefficients described in the text. Finally, a cartoon of the band structure consistent with the data and calculations is shown in Figure S5.

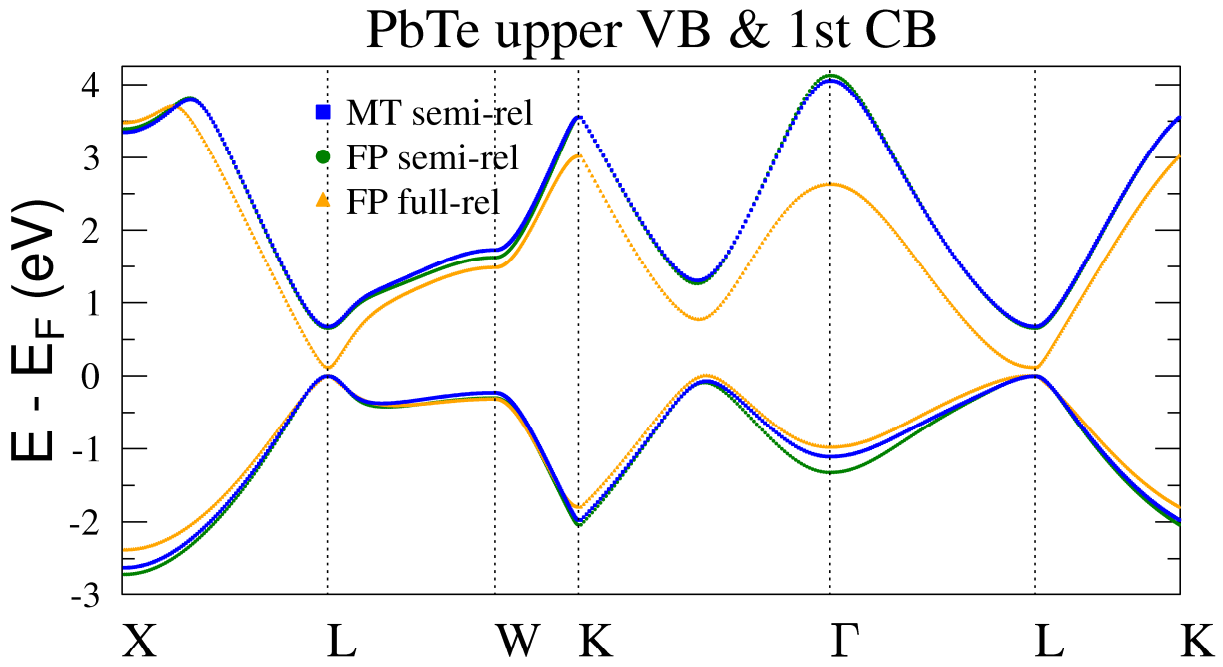

Figure S1. Comparison of the last valence band and first conduction band from (i) spherical-potential (muffin-tin) and semi relativistic calculations (MT semi-rel, in blue) (ii) full-potential semi-relativistic calculations (FP semi-rel, in green) and (iii) full-potential fully-relativistic (FP full-rel, in orange) calculations. The main relativistic effect is a shift of the conduction band, reducing the band gap.

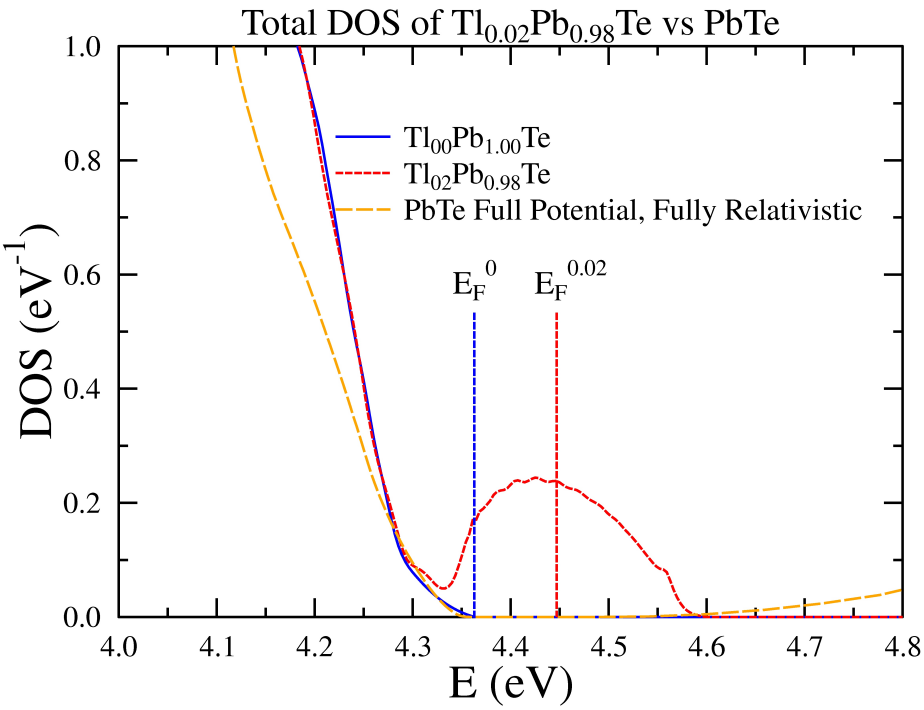

Figure S2. Comparison of DOS near the valence band edge for PbTe from full-potential fully-relativistic calculations (orange), spherical-potential semi-relativistic $Tl_{0.00}Pb_{1.00}Te$ (blue) and $Tl_{0.02}Pb_{0.98}Te$ (red). Relativistic and semi-relativistic results close to the valence band edge are similar. Tl atoms form "hump" in DOS, leaving the deeper states unaffected.

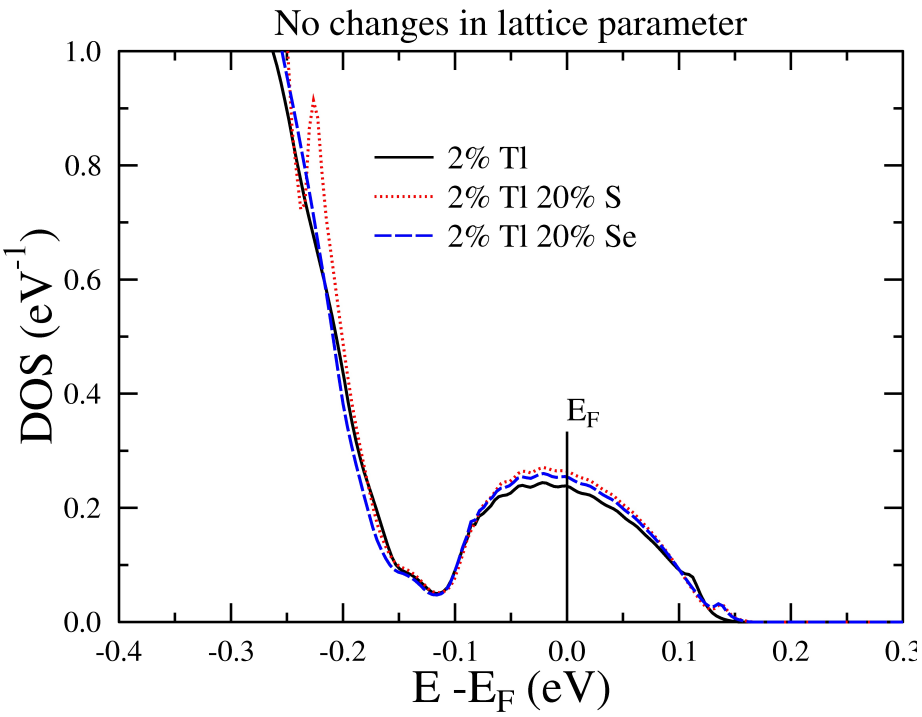

Figure S3. DOS near E_F computed for 20% of Se/Te (blue dashed line) and 20% of S/Te (red dotted line) substitution in $Tl_{0.02}Pb_{0.98}Te$ without adjusting the lattice parameter, compared with DOS of $Tl_{0.02}Pb_{0.98}Te$ (black continuous line). All DOSes are very similar, showing that changes in lattice parameter are main cause of DOS changes upon substitution.

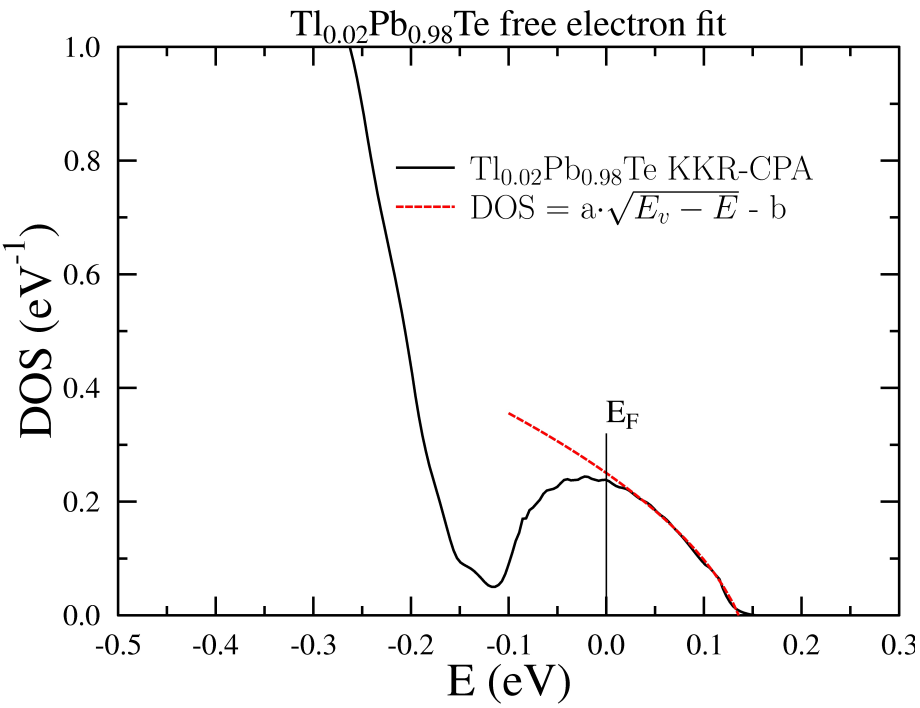

Figure S4. KKR-CPA DOS of $Tl_{0.02}Pb_{0.98}Te$ compared to the shifted free-electron-like formula for DOS, the fitting gives $m^* \sim 1.5\ m_e$ (see main text).

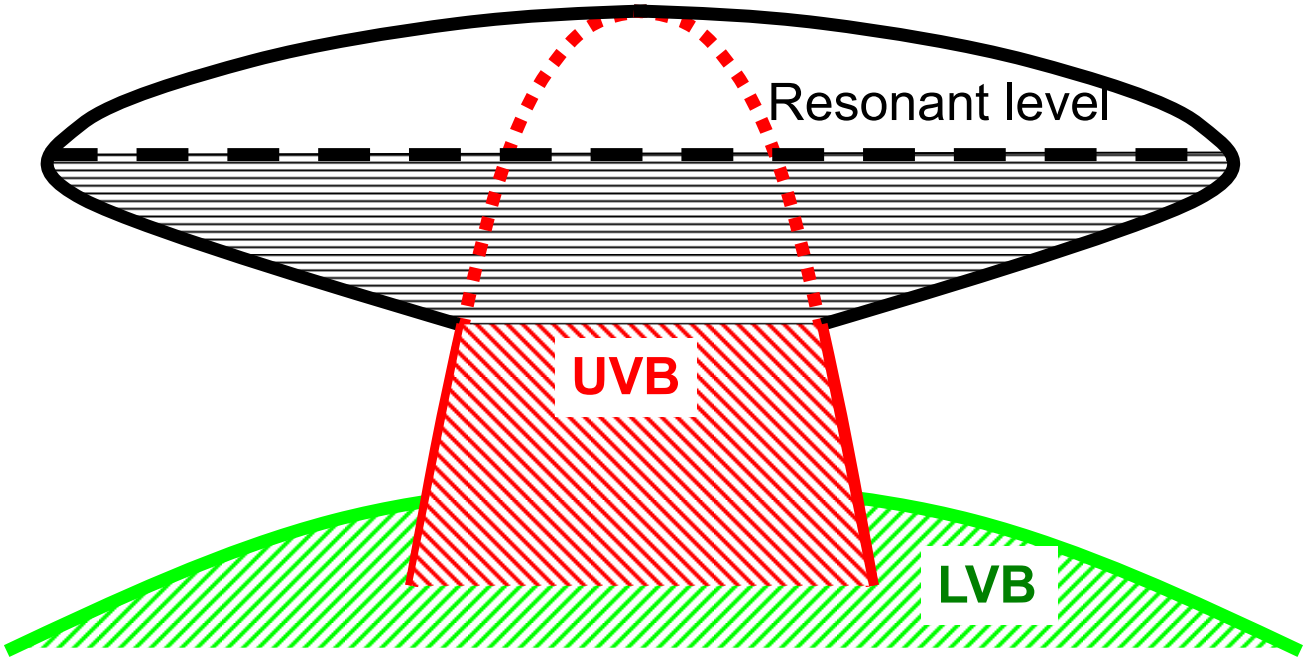

Figure S5 Cartoon of the valence band structure of Tl-doped PbTe, showing schematically the upper valence band (UVB, red) at the L-points of the Brillouin zone, the lower heavy hole band (LVB, green) which, when populated, forms a crown-like Fermi surface around the Σ-points of the Brillouin zone, and the Tl-induced resonant level (black). The latter has a free-electron-like shape, yet with a heavy density-of-states mass. When the Fermi level is about 60 meV from the valence band edge, as shown by the dashed line, the thermopower is pinned to ~120 μV K^{-1} at 300 K. When the Fermi level reaches the LVB, the thermopower at 300 K is only ~55 μV K^{-1}.