ADVANCED MATERIALS

Supporting Information

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Ultralow Thermal Conductivity, Multiband Electronic Structure and High Thermoelectric Figure of Merit in TlCuSe

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Synthesis. The handling and loading of precursor materials were carried out in an Ar gas filled inert glovebox. Polycrystalline TlCuSe of 100 g raw material was synthesized by a reaction of the high purity grade elements (Tl chunks, 99.999%; Cu shots, 99.999%; Se shots, 99.999%; all from Alfa Aesar). The oxidized layer on the surface of Tl metal was scraped off using a blade before the reaction. The stoichiometric mixture for TlCuSe was loaded in a carbon-coated quartz ampoule (14 mm inner diameter) and evacuated under 10-4 mbar, then heated at 773 K in a rocking furnace for 24 h, followed by 12 h of slow cooling.

Spark Plasma Sintering (SPS). The synthesized polycrystalline ingot of TlCuSe (28 g) was crushed into fine powder and subsequently densified by the SPS method (SPS-211LX, Fuji Electronic Industrial Co., Ltd.) in a 12.7 mm diameter graphite die under an axial compressive stress of 40 MPa at 573 K for 10 minutes. High density disk-shaped pellets with a thickness of 2.0 cm with ~92.6% of its theoretical density (8.41 g·cm-3) were obtained.

Powder X-ray Diffraction (PXRD). The purity and phase identification of the synthesized TlCuSe were examined by Rigaku Miniflex powder X-ray diffractometer with Ni-filtered Cu Kα radiation operating at 40 kV and 15 mA. Mercury software was used to calculate the PXRD spectra by using the CIFs of refined structures.

Thermal Analysis. The thermal stability of TlCuSe was assessed by differential thermal analysis (DTA) using a Netzsch STA 449F3 Jupiter thermal analyzer. Powdered crystalline material (40 mg) was flame-sealed in a tiny carbon coated quartz ampoule evacuated to 10−4 mbar. A similarly sealed ampoule of ∼40 mg of Al2O3 was used as a reference sample. The sample was heated to 873°C at a rate of 10 K·min-1 and then cooled at -10 K·min-1 to 343 K.

Optical diffuse reflectance measurement. Optical diffuse reflectance measurement was carried out at room temperature using a Shimadzu UV-3600PC double-beam, double-monochromator spectrophotometer operating in the 400-3600 nm region. BaSO4 was adopted as a 100% reflectance reference. The specimen was prepared by grinding crystals into powder and spreading it onto a compacted surface of the standard material. The reflectance versus photon energy data were used to determine bandgap by converting reflectance into absorption data using Kubelka-Munk equation.

Table S1. Various fitting parameters for Debye model and Debye + 2 Einstein model.

Debye model		Debye + 2 Einstein model	
γ	5.25×10^{-3} J·mol^{-1}·K^{-2}	γ	1.391×10^{-2} J·mol^{-1}·K^{-2}
β	4.9×10^{-3} J·mol^{-1}·K^{-4}	β	1.72×10^{-3} J·mol^{-1}·K^{-4}
		$A1$	1.20184
		θ_{E1}	24.5 K
		$A2$	10.0
		θ_{E2}	45.5 K
		θ_{D}	94.3 K

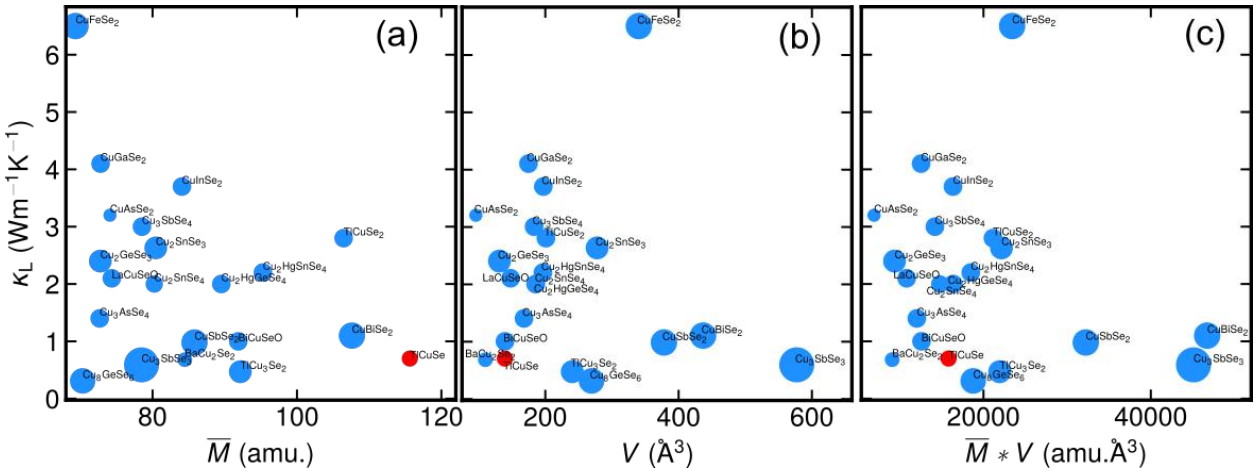

Figure S1. Lattice thermal conductivity of Cu-Se compounds as a function of average atomic mass M **(a),** volume of the primitive unit cell V **(b),** and the product of M and V **(c).** The size of the dot is proportional to the number of atoms in the primitive unit cell.

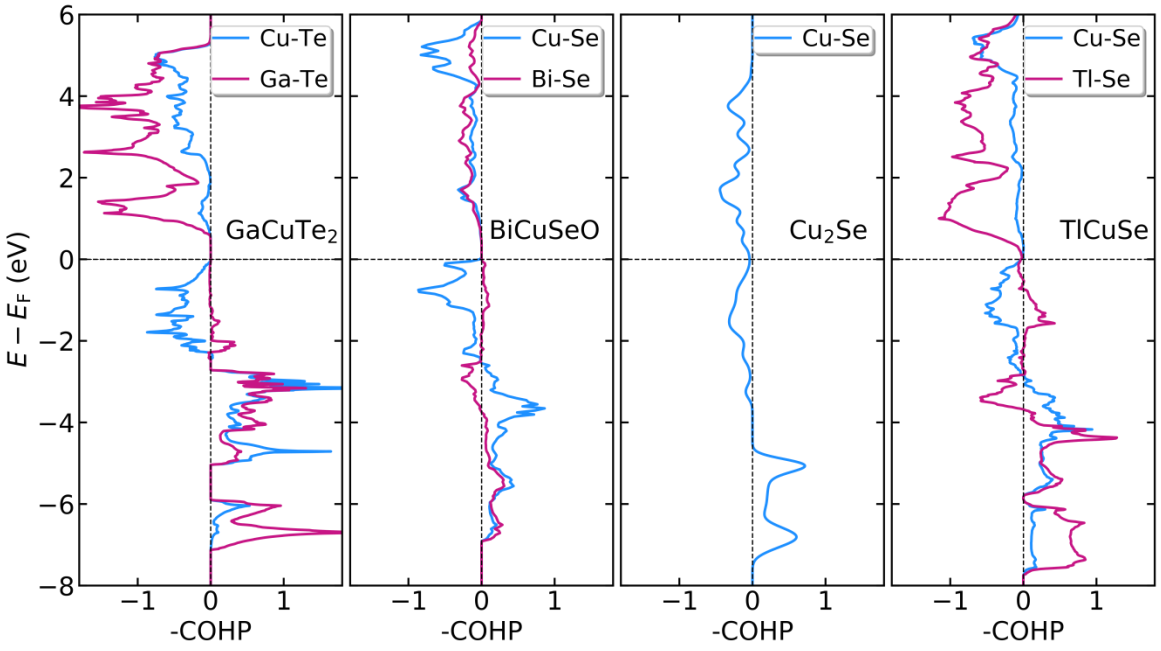

Figure S2. Atom projected crystal orbital Hamilton population (COHP) of Cu-based compounds, $CuGaTe_2$, BiCuSeO, Cu_2Se (antifluorite structure), and TlCuSe. The negative and positive -COHP indicate anti-bonding and bonding between atom pair, respectively.

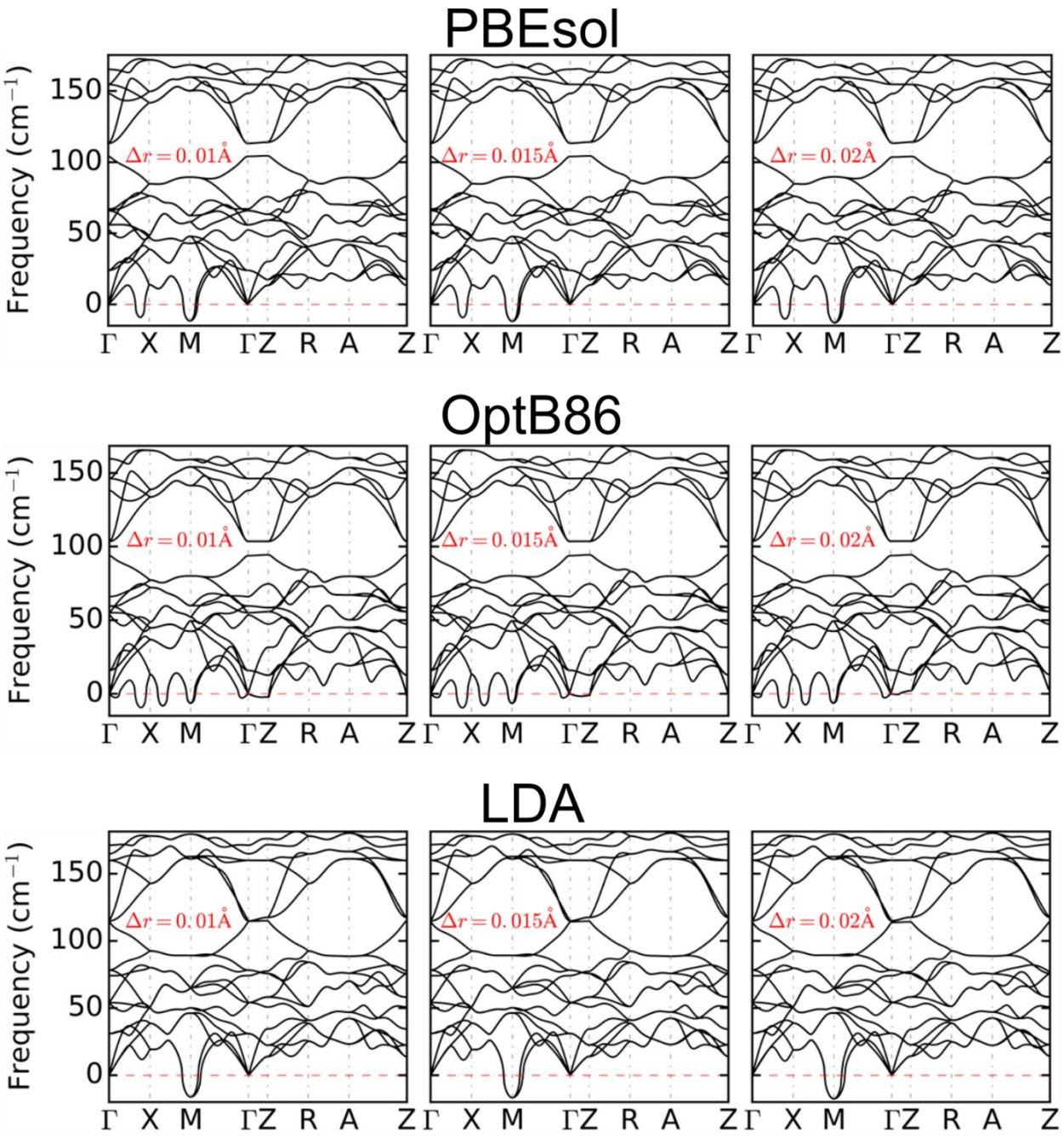

Figure S3. Phonon band structures of TlCuSe at 0 K with different exchange-correction functionals (PBEsol, OptB86, and LDA) and displacement amplitude in force constants calculations.

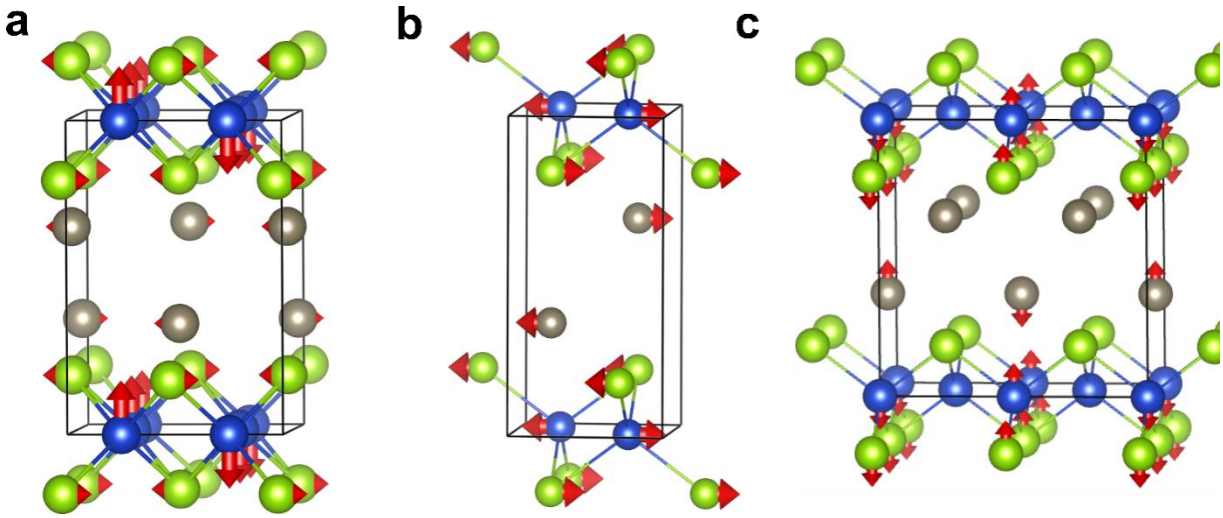

Figure S4. **a-c** are atom displacement of M_1, Γ_5^+, and X_1 phonon modes, respectively. The length of the red arrow is proportional to atom displacement amplitude.

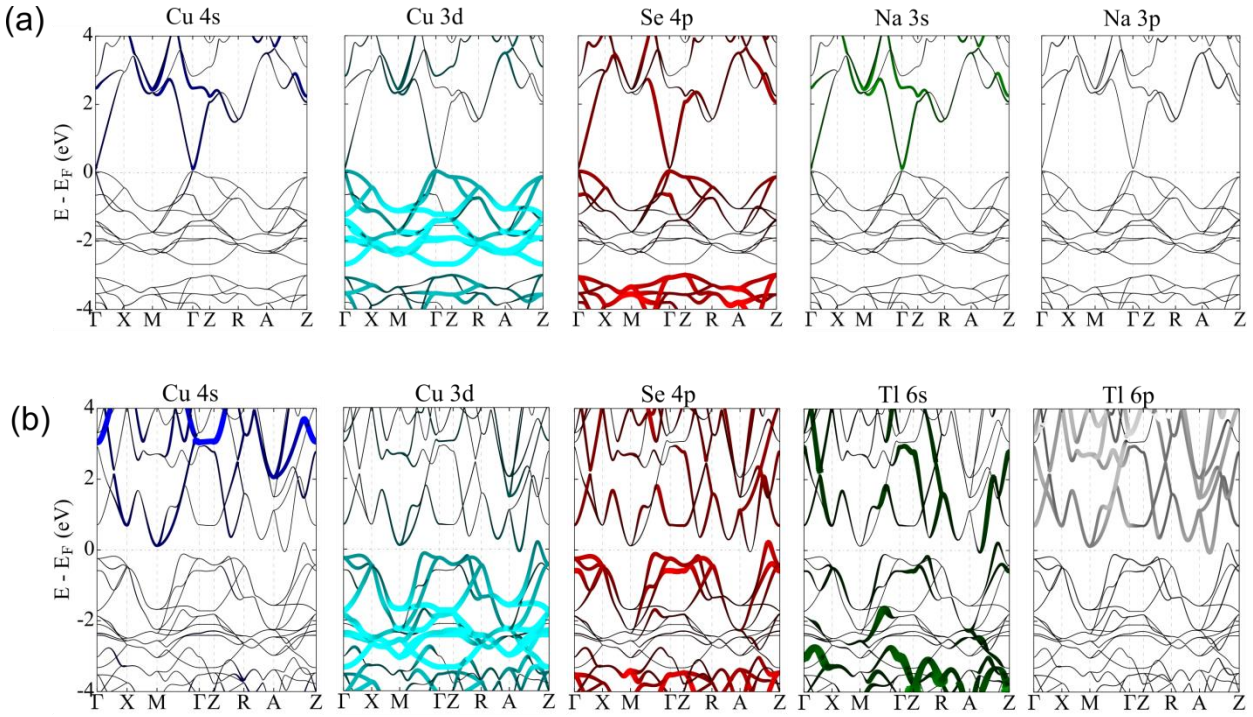

Figure S5. Band structures of NaCuSe **(a)** and TlCuSe **(b).** The Cu-4*s*, Cu-3*d*, Se-4*p*, Na-3*s* (Tl-6*s*), Na-3*p* (Tl-6*p*) orbitals are highlighted using blue, cyan, red, green, and gray color, respectively. The thickness of the band is proportional to the relative contribution of the highlighted orbital to the bands.

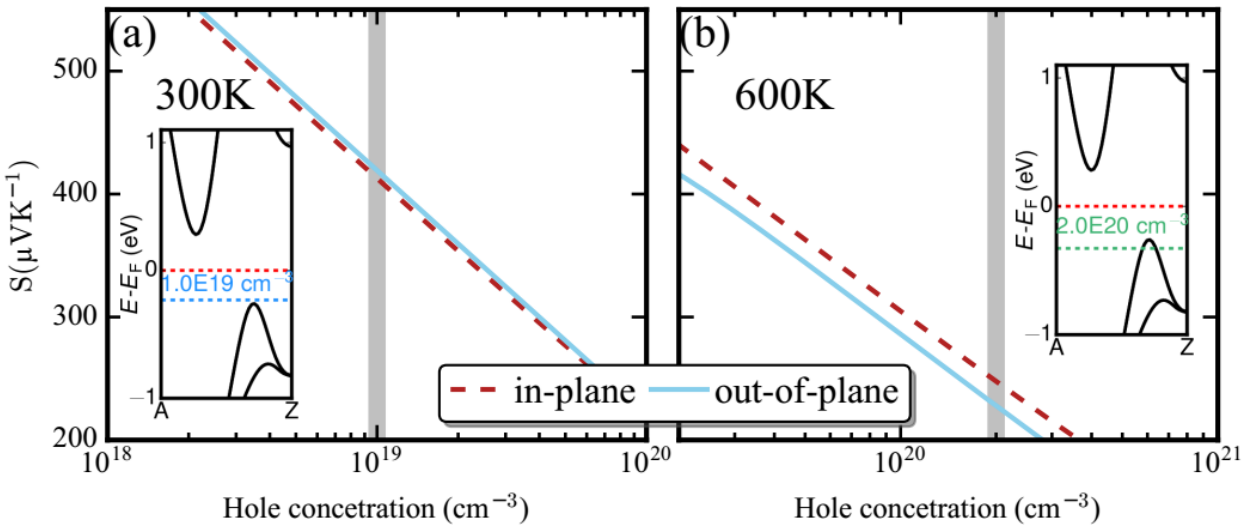

Figure S6. Calculated Seebeck (*S*) coefficient as a function of the hole concentration at **(a)** 300 K and **(b)** 600 K.

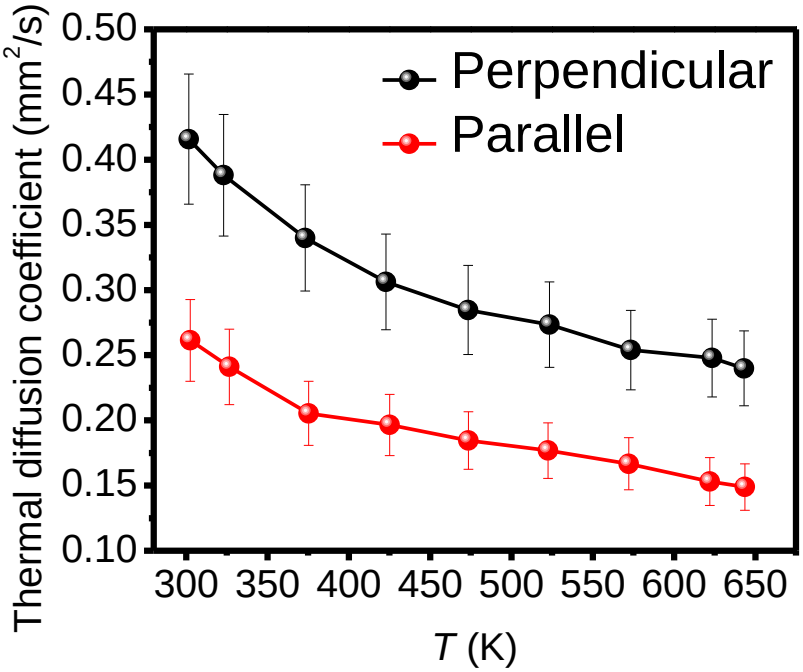

Figure S7. Temperature of total thermal conductivity for TlCuSe along two different directions (parallel and perpendicular to the pressing direction).