Supplementary Material for
Pressure induced phase transitions in topological crystalline insulator SnTe and its comparison with semiconducting SnSe: Raman and First-principles studies

Sukanya Pal^{1,*}, Raagya Arora^{2,*}, Subhajit Roychowdhury³, Luminita Harnagea⁴, Kumar Saurabh⁴,
Sandhya Shenoy², D.V.S. Muthu¹, Kanishka Biswas³, U.V. Waghmare², and A.K. Sood^{1†}

¹*Department of Physics, Indian Institute of Science, Bangalore 560012, India*

²*Theoretical Sciences Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur P.O., Bangalore 560064, India*

³*New Chemistry Unit, Jawaharlal Nehru Center for Advanced Scientific Research, Jakkur P.O., Bangalore 560064, India and*

⁴*Department of Physics, Indian Institute of Science Education and Research, Pune 411008, India*

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Fig. S 1: (color online) Raman spectra of SnTe at a few typical pressures in the reverse pressure cycle. Black solid circles are the experimental data. The solid red lines are Lorentzian fit to the experimental data. The blue solid lines are individual fits of the Raman modes. Appearance of new modes is indicated by arrows.

Fig. S 2: (color online) Raman shift of SnTe is plotted against applied pressure in the reverse pressure cycle. The error bars are obtained from the fitting procedure. The solid red lines are the linear fits to the frequencies of the Raman modes. The dotted lines indicate the pressure where the possible transitions are taking place. The numbers are the value of the slope $d\omega/dP$ in $\text{cm}^{-1}/\text{GPa}$ obtained from linear fits.

* Equal contributions

† Electronic address: asood@iisc.ac.in

TABLE I: Raman modes and pressure coefficients ($d\omega/dP$) of SnTe observed for various phases.

Phase	Mode	Mode assignment	Frequency (ω_0) (cm^{-1})	$d\omega/dP$ ($\text{cm}^{-1}/\text{GPa}$)
Phase I ($Fm\bar{3}m$) (0 to 1.5 GPa)	M1	Optical phonon at W point in BZ	89.5 ± 0.6	4.7 ± 0.7
	M2	Optical phonon at W point in BZ	101.6 ± 0.7	4.7 ± 0.9
	M3	Optical phonon at L point in BZ	125.8 ± 0.3	-2.9 ± 0.2
	M4	second-order Raman mode	144.0 ± 0.3	-0.7 ± 0.4
Phase II ($Fm\bar{3}m$) (1.5 to 5.0 GPa)	M1		88.6 ± 0.9	2.1 ± 0.2
	M2		100.6 ± 0.4	2.3 ± 0.1
	M3		113.1 ± 0.9	2.4 ± 0.2
	M4		137.8 ± 1.3	3.2 ± 0.2
	M5(new)		54.5 ± 0.4	3.0 ± 0.1
	M6(new)		125.6 ± 0.3	3.4 ± 0.1
Phase III ($Pnma$) (5.0 to 12.0 GPa)	M1		92.1 ± 1.1	0.9 ± 0.1
	M2		101.0 ± 1.2	2.9 ± 0.1
	M3		disappears	-
	M6		131.1 ± 1.0	2.4 ± 0.1
Phase IV ($Pnma[\text{GeS}]$) (12.0 to 18.0 GPa)	M1		88.2 ± 1.7	1.4 ± 0.1
	M4		disappears	-
	M5		70.4 ± 0.7	1.2 ± 0.03
	M6		137.6 ± 0.9	1.8 ± 0.05
	M7(new)		96.1 ± 1.5	2.7 ± 0.1
	M8(new)		94.0 ± 3.2	3.5 ± 0.2
Phase V ($Pm\bar{3}m$) (18.0 to 25.0 GPa)	M8		disappears	-

Fig. S 3: (color online) Raman spectra of SnSe at a few typical pressures in the reverse pressure run. The solid blue lines are Lorentzian fit to the experimental data in black line. The red solid lines are individual fits of the Raman modes.

Fig. S 4: (color online) Raman shift of SnSe is plotted against applied pressure in the reverse pressure run. The error bars are obtained from the fitting procedure. The solid red lines are the linear fits to the frequencies of the Raman modes. The black dashed lines indicate the pressure where the transitions are taking place. The numbers are the value of the slope $d\omega/dP$ in $\text{cm}^{-1}/\text{GPa}$ obtained from linear fits.

TABLE II: Raman modes and pressure coefficients of SnSe ($d\omega/dP$) observed for various phases.

Phase	Mode	Mode assignment	Frequency (ω_0) (cm^{-1})	$d\omega/dP$ ($\text{cm}^{-1}/\text{GPa}$)
Phase I (<i>Pnma</i>) (0 to 6.0 GPa)	M1	A_g	36.1 ± 0.4	-1.2 ± 0.1
	M2	A_g	71.9 ± 0.2	2.3 ± 0.02
	M3	B_{3g}	109.9 ± 0.5	-0.01 ± 0.2
	M4	A_g	131.3 ± 0.5	-2.1 ± 0.1
	M5	A_g	153.7 ± 0.3	4.9 ± 0.03
	M6	second order	231.7 ± 3.2	5.2 ± 0.9
	M7	second order	295.6 ± 2.4	5.5 ± 0.7
Phase II (<i>Cmcm</i>) (6.0 to 13.0 GPa)	M3		97.4 ± 2.8	2.4 ± 0.3
	M4		disappears	-
	M6		256.1 ± 4.5	-0.6 ± 0.5
	M7		342.4 ± 3.1	-2.9 ± 0.3
	M8(new)		81.9 ± 1.3	-0.1 ± 0.1
	M9(new)		125.2 ± 1.5	2.7 ± 0.1
Phase III (<i>Cmcm</i>) (13.0 to 21.0 GPa)	M2		86.7 ± 2.0	1.1 ± 0.1
	M5		200.2 ± 4.3	1.4 ± 0.2
	M6		disappears	-
	M7		235.8 ± 17.5	3.0 ± 1.0
	M10(new)		31.6 ± 0.7	0.3 ± 0.04

Fig. S 5: (color online) Electronic structure and the corresponding density of states of the orthorhombic ($Pnma$) structure of SnTe at (a) $P = 6$ GPa, (b) 8 GPa, (c) 11 GPa, (d) 12 GPa, (e) 13 GPa and (f) 16 GPa are calculated with the inclusion of effects of the spin orbit coupling and corresponding electronic density of states showing enhanced metallicity with increasing pressure. The red shaded region within the square indicates the metallization of the $Pnma$ phase at 8 GPa. The shaded region within the red circle indicates the Fermi energy crossing of VBM at the T point at 11 GPa.

Fig. S 6: (color online) Electronic structure and corresponding electronic density of states of the orthorhombic $Pnma$ (GeS type) structure of SnTe at (a) $P = 6$ GPa, (b) 8 GPa, (c) 10 GPa, (d) 12 GPa, (e) 13 GPa and (f) 16 GPa calculated with the inclusion of spin-orbit coupling.

Fig. S 7: (color online) Electronic structure and corresponding electronic density of states of the orthorhombic ($Pnma$) structure of SnSe at (a) $P = 0$ GPa, (b) 2 GPa, (c) 4 GPa and (d) 6 GPa calculated with the inclusion of effects of the spin-orbit coupling and (f) corresponding electronic density of states showing enhanced density of states at Fermi level with increasing pressure. The red arrow shows the indirect nature of the band-gap at 0 GPa.

Fig. S 8: (color online) Electronic structure and corresponding electronic density of states of the orthorhombic ($Cmcm$) structure of SnSe at (a) 7 GPa (b) 8 GPa (c) 9 GPa (d) 12 GPa (e) 13 GPa and (f) 16 GPa calculated with the inclusion of spin-orbit coupling. The shaded region within the red circle indicates the Fermi level crossing of valence bands at ~ 12 GPa along the Γ X direction.

Fig. S 9: Phonon dispersion of orthorhombic ($Cmcm$) structure of SnSe at $P = 9$ GPa, 12 GPa and 16 GPa calculated along the $X\Gamma$ direction. The yellow shaded region highlights the negative region and the green circles highlight the negative to positive crossover.