Supplementary Information

of

Chemical Bonding in Dense $A^{IV}X^{VI}$ and $A_2^{V}X_3^{VI}$ Chalcogenides: Electron-Deficient Multicenter Bonds in Electron-Rich Elements

Hussien Helmy Hassan Osman*[a,b] and Francisco Javier Manjon[b]

[a]Instituto de Ciencia de los Materiales de la Universitat de València, MALTA Consolider Team, Universitat de València, 46100, Burjassot, Valencia, Spain.

[b]Instituto de Diseño para la Fabricación y Producción Automatizada, MALTA Consolider Team, Universitat Politècnica de València, 46022, València, Spain.

*Corresponding author E-mail: hussien.helmy@uv.es

Table S1. Computational details of VASP calculations including the cutoff energy (E_{cutoff}) and *k*-mesh, experimental and calculated lattice parameters, and unit cell volume of GeS, SnSe, PbTe, As_2S_3, Sb_2Se_3, and Bi_2Te_3.

Species	Space group	E_{cutoff} (ev)	*k*-mesh	lattice parameters (Å)		unit cell volume (Å^3)	
				Exp.	Calc.	Exp.	Calc.
GeS	*Pnma* (62)	450	3 × 8 × 7	10.470 3.641 4.297[1]	10.296 3.664 4.150	163.81[1]	156.54
SnSe	*Pnma* (62)	350	2 × 8 × 7	11.156 4.095 4.228[2]	11.353 4.166 4.410	193.19[2]	208.57
PbTe	*Fm-3m (225)*	350	8 × 8 × 8	6.454[3]	6.440	268.84[3]	267.14
As_2S_3	*$P2_1/c$* (14)	360	6 × 4 × 2	4.220 9.570 12.178[4] β = 109.78°	4.143 9.492 12.167 β = 108.92°	462.80[4]	452.59
Sb_2Se_3	*Pnma* (62)	350	2 × 8 × 2	11.794 3.986 11.648[5]	11.784 3.976 11.322	547.54[5]	530.54
Bi_2Se_3	*R-3m (166)*	380	10 ×10 × 1	4.161 4.161 28.630[6]	4.175 4.175 28.793	429.29[6]	434.57
Bi_2Te_3	*R-3m* (166)	350	10 × 10 × 1	4.385 4.385 30.497[7]	4.383 4.383 29.903	507.82[7]	497.48

Table S2. Calculated topological descriptors of PbTe, Bi_2Se_3 and Bi_2Te_3 at room pressure. Bond distance (*d*, Å), electrons shared (ES), charge density (ρ_b), laplacian of charge density ($\nabla^2\rho_b$), and three energy density ratios H_b/ρ_b, c) G_b/ρ_b, and $|V_b|/G_b$ are summarized.

Species	Bond	*d* (Å)	ES	ET	ρ_b	$\nabla^2\rho_b$	H_b/ρ_b	G_b/ρ_b	$\lvert V_b\rvert/G_b$
PbTe	Pb-Te	3.22019	0.87	0.31	0.029	0.035	–0.173	0.473	1.365
Bi_2Se_3	Bi-Se1	2.87073	1.08	0.29	0.048	0.016	–0.354	0.438	1.810
	Bi-Se2	3.08830	0.90	0.29	0.032	0.022	–0.236	0.381	1.752
Bi_2Te_3	Bi-Te1	3.06727	1.16	0.16	0.042	0.044	–0.434	0.176	1.472
	Bi-Te2	3.22996	0.82	0.18	0.031	0.021	–0.226	0.392	1.580

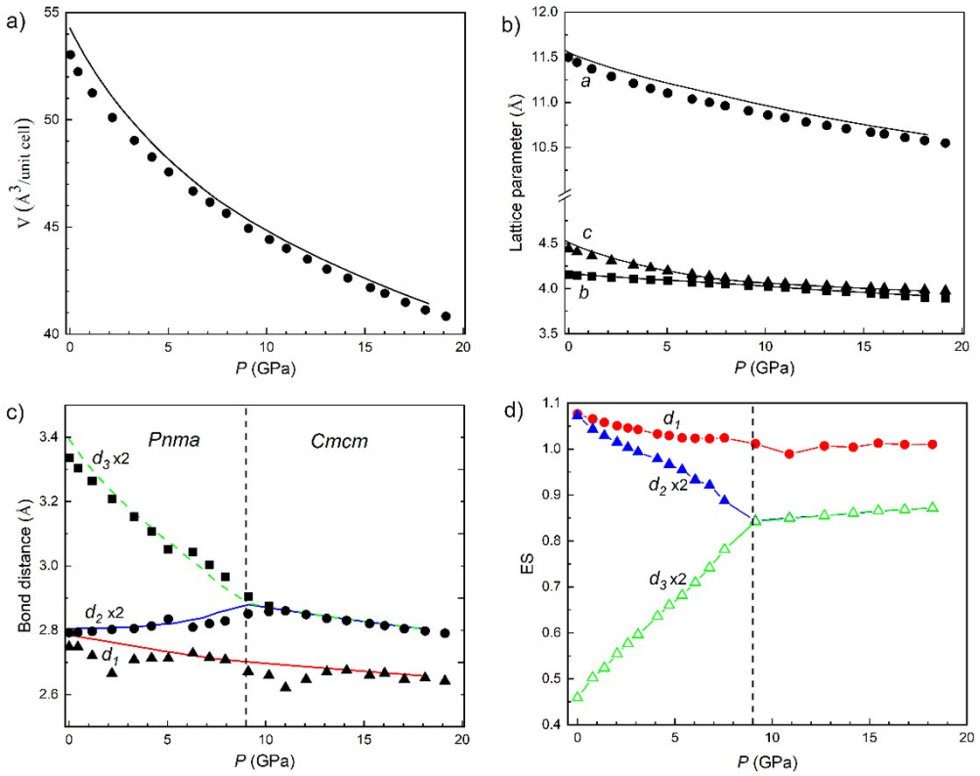
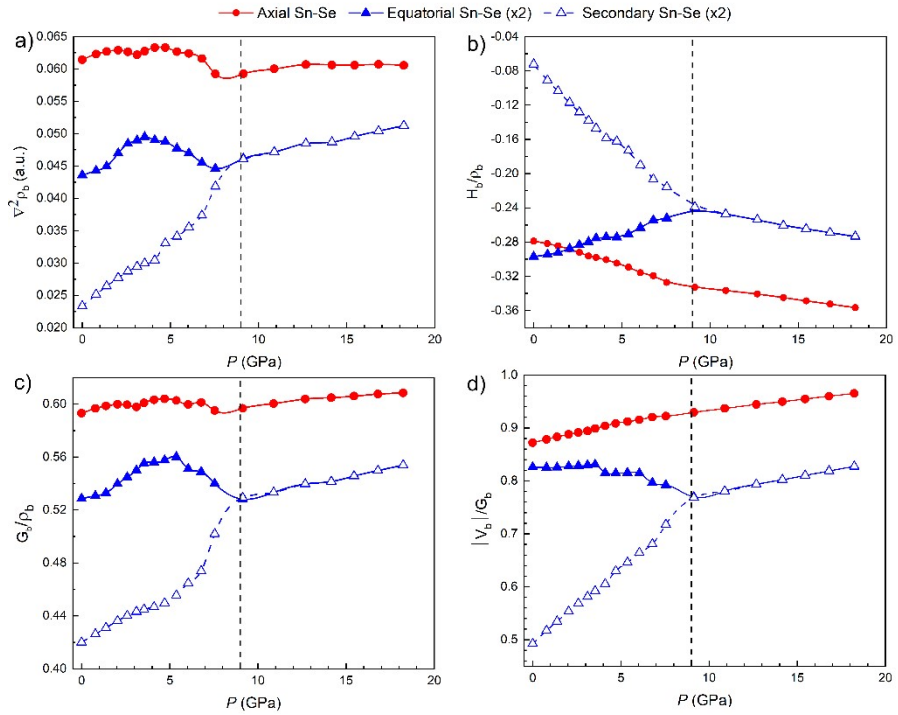


Fig. S1. SnSe: Pressure dependence of the structural parameters in SnSe: a) unit-cell volume, b) lattice parameters, and c) three nearest intralayer Sn–Se bonds (axial (d_1) and equatorial (d_2)) and the two next nearest intralayer equatorial Sn···Se distance (d_3). Lines and symbols correspond to theoretical and experimental[2] results. d) Calculated electron sharing (ES) along the three main bond types. The vertical dashed line in c) and d) indicates the theoretical phase transition pressure between the *Pnma* and *Cmcm* phases leading to the formation of electron-deficient



multicenter bonds (EDMBs).

Fig. S2. SnSe: Pressure dependence of topological parameters along the three Sn-Se distances (axial (d_1), equatorial (d_2), and secondary equatorial (d_3)) at the bond critical point (BCP): a) Laplacian of charge density, $\nabla^2\rho_b$; b) and c) ratios of total and kinetic local energy densities, H_b and G_b, to the charge density, ρ_b, , respectively; d) $|V_b|/G_b$ ratio.

The vertical dashed line indicates the theoretical phase transition pressure between the *Pnma* and *Cmcm* phases leading to the formation of electron-deficient multicenter bonds (EDMBs).

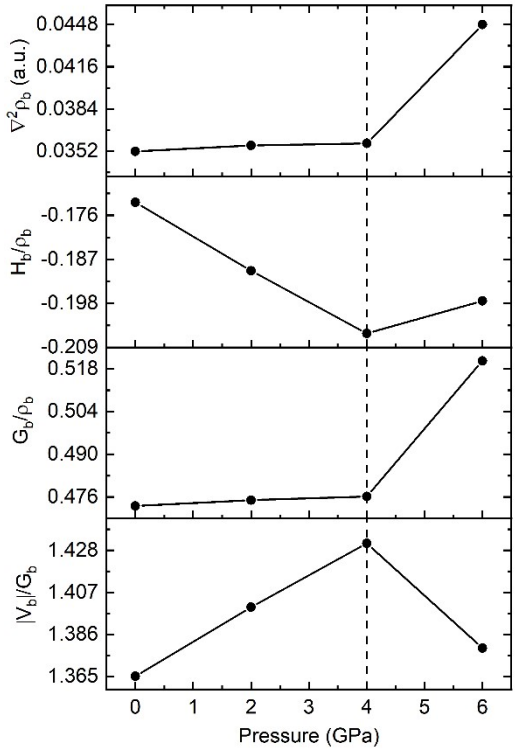


Fig. S3. PbTe: Pressure dependence of a) the Laplacian of charge density ($\nabla^2\rho$) and the ratios of the different local energy densities (H_b/ρ_b, G_b/ρ_b, and $|V_b|/G_b$) at the BCP along the only Pb-Te bonds in rocksalt-PbTe. The topological properties of the Pb–Te bond in *rs*-PbTe are consistent with its EDMB nature.

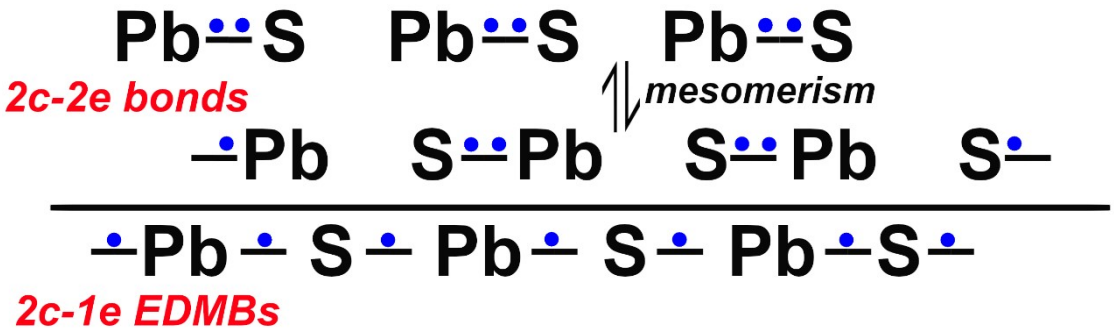


Fig. S4. Mesomeric representation of electron-deficient multicenter bonding (EDMB, 2c–1e) in PbS, adapted from reference [8] and refined according to the discussion provided on pages 185–186.

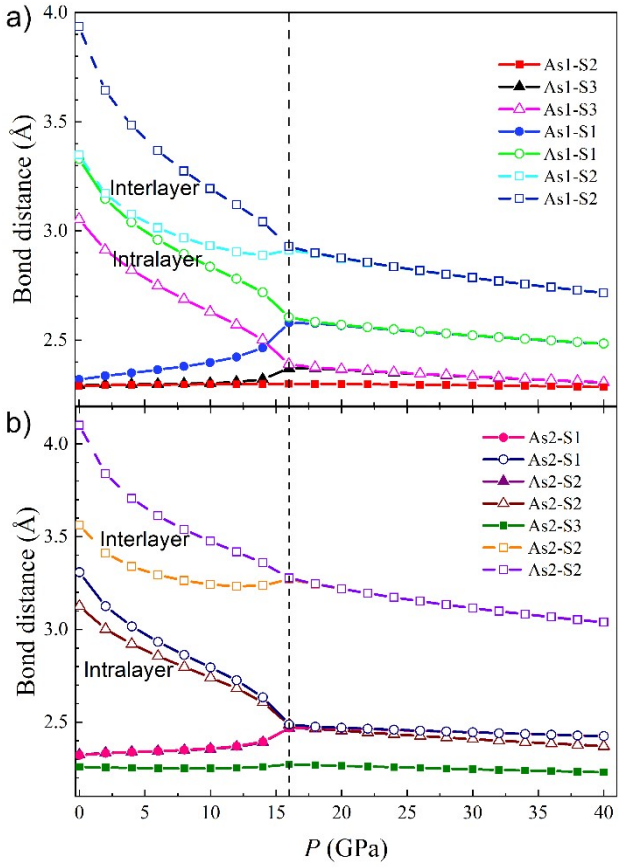


Fig. S5. As_2S_3: Pressure dependence of the theoretical a) As1–S and b) As2–S interatomic distances in α-As_2S_3. The short covalent bonds as well as the long intra- and inter-layer non-covalent interactions at room pressure are indicated. The vertical dashed line indicates the pressure of equalization of bond lengths leading to the formation of EDMBs.

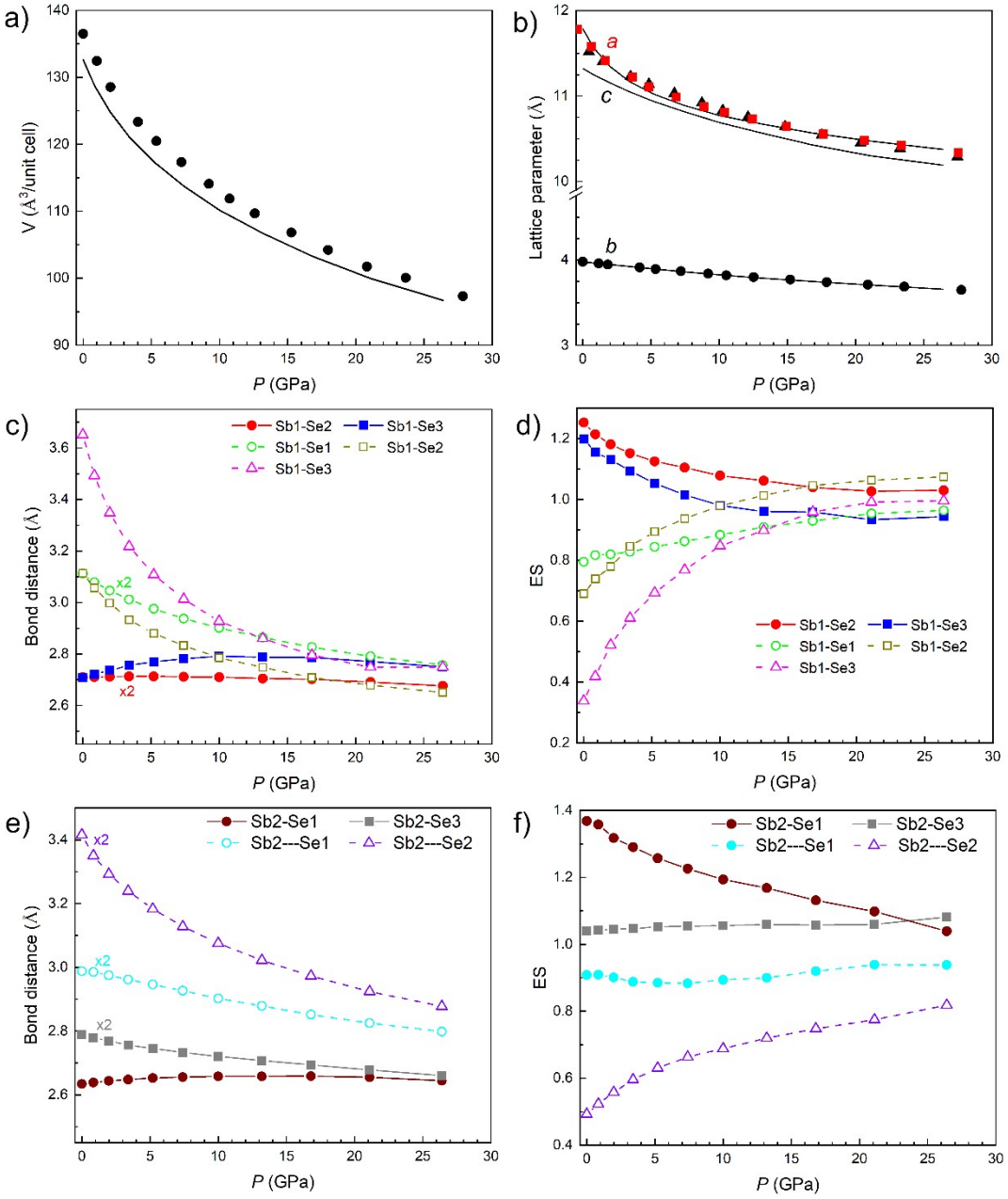


Fig. S6. Sb_2Se_3: Pressure dependence of the a) calculated unit cell volume and b) lattice parameters of the *Pnma* phase of Sb_2Se_3. Solid symbols represent the experimental data obtained from Ref. [9]. (c, e) Pressure-induced changes of the Sb1–Se and the Sb2–Se bond lengths. (d, f) Calculated number of shared electrons (ES) for the corresponding Sb1–Se and Sb2–Se bonds. The formation of EDMBs in *Pnma*-type Sb_2Se_3 occurs at a much smaller pressure (typically around 10 GPa).

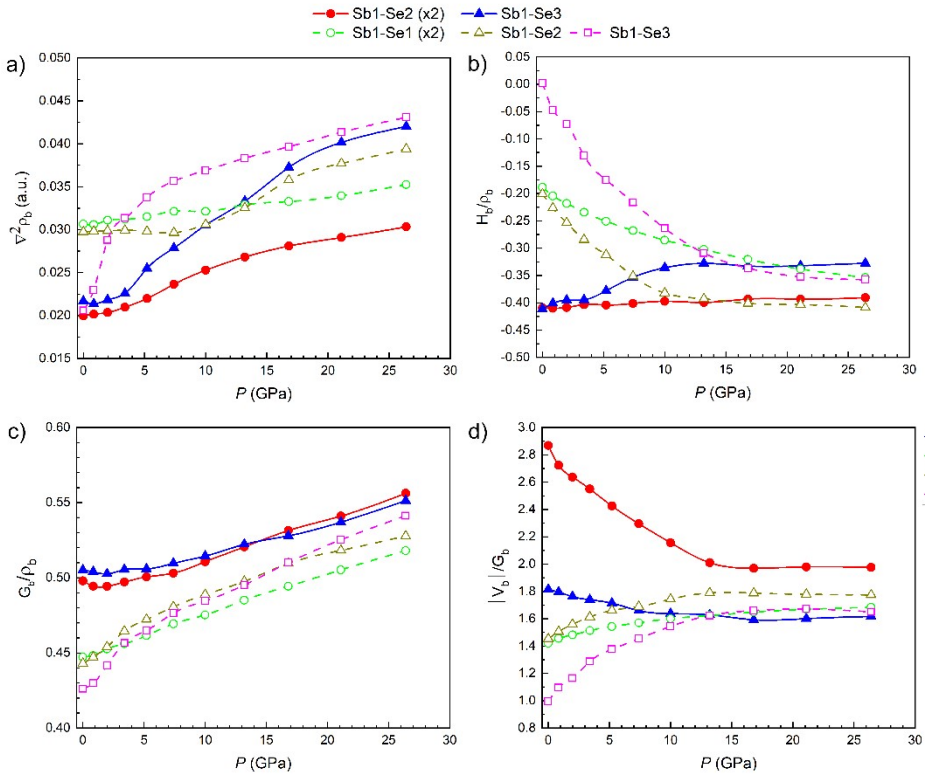


Fig. S7. Sb_2Se_3: Pressure dependence of the topological parameters of Sb1–Se bonds at BCPs: a) $\nabla^2\rho_b$; b) H_b/ρ_b; c) G_b/ρ_b; d) $|V_b|/G_b$.

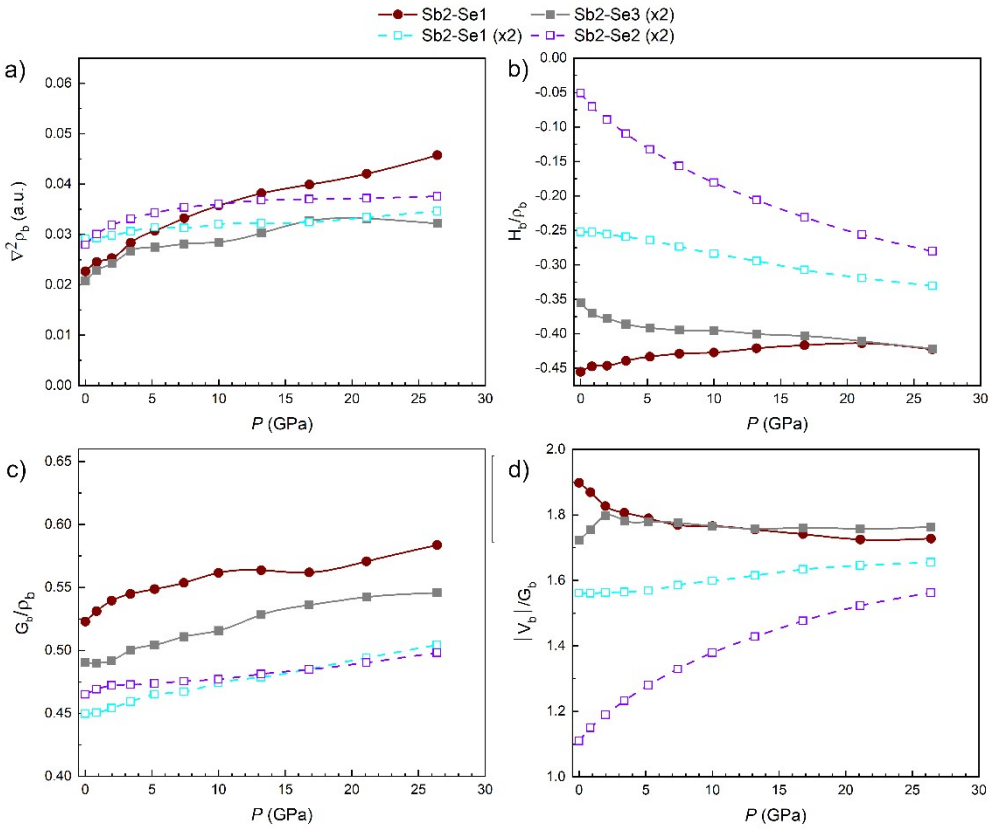


Fig. S8. Sb_2Se_3: Pressure dependence of the topological parameters of Sb2–Se bonds at BCPs: a) $\nabla^2\rho_b$; b) H_b/ρ_b; c) G_b/ρ_b; d) $|V_b|/G_b$.

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