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Electronic Supplementary Information

Metavalent Bonding in Chalcogenides:

DFT-Chemical Pressure Approach

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Table S1. Optimized crystal structures of GeSe at selected pressures.

Structure (pressure)	GeS-type (0 GPa)	GeS-type (10 GPa)	GeS-type (20 GPa)	GeS-type (30 GPa)	TlI-type (40 GPa)
Lattice parameters (Å)	a = 3.81 b = 4.30 c = 10.72	a = 3.73 b = 4.05 c = 10.38	a = 3.65 b = 3.82 c = 10.10	a = 3.54 b = 3.71 c = 9.78	a = 3.48 b = 3.63 c = 9.59

Table S2. Optimized crystal structures of PbSe at selected pressures.

Structure (pressure)	rock-salt (0 GPa)	rock-salt (2.5 GPa)	TlI-type (5.5 GPa)	TlI-type (7.5 GPa)	TlI-type (10 GPa)
Lattice parameters (Å)	a = 6.08	a = 5.92	a = 4.35 b = 4.19 c = 11.46	a = 4.29 b = 4.12 c = 11.28	a = 4.22 b = 4.07 c = 11.14

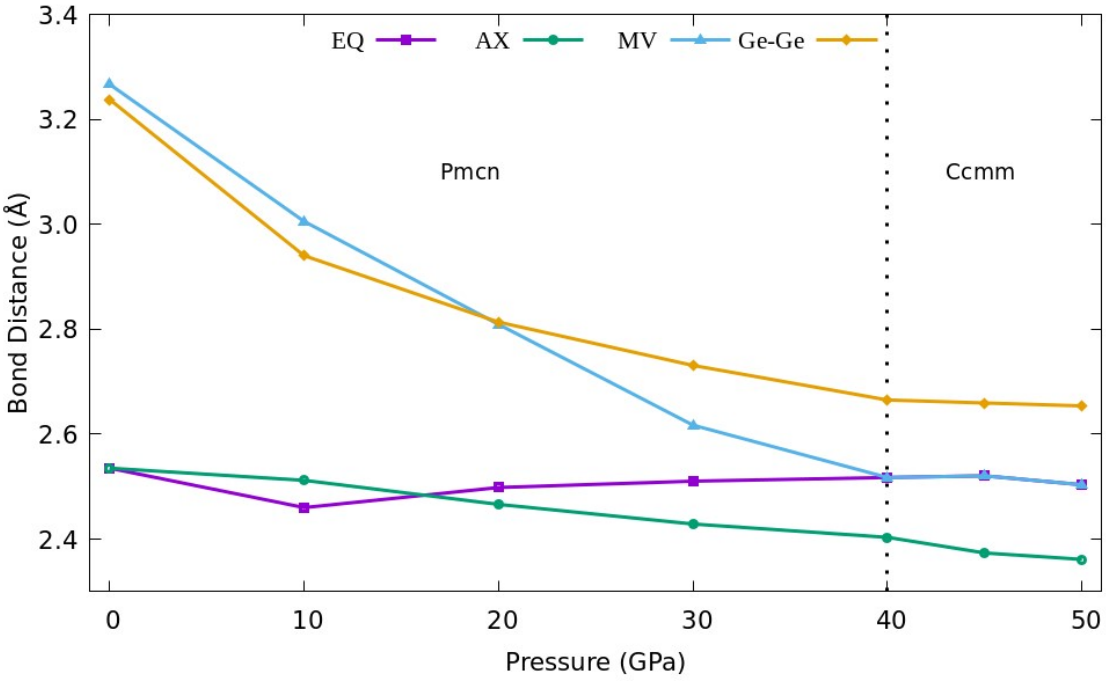

Fig. S1 Pressure dependence of Ge-Se and Ge-Ge distances in *Pmcn* and *Ccmm* GeSe. The vertical dotted line represents the calculated phase transition pressure near 40 GPa.

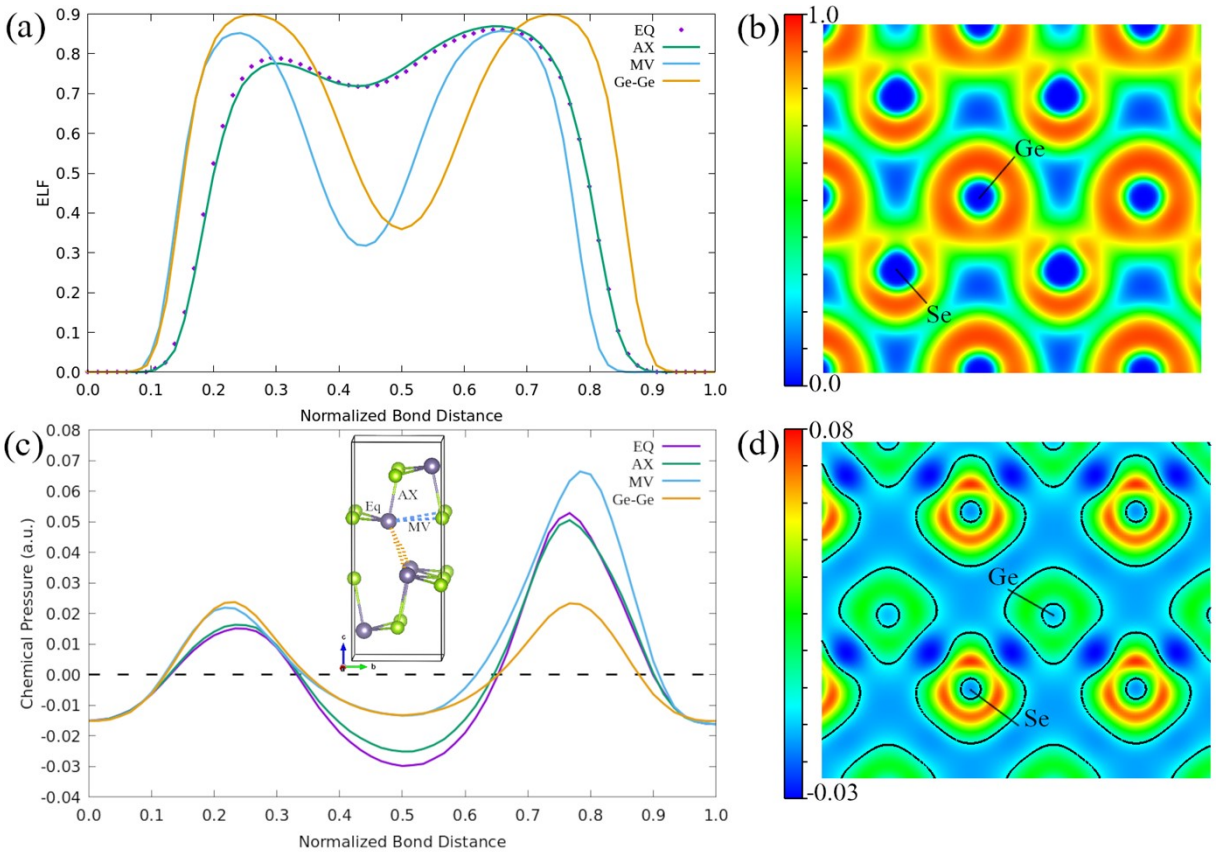

Fig. S2 ELF and chemical pressure plots of GeSe crystal (*Pmcn*) at 10 GPa. (a) 1D ELF, (b) 2D ELF, (c) 1D CP with an inset of the unit cell showing the main distances, and (d) 2D cross-section of the total CP map through the [001] plane. A black contour is shown for CP = 0.

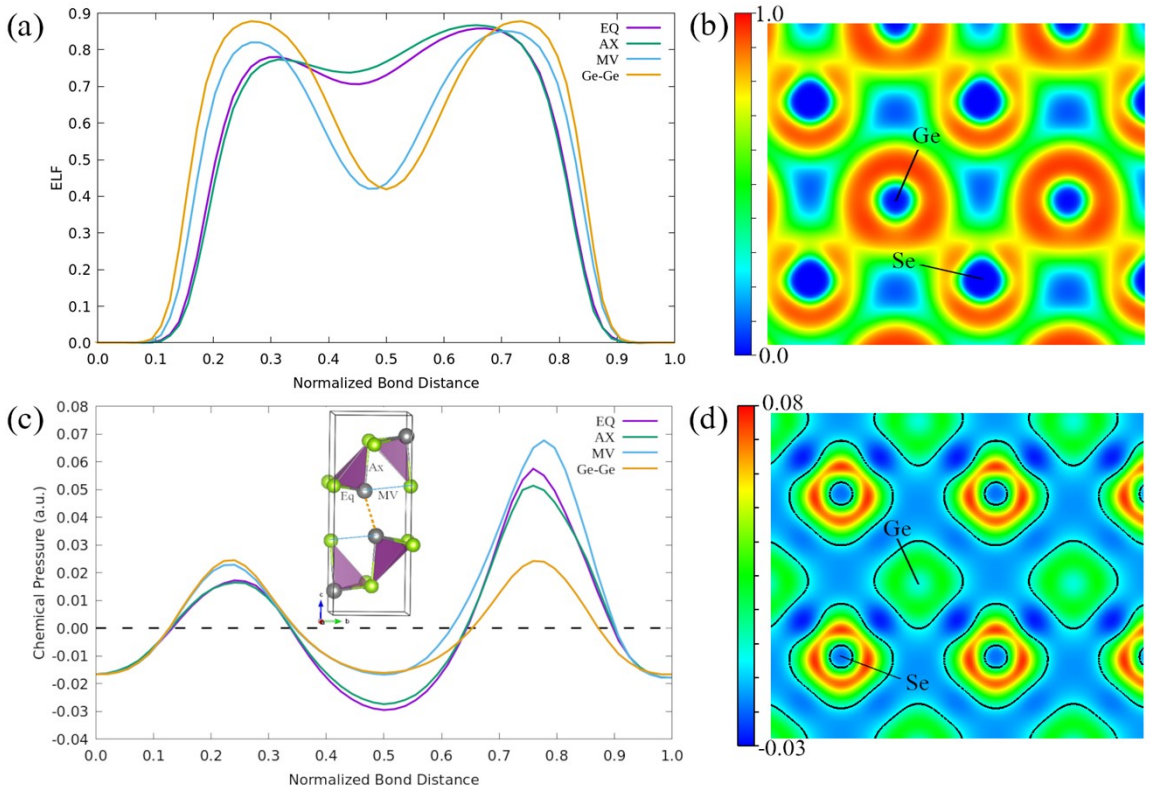

Fig. S3 ELF and chemical pressure plots of GeSe crystal (*Pmcn*) at 20 GPa. (a) 1D ELF, (b) 2D ELF, (c) 1D CP with an inset of the unit cell showing the main distances, and (d) 2D cross-section of the total CP map through the [001] plane. A black contour is shown for CP = 0.

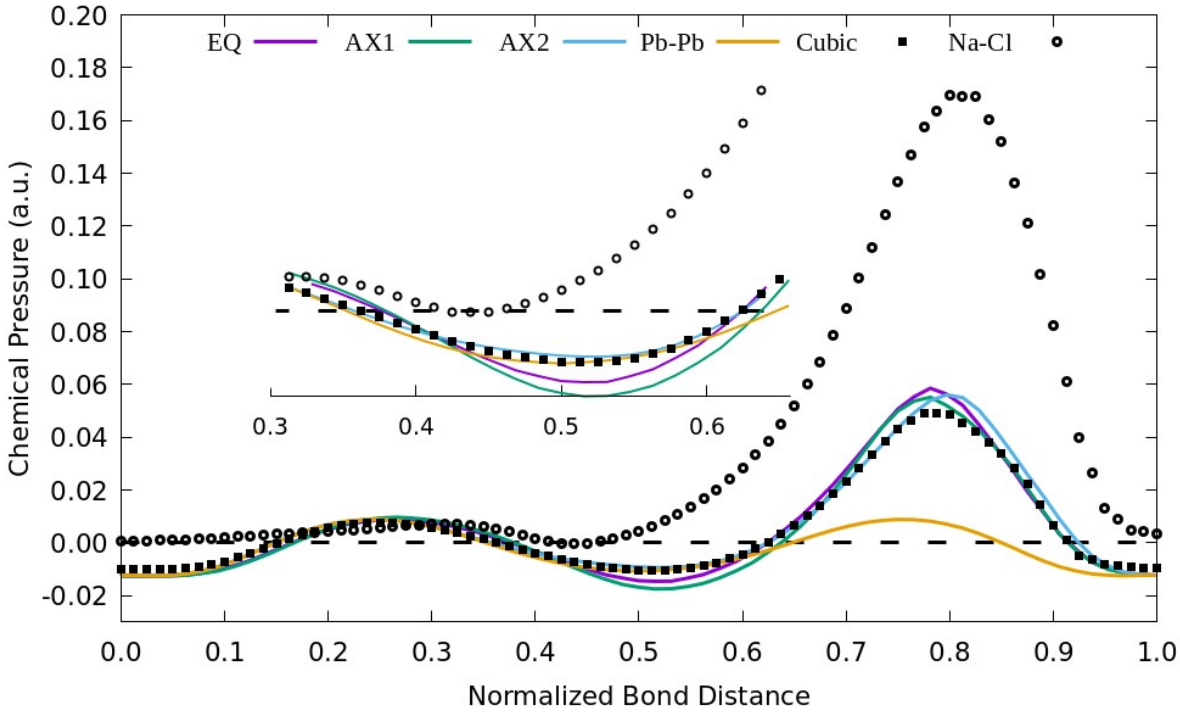

Fig. S4 Comparison between the CP profiles of the different bonds in the orthorhombic (*Ccmm,* EQ, AX1, AX2 and Pb-Pb) and cubic (*Fm-3m*) phases of PbSe and NaCl at ambient pressure.

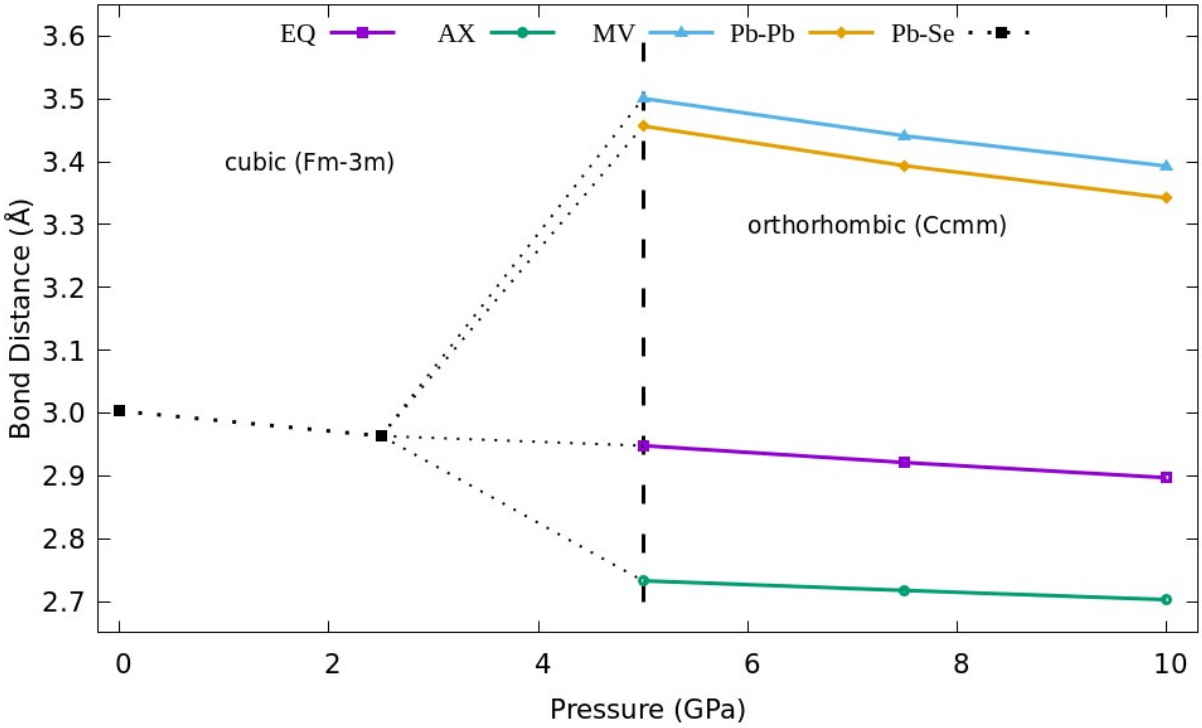

Fig. S5 Pressure dependence of the Pb-Se in *Fm-3m* PbSe and Pb-Se and Pb-Pb distances in *Ccmm* PbSe. The vertical dashed line represents the calculated phase transition pressure at 5 GPa.