Electronic Supplementary Information

Ferroelastic lattice rotation and band-gap engineering in quasi 2D layered-structure $PdSe_2$ under uniaxial stress

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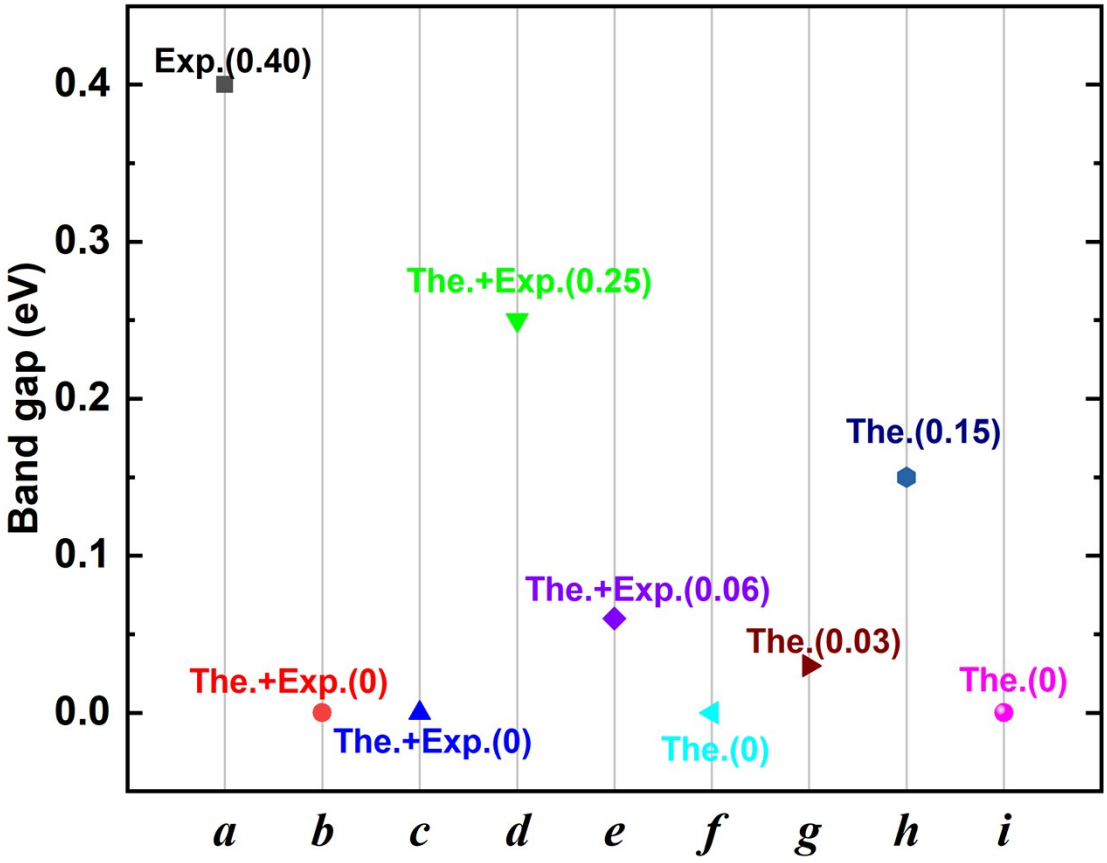
Table S1 Theoretical predicted together with experimental measured equilibrium lattice constants, cell volume and positional parameters (Pd(0, 0, 0) and Se(x, y, z)) of the orthorhombic $PdSe_2$. The data calculated within GGA-PBE and DFT-D (TS) are from present work.

	a (Å)	*b* (Å)	*c* (Å)	V (Å^3)	x	y	z
Exp. [1]	5.741	5.866	7.691	259.01	0.112	0.117	0.407
Exp. [2]	5.746	5.868	7.695	259.43	0.111	0.118	0.406
GGA-PW91 [2]	5.875	5.982	7.772	273.14			
LDA [3]	5.866	6.0	7.357	258.94	0.112	0.118	0.404
optPBE [4]	5.85	5.99	7.95	287.58			
SCAN+rVV10 [4]	5.73	5.87	7.74	260.33			
GGA-PBE	5.726	5.875	8.432	283.64	0.109	0.117	0.413
DFT-D (TS)	5.805	5.892	7.677	262.61	0.114	0.118	0.410

Table S2 Calculated bond lengths, interatomic distances and interlayer distances for the orthorhombic $PdSe_2$ compared with experimental data. As shown in the insets of Fig. 2(c) in the main text, here d1 is the interlayer Pd-Se distance, d2 and d3 are the Pd-Se bond lengths in the square-planar $(PdSe_4)^{2-}$ structural units, d4 is the Se-Se bond lengths in the $(Se_2)^{2-}$ anions, and d_{layers} is interlayer spacing. The data calculated within GGA-PBE and DFT-D (TS) are from present work.

	Exp. [1]	Exp. [2]	LDA [3]	GGA-PBE	DFT-D (TS)
d1 (Å)	3.268	3.261	3.125	3.604	3.288
d2 (Å)	2.438	2.449	2.486	2.454	2.447
d3 (Å)	2.444	2.440	2.487	2.448	2.448
d4 (Å)	2.360	2.378	2.393	2.367	2.363
d_{layers} (Å)	2.415	2.40	2.266	2.753	2.452



	Reference	Band gap (eV)	Method
a	Journal of Physics and Chemistry of Solids 26 (1965): 639-645	0.4	Exp.
b	Journal of the American Chemical Society 139 (2017): 14090-14097	0 (semimetal)	The.+ Exp.
c	Advanced Functional Materials 29 (2019): 1806878	0 (semimetal)	The.+ Exp.
d	Physical Review B 96 (2017): 060509	0.25	The.+ Exp.
e	Physical Review Letters 121 (2018): 086101	0.06	The.+ Exp.
f	Journal of Physics and Chemistry of Solids 71 (2010): 42-46	0 (semimetal)	The.
g	Applied Physics Letters 107 (2015): 153902	0.03	The.
h	Advanced Materials 29 (2017): 1602969	0.15	The.
i	ACS Omega 3 (2018): 5971-5979	0 (semimetal)	The.

Fig. S1 A summary of the band gap for bulk $PdSe_2$ by experimental measurements (Exp.) or theoretical calculations (The.) from available literature.

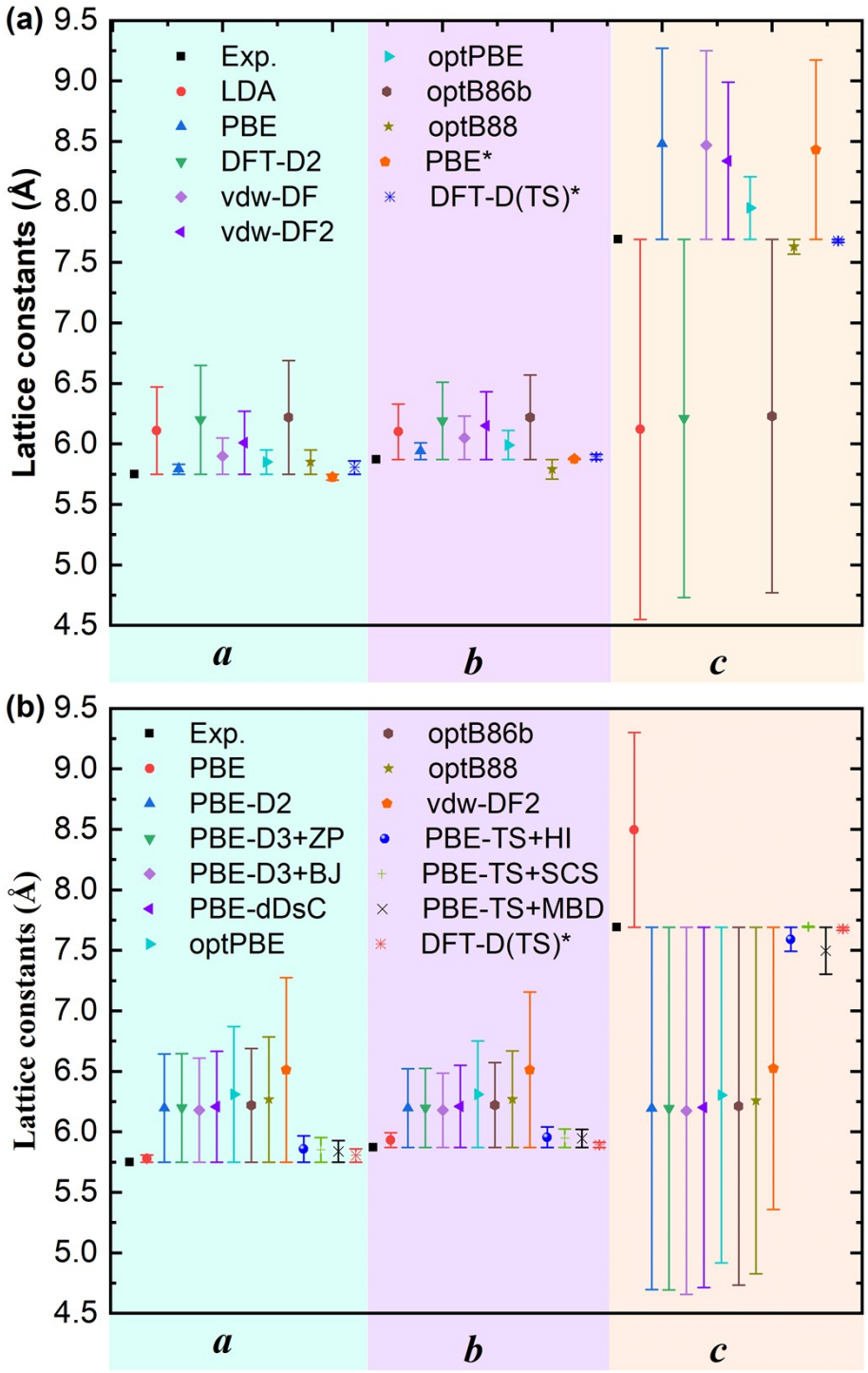


Fig. S2 The calculated lattice constants of bulk $PdSe_2$ using different DFT functionals, and the relative error (Δ) with respect to the experimental data. The theoretical calculated results are from: (a) "Journal of the American Chemical Society 2017, 139, 14090-14097" and (b) "ACS Omega 2018, 3, 5971−5979". The experimental (Exp.) data are from "Inorganic Chemistry 43 (2004): 1943-1949". The data of PBE* and DFT-D (TS)* are from present work.

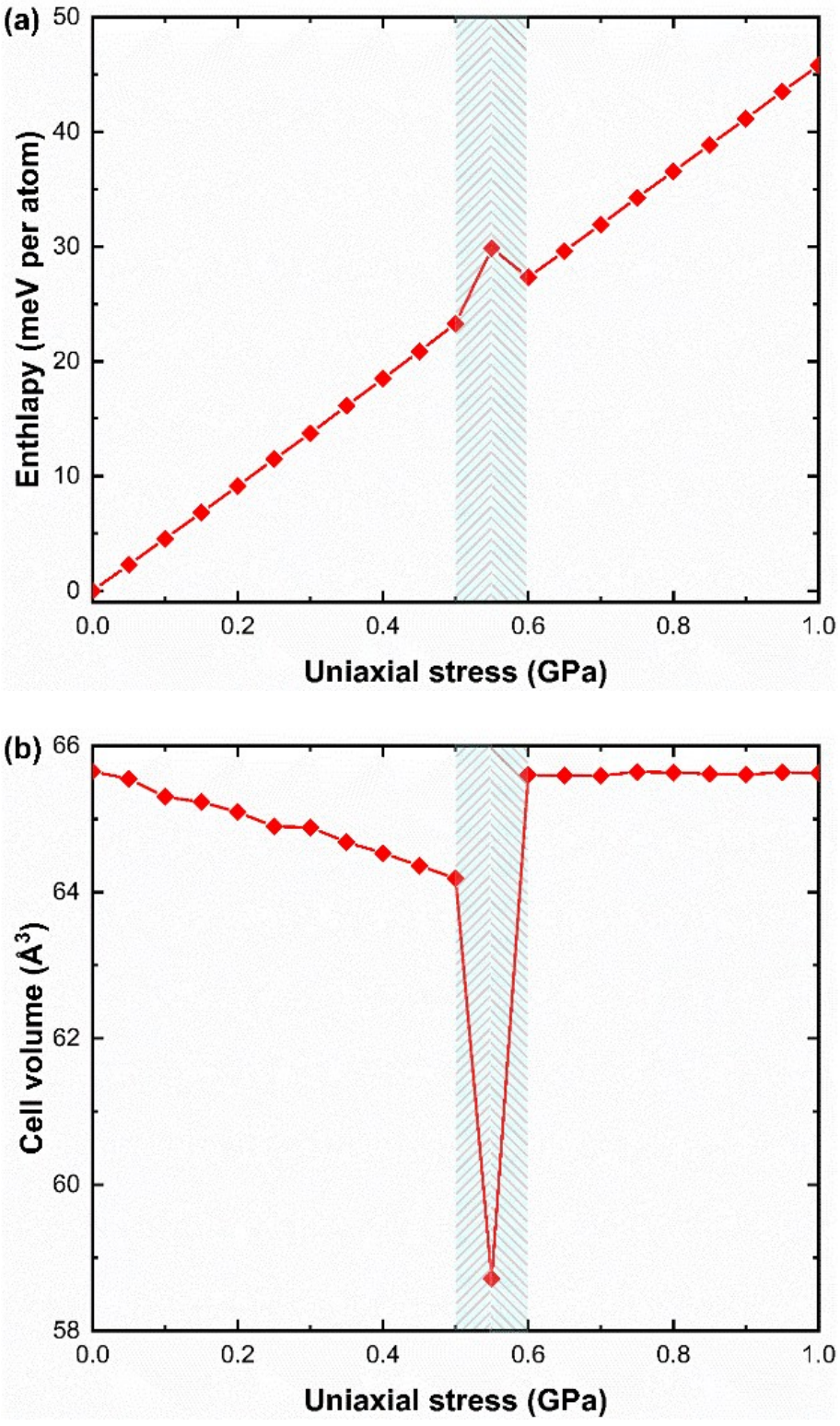


Fig. S3 The calculated resultant enthlapy (a) and cell volume (b) in response to the uniaxial compressive stress along the *c*-axis.

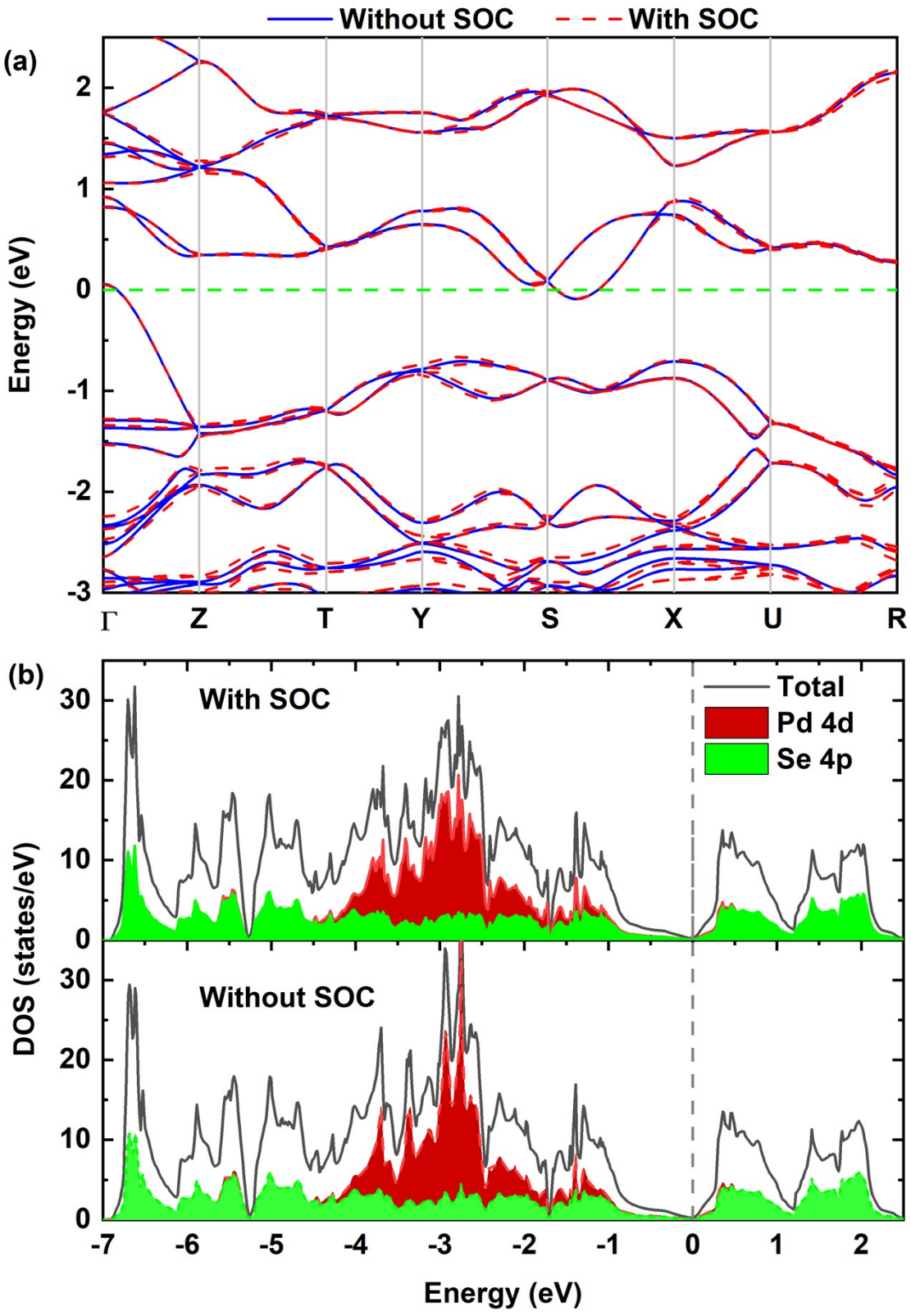


Fig. S4 Calculated electronic band structure (a) and DOS (b) of bulk $PdSe_2$ with DFT-D (TS) without/with SOC. The Fermi energy is set to zero for both cases.

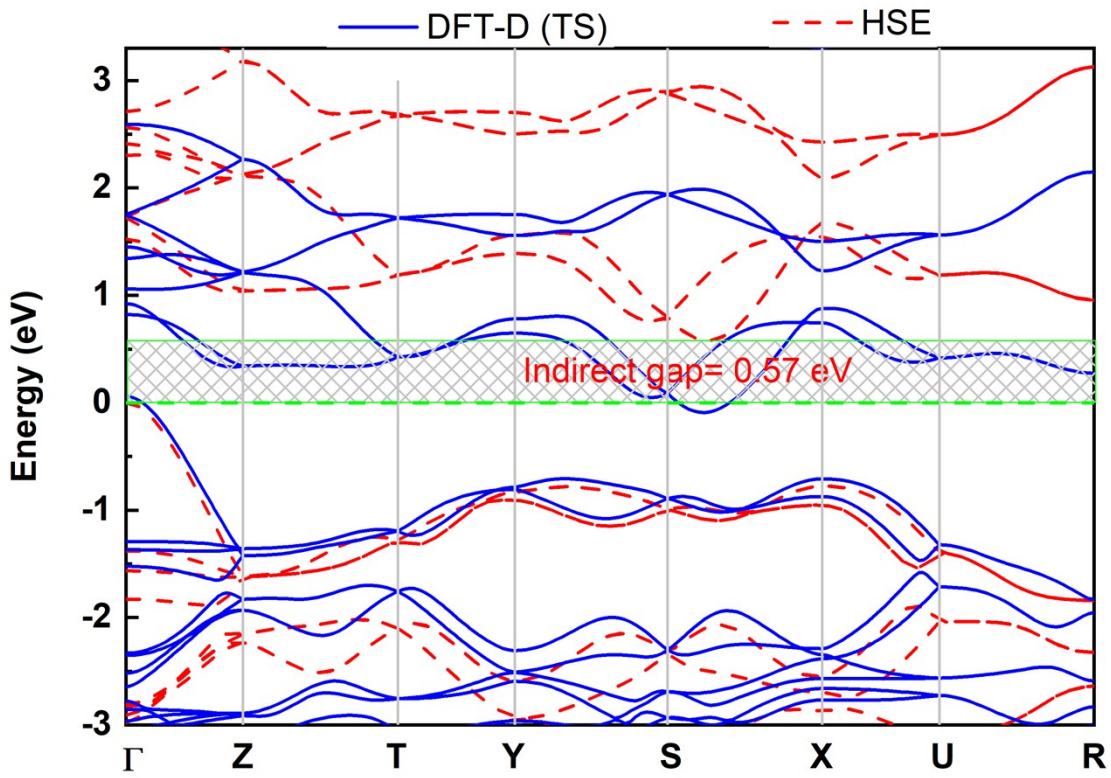


Fig. S5 Calculated electronic band structure for bulk $PdSe_2$ with DFT-D (TS) and HSE06 functionals at ambient condition. The Fermi level is set to zero for both cases.

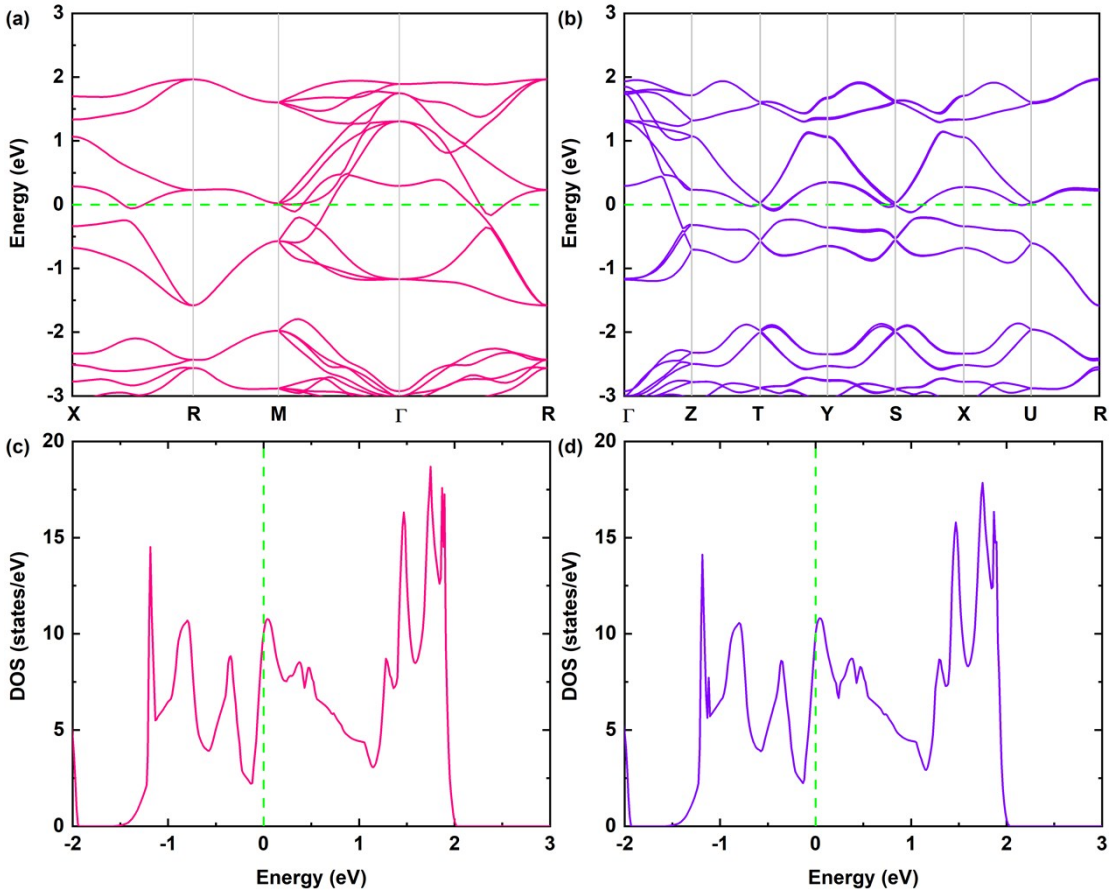
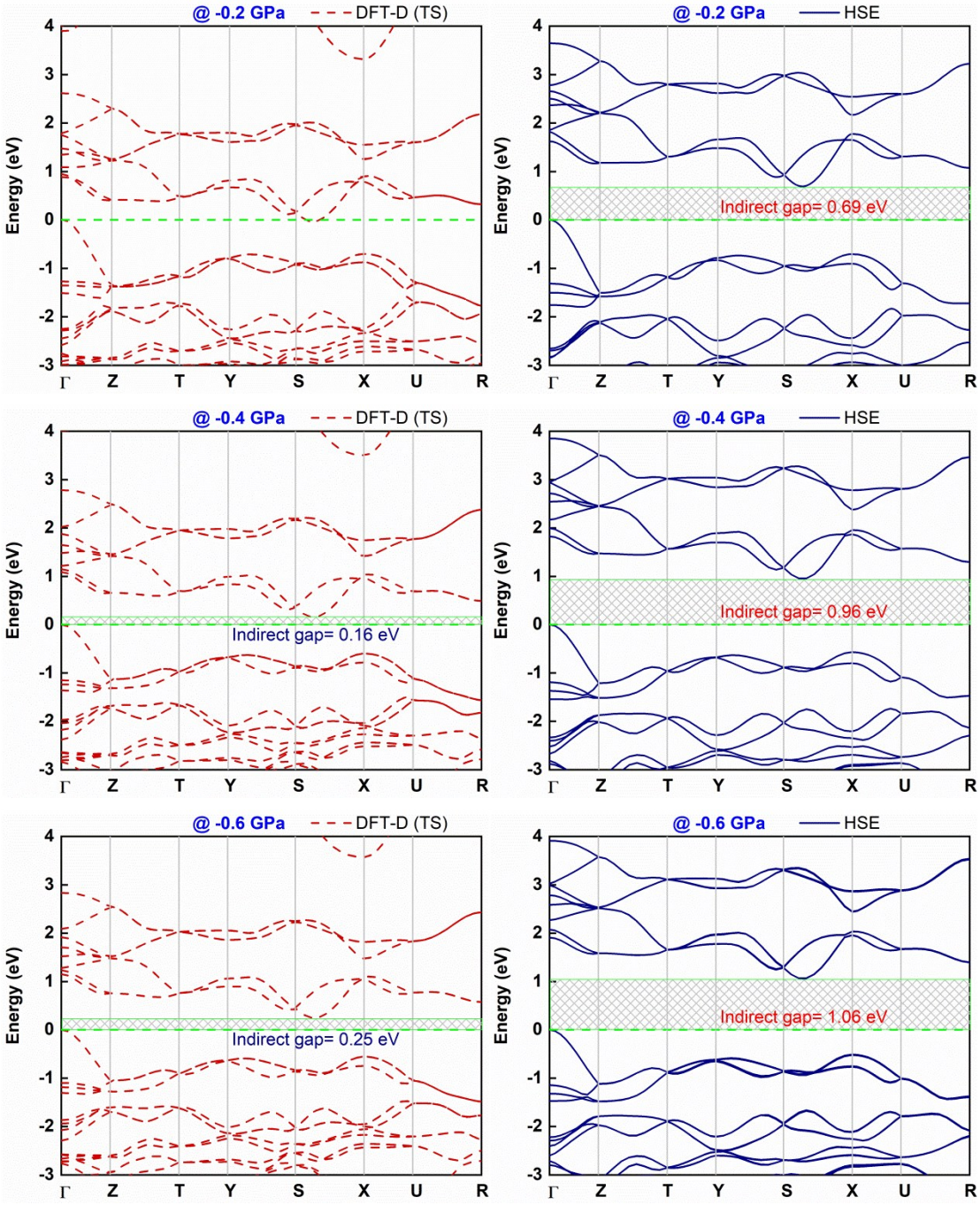


Fig. S6 Electronic structure of bulk $PdSe_2$ calculated with DFT-D (TS) at 0.55 GPa (intermediate state Ⅱ). Because the intermediate state Ⅱ is a nearly cubic phase with pyrite structure, whose lattice constants are almost equal to each other (a = 6.208, b = 6.175, and c = 6.126 Å). We search the symmetry of the optimized structure at 0.55 GPa with different tolerance factor (low and high precision), and impose the resultant symmetry and space group to the structure model with space group (a) $Pa\bar{3}$ and (b) *P*bca, respectively. To exclude the influence of the imposing symmetry, we calculate the corresponding density of states (DOS) of bulk $PdSe_2$ by imposing symmetry $Pa\bar{3}$ (c) or not (d). The calculated results demonstrate the metallic nature is robust for the intermediate state even using HSE06 functional.


@ -0.2 GPa
DFT-D (TS)
@ -0.2 GPa
HSE
Indirect gap= 0.69 eV
@ -0.4 GPa
DFT-D (TS)
Indirect gap= 0.16 eV
@ -0.4 GPa
HSE
Indirect gap= 0.96 eV
@ -0.6 GPa
DFT-D (TS)
Indirect gap= 0.25 eV
@ -0.6 GPa
HSE
Indirect gap= 1.06 eV
Energy (eV)
Γ Z T Y S X U R

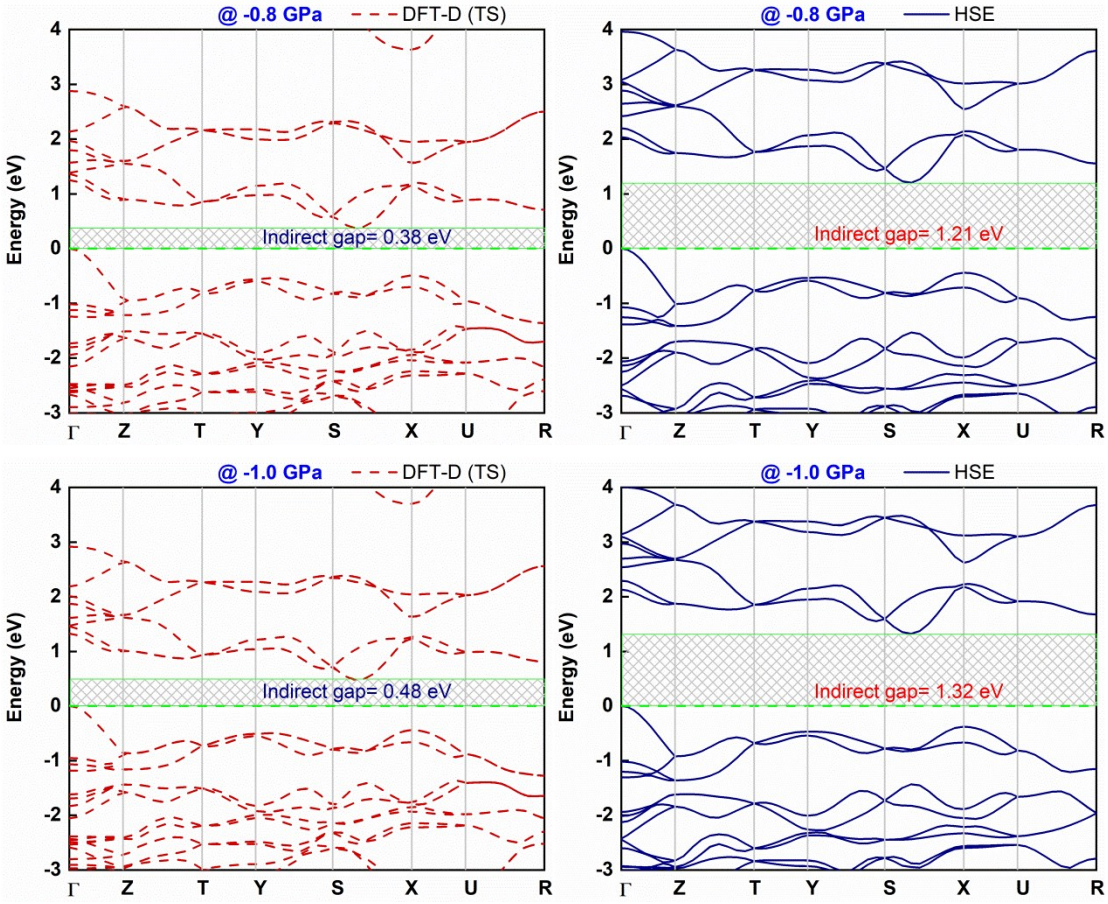


Fig. S7 Calculated electronic band structure for bulk $PdSe_2$ with DFT-D (TS) and HSE06 functionals under tensile stress. The Fermi level and VBM are set to zero for both cases. In fact, real Fermi level and VBM are gruadually decreases along with the increase of the tensile stress.

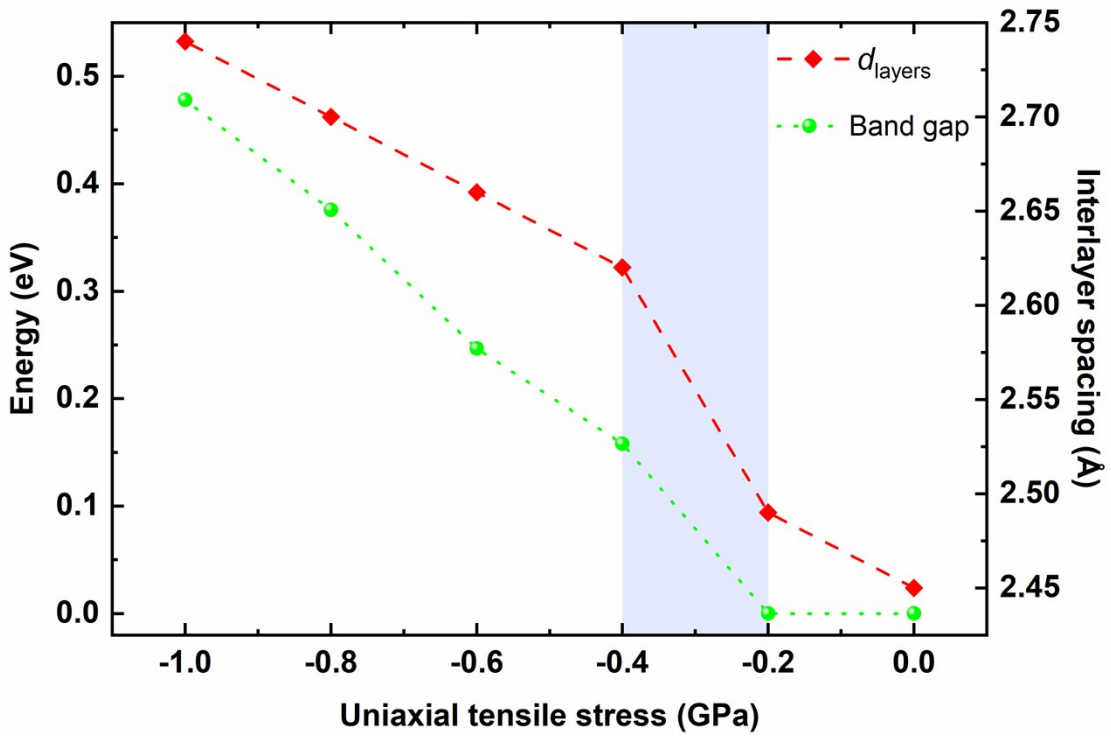


Fig. S8 The evolution of bandgap and interlayer spacing (d_{layers}) along with the uniaxial tensile stress calculated with DFT-D (TS) functional. The shadow region indicates the rapid increasing of the interlayer spacing and the transition from semimetal to semmiconductor.

Reference

[1]. Grønvold, F., and E. Røst. "The crystal structure of $PdSe_2$ and PdS_2." *Acta Crystallographica* **10** (1957): 329-331.

[2]. Soulard, C., et al. "Experimental and theoretical investigation on the relative stability of the PdS_2-and pyrite-type structures of $PdSe_2$." *Inorganic Chemistry* **43** (2004): 1943-1949.

[3]. Hamidani, A., B. Bennecer, and K. Zanat. "Structural and electronic properties of the pseudo-binary compounds PdX_2 (X= P, S and Se)." *Journal of Physics and Chemistry of Solids* **71** (2010): 42-46.

[4]. Oyedele, Akinola D., et al. "$PdSe_2$: pentagonal two-dimensional layers with high air stability for electronics." *Journal of the American Chemical Society* **139** (2017): 14090-14097.

[5]. Zeng, Long-Hui, et al. "Controlled Synthesis of 2D Palladium Diselenide for Sensitive Photodetector Applications." *Advanced Functional Materials* **29** (2019): 1806878.