Supplemental Material: Spontaneous interlayer compression in commensurately stacked van der Waals heterostructures

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bulk	a(Å)	c(Å)	d(Å)		Symmetry
MoS_2	3.162	12.301	2.97	[2.96]	$P6_3/mmc$
$MoSe_2$	3.287	13.003	3.13	[3.22]	$P6_3/mmc$
WS_2	3.155	12.398	3.05		$P6_3/mmc$
WSe_2	3.270	12.957	3.10		$P6_3/mmc$
TiS_2	3.478	5.749	2.60	(2.84)	$P\bar{3}m1$
$TiSe_2$	3.639	6.180	3.15		$P\bar{3}m1$
ZrS_2	3.687	5.812	2.60		$P\bar{3}m1$
$ZrSe_2$	3.793	6.160	3.02		$P\bar{3}m1$

heterostructure	a(Å)	c(Å)	d(Å)	Symmetry
WS_2/MoS_2	3.147	12.329	3.019	$P\bar{6}m2$
$WS_2/MoSe_2$	3.205	11.942	2.72	$P\bar{6}m2$
$MoSe_2/WSe_2$	3.117	12.958	2.705	$P\bar{6}m2$
	3.34[1]			
WS_2/WSe_2	3.202	11.994	2.724	$P\bar{6}m2$
$TiS_2/TiSe_2$	3.437	11.006	2.511	$P\bar{3}m1$
TiS_2/ZrS_2	3.202	12.000	2.800	$P\bar{3}m1$
$TiSe_2/ZrSe_2$	3.660	12.047	2.875	$P\bar{3}m1$

TABLE I. Comparison of the structural parameters (in-plane and out-of-plane lattice parameters and vdW gap) for both the parent structures (left) and heterostructures (right). Calculated lattice parameters for the bulk compounds come from Ref. 2 literature values of the vdW gap, in square brackets, from Ref. 3 and in parentheses from Ref. 4.

heterostructure	E_g(eV)	bulk-constrained	E_g(eV)
WS_2/MoS_2	1.04	MoS_2	1.006
		WS_2	0.722
$WS_2/MoSe_2$	0.722	$MoSe_2$	0.338
		WS_2	0.813
$MoSe_2/WSe_2$	0.879	$MoSe_2$	0.473
		WSe_2	0.614
WS_2/WSe_2	0.818	WS_2	0.851
		WSe_2	0.477
$TiS_2/TiSe_2$	–	TiS_2	0.025
		$TiSe_2$	--
TiS_2/ZrS_2	0.254	TiS_2	0.222
		ZrS_2	0.889
$TiSe_2/ZrSe_2$	–	$TiSe_2$	--
		$ZrSe_2$	0.032

TABLE II. Calculated electronic band gap energies for each of our heterostructures and their bulk-constrained counterparts. Here, we report data for the bulk compounds constrained to the c lattice parameters of the corresponding heterostructure. – indicates that the calculated structure is metallic.

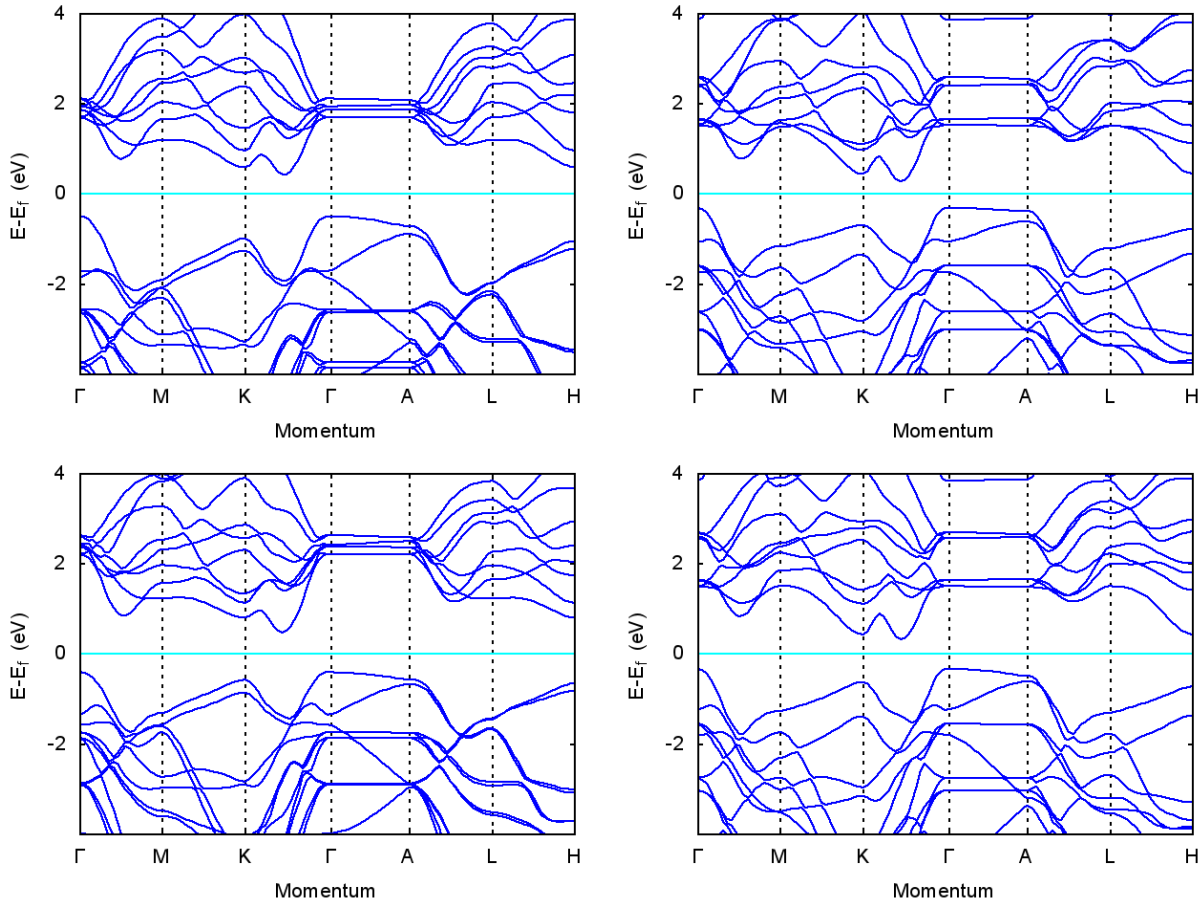

FIG. 1. (Color Online) Calculated Kohn-Sham band structures for the hexagonal heterostructures investigated here. Left to right, top row: WS_2/MoS_2 and $WS_2/MoSe_2$. Left to right, bottom row: $MoSe_2/WSe_2$ and WS_2/WSe_2. The horizontal teal line corresponds to the Fermi level.

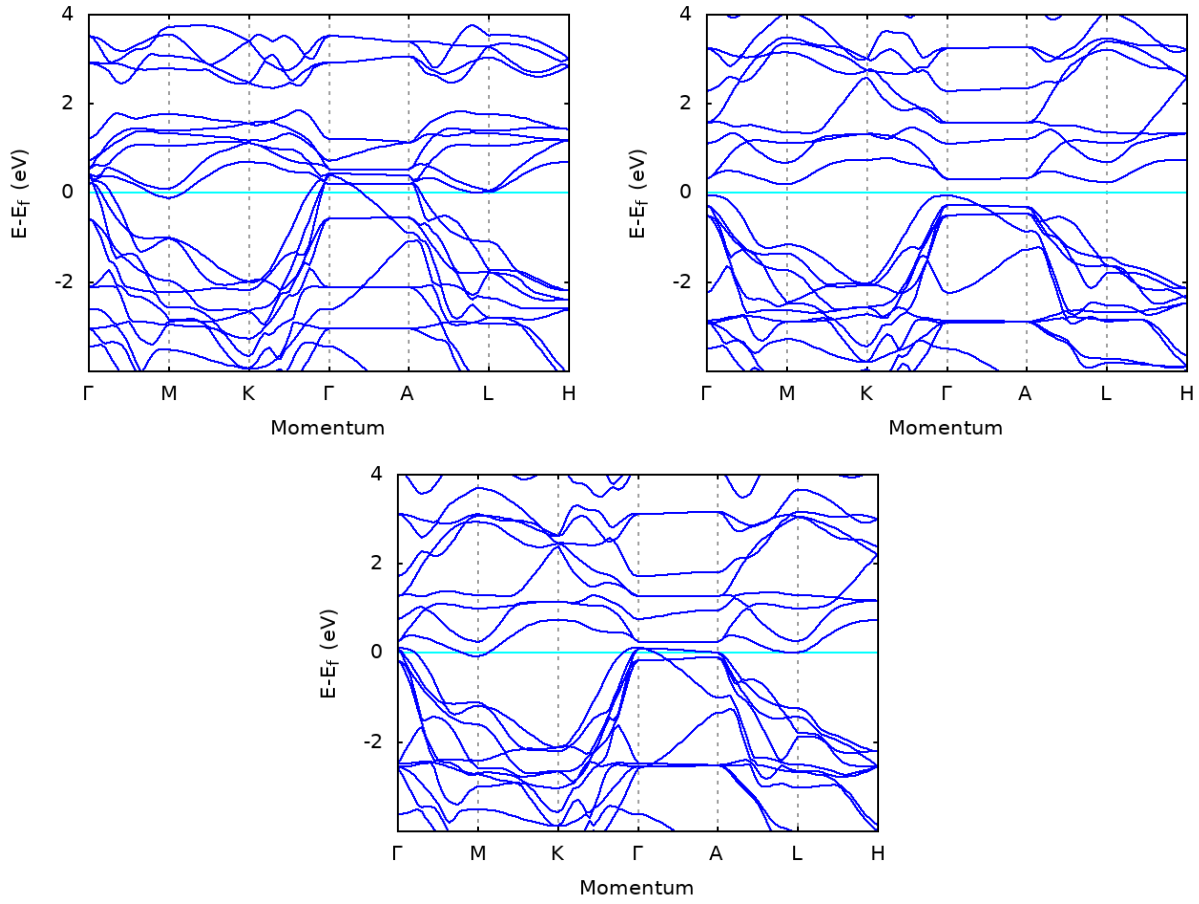

FIG. 2. (Color Online) Calculated Kohn-Sham band structures for the trigonal heterostructures investigated here. Left to right, top row: $TiS_2/TiSe_2$ and TiS_2/ZrS_2. Bottom row: $TiSe_2/ZrSe_2$. The horizontal teal line corresponds to the Fermi level. $TiS_2/TiSe_2$ is fully metallic, TiS_2/ZrS_2 is semi-conducting, and $TiSe_2/ZrSe_2$ is semi-metallic.

	atom	$q_{B,h}$ (e)	$q_{B,b}$ (e)
WS_2/MoS_2	Mo	1.161	1.155
	S	−0.579	−0.577
	Lay	0.003	0
	W	1.397	1.400
	S	−0.695	−0.700
	Lay	0.007	0
$WS_2/MoSe_2$	Mo	0.874	0.910
	Se	−0.422	−0.455
	Lay	0.030	0
	W	1.409	1.400
	S	−0.717	−0.700
	Lay	−0.025	0
$MoSe_2/WSe_2$	Mo	0.896	0.910
	Se	−0.448	−0.455
	Lay	0.000	0
	W	1.082	1.081
	Se	−0.537	−0.540
	Lay	0.008	0
WS_2/WSe_2	W	1.407	1.400
	S	−0.717	−0.700
	Lay	−0.027	0
	W	1.049	1.081
	Se	−0.507	−0.540
	Lay	0.035	0
$TiS_2/TiSe_2$	Ti	1.762	1.764
	S	−0.897	−0.882
	Lay	−0.032	0
	Ti	1.590	1.599
	Se	−0.780	−0.799
	Lay	0.03	0
TiS_2/ZrS_2	Ti	1.780	1.764
	S	−0.889	−0.882
	Lay	0.002	0
	Zr	1.972	2.010
	S	−0.989	−1.006
	Lay	−0.006	0
$TiSe_2/ZrSe_2$	Ti	1.625	1.599
	Se	−0.807	−0.799
	Lay	0.011	0
	Zr	1.787	1.846
	Se	−0.897	−0.921
	Lay	−0.007	0

TABLE III. Calculated Bader charge (q_b) for the heterostructures and bulk compounds using the Atom-in-molecule approach[5]. The first column of charges corresponds to $q_{B,h}$ of the heterostructure and the second column corresponds to $q_{B,b}$ of the bulk structure. The calculated Bader charge is identical for both chalcogen atoms in each structure. Departures from charge neutrality of order 0.01 are due to numerical errors in the Bader algorithm. The "Lay" line is the total layer charge to show charge transfers. Bader charges for the bulk structures come from Ref. 6 except ZrS_2 and $ZrSe_2$ which are calculated in this work.