

Ultra-weak Interlayer Coupling in Two-Dimensional Gallium Selenide

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Supplementary Material

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1 Energy differences – Stability

In our model, a given N QL geometry has the same number of atoms and about the same cell volume for both polytypes. Thus we can use the total energy difference of the two polytypes with same N QL number, normalized by the number of vdW gaps n^{vdW} (the number of interlayer regions in a unit cell), $\delta E_{\varepsilon/\beta} = (E_{\varepsilon} - E_{\beta})/n^{\text{vdW}}$, to estimate the most stable polytype for the N QL crystal. From this definition, a value $\delta E_{\varepsilon/\beta} < 0$ indicates that the ε phase is energetically more stable than the β phase for the N QL geometry considered. In Table S1 (supporting information), we present these energy differences, using the rVV10 functional, $\delta E_{\varepsilon/\beta}^{\text{rVV10}}$ (the same trend is obtained by using LDA).

Table S1 $\delta E_{\varepsilon/\beta}^{\text{rVV10}}$ for bulk and N QL geometry for ε - and β -polytypes of GaSe

	bulk	7L	6L	5L	4L	3L	2L
$\delta E_{\varepsilon/\beta}^{\text{rVV10}}$ (meV)	-3.83	-3.85	-3.89	-3.50	-3.59	-3.65	-3.22

For completeness of our study about the relative stability of β and ε phases of few-layer GaSe, we calculated $\delta E_{\varepsilon/\beta}$ for 3 QL GaSe using the semi-empirical correction proposed in Ref. 1 (grimme-D2) and the nonlocal functional vdW-DF2.² The results in Table S2 are in agreement with the trends observed in our rVV10 and LDA calculations.

Table S2 Relative stability of ε and β phases for 3 QL using two different descriptions of the van der Waals interactions, the grimme-D2 and the vdW-DF2.

$\delta E_{\varepsilon/\beta}^{\text{grimme-D2}}$ (meV)	-0.39
$\delta E_{\varepsilon/\beta}^{\text{vdw-DF2}}$ (meV)	-2.55

2 Cleavage Energies

The surface energy (E_{surf}) can be defined as:

$$E_{\text{surf}} = \frac{1}{2A} (E_{\text{slab}} - nE_{\text{bulk}}) \quad (1)$$

where E_{slab} , n , E_{bulk} and A are the slab energy, the ratio of the number of atoms (or unit formula) in the slab and bulk, the bulk energy and the area of the created surface. The energy to cleave the bulk and form two surfaces, i.e., the cleavage energy, is defined by $E_{\text{cleave}} = 2E_{\text{surf}}$.

A naive approach to obtain the surface energy from Eq. (1) is to obtain the needed parameters from well converged bulk and slab calculations. This approach suffer from divergence with n ,³ even when carefully converged bulk and

slab calculations are performed.¹ A free divergence approach is to fit the $E_{\text{slab}}(N_l)$,³ where N_l is the number of layers in the slab:

$$E_{\text{slab}} = E_{\text{surf}} 2A + N_l E_{\text{bulk}} \quad (2)$$

$$y = b + N_l a; \quad b = E_{\text{surf}} 2A; \quad a = E_{\text{bulk}}/2 \quad (3)$$

Eq. (3) provides an estimation of E_{bulk} from slab calculations and allows to evaluate Eq. (1) using slab calculations only. For further discussion, we call the difference between the fitting approach and the naive one as δE_{bulk} .

We calculated the cleavage energies from the two estimations of E_{bulk} , from the naive approach and from the fitting approach, using the rrv10 functional and considering slabs with 7, 9, 11 and 13 layers. Fig. S1(a) and (b) show the results for Graphite (Bernal-stacking) and ϵ -GaSe, respectively. We note that while the fitting approach converge to a value, the naive approaches diverges with N .

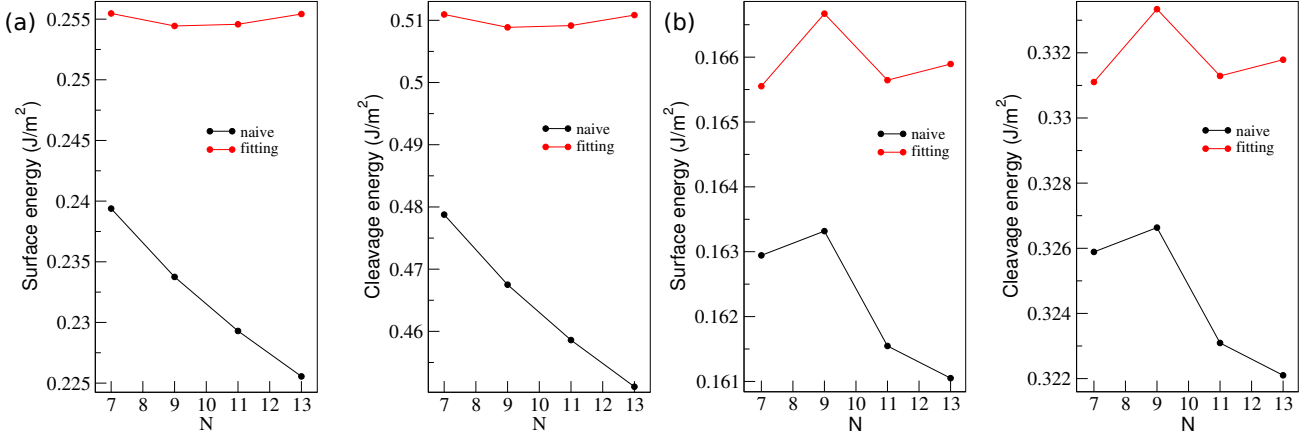


Figure S1 Surface and Cleavage energies from the naive approach and the fitting approach for (a) Graphite Bernal-stacking and (b) ϵ -GaSe.

The results for the ϵ -GaSe and β -GaSe and the more stable phases of graphite (Bernal-stacking) and MoS₂ (2H-MoS₂) are summarized in Table S3.

Table S3 Cleavage energy and δE_{bulk} (see text).

crystal	$E_{\text{cleave}} \text{ (J m}^{-2}\text{)}$		$\delta E_{\text{bulk}} \text{ (meV)}$
	E_{bulk} from bulk calculation	E_{bulk} from fitting of Eq. (3)	
ϵ -GaSe	0.32	0.33	-1.19
β -GaSe	0.32	0.33	-1.55
graphite	0.45	0.51	-3.02
MoS ₂	0.50	0.50	0.17

From our calculations, among the considered layered materials, the GaSe crystals are the most easiest to cleave, in agreement with our results for the breathing force constant obtained from the linear-chain model.

3 Lattice parameters of optimized structures

Our calculations indicate that the in-plane lattice parameter a , defined by the bonds within the QL, is essentially the same for all N QL and bulk for both polytypes. The values obtained for a using the LDA, (a^{LDA}), and the rVV10 (a^{rVV10}) functionals, underestimates by 1.3% and overestimates by 2.7%, respectively, the experimental value of 3.75 Å.⁴ For the bulk geometries, the out-of-plane lattice parameter c is defined by the vdW interaction between adjacent QLs. Both LDA and rVV10 functionals indicate that the separation of adjacent QLs in the β polytype is

¹ In the slab calculations and bulk reference we use same convergence criterion for force (1.0×10^{-3} Ry/bohr), energy (1.0×10^{-4} Ry) and self-consistency (1.0×10^{-10} Ry). For both GaSe crystals, we use a basis set to expand the wave-functions (charge-density) of 42 (336) Ry and a k-grid of $8 \times 8 \times 1$ (for bulk we use $8 \times 8 \times 2$); for Graphite, 36 (216) Ry and $14 \times 14 \times 1$ (for bulk we use $14 \times 14 \times 2$); for MoS₂, 44 (352) Ry and $8 \times 8 \times 1$ (for bulk we use $8 \times 8 \times 2$).

$\sim 0.6\%$ greater than the value in the ε -type. This is in agreement with experimental results, where the bulk of both polytypes show same c .⁴ The values obtained for c in bulk ε -GaSe using the LDA, $c_{\varepsilon}^{\text{LDA}}$, and using the rVV10, $c_{\varepsilon}^{\text{rVV10}}$, underestimate by 1.8% and overestimate by 0.3% respectively the experimental value of 15.95Å.⁴

Indeed, LDA provides good description of lattice parameters in solids.⁵ LDA tends to slightly underestimate lattice parameters in solids, yet the predicted values are in better agreement with the experiments than some GGA-based functionals (e.g.: PBE) and vdW-based functionals, which tend to overestimate the lattice parameters. These trends are valid also for layered materials, as shown by our results for GaSe. As another examples, LDA calculations underestimate the lattice parameters a and c for bulk MoS₂ and WS₂ by $\sim 0.7\%$ and $\sim 2.1\%$, respectively.⁶ In the case of bulk h-BN, experiments indicate that the interlayer distance is about 3.3Å,^{7,8} the out of plane lattice parameter $c = 6.65\text{Å}$,^{8,9} the in-plane lattice parameter $a = 2.504\text{Å}$,^{8,9} while LDA predicts the interlayer distance of 3.254Å, and $a = 2.496\text{Å}$ ¹⁰ which are within 1.4% and 0.32%, respectively, from the experimental values.

4 Raman Tensors

1. N -odd β and ε polytypes (D_{3h}^1 space group):

$$A_1' : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix},$$

$$E'_{(x)} : \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad E'_{(y)} : \begin{pmatrix} 0 & -d & 0 \\ -d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$E'' : \begin{pmatrix} 0 & 0 & -c \\ 0 & 0 & 0 \\ -c & 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{pmatrix}.$$

2. N -even β polytype (D_{3d}^3 space group):

$$A_{1g} : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix},$$

$$E_g : \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}.$$

3. N -even ε polytype (C_{3v}^1 space group):

$$A_{1(z)} : \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix},$$

$$E_{(x)} : \begin{pmatrix} 0 & c & d \\ c & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \quad E_{(y)} : \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}.$$

4. Bulk β polytype (D_{6h}^4 space group):

$$E_{2g} : \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & -d & 0 \\ -d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

5. Bulk ε polytype (D_{3h}^1 space group):

$$E'_{(x)} : \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad E'_{(y)} : \begin{pmatrix} 0 & -d & 0 \\ -d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

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