

Comparative study of structural and electronic properties of GaSe and InSe polytypes



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Juliana Srour

*LCP-A2MC, Institute Jean Barriol, Université de Lorraine, 1 Bd Arago,
F-57078 Metz, France*

Michaël Badawi

*LCP-A2MC and LPCT – Laboratoire de Physique et Chimie Théoriques
(UMR CNRS UL 7019), Université de Lorraine, Rue Victor Demange,
F-57500 Saint-Avold, France*

Fouad El Haj Hassan

*Université Libanaise – Faculté de Sciences (I), LPE – Laboratoire de
Physique et d'Electronique, Campus Rafic Hariri – Hadath, Beirut,
Lebanon*

Andrei Postnikov^{a)}

*LCP-A2MC, Institute Jean Barriol, Université de Lorraine, 1 Bd Arago,
F-57078 Metz, France*

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Equilibrium crystal structures, electron band dispersions and band gap values of layered GaSe and InSe semiconductors, each being represented by four polytypes, are studied via first-principles calculations within the density functional theory (DFT). A number of practical algorithms to take into account dispersion interactions are tested, from empirical Grimme corrections to many-body dispersion schemes. Due to the utmost technical accuracy achieved in the calculations, nearly degenerate energy-volume curves of different polytypes are resolved, and the conclusions concerning the relative stability of competing polytypes drawn. The predictions are done as for how the equilibrium between different polytypes will be shifted under the effect of hydrostatic pressure. The band structures are inspected under the angle of identifying features specific for different polytypes, and with respect to modifications of the band dispersions brought about by the use of modified Becke-Johnson (mBJ) scheme for the exchange-correlation (XC) potential. As another way to improve the predictions of band gaps values, hybrid functional calculations according to the HSE06 scheme are performed for the band structures, and the relation with the mBJ results discussed. Both methods nicely agree with experimental results and with state-of-the-art GW calculations. Some discrepancies are identified in cases of close competition between the direct and indirect gap (e.g., in GaSe); moreover, the accurate placement of bands revealing relatively localized states is slightly different according to mBJ and HSE06 schemes.

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^{a)}Corresponding author: andrei.postnikov@univ-lorraine.fr

I. INTRODUCTION



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Layered nature of III-VI semiconductors, known since long, experiences in the last decades a renaissance of interest, related to two-dimensionality of properties and promising applications. The structure of these materials is such that cations (Ga or In, the the present work) are bonded, in the tetrahedral coordination, to another similar cation and to three anions (Se, in the present work). The anions place themselves in hexagonal arrangement at two surfaces of what is in the following referred to as *double layer*, each anion being bonded to three cation beneath (within the layer). The inner cation-cation bond directs at normal to the surface, and the anions at the two opposite surfaces are (in all known structure modifications) in the eclipsed (wurtzite-like) configuration.¹ The double layers can be stockpiled in a variety of sequences, giving rise to polytypes with the globally hexagonal symmetry. The anions' valences being saturated, there is formally no covalent bonding between the adjacent double layers, hence an important role of dispersion interactions (DI) in holding the layer system together.

From the point of view of experiments or applications, the step of bulk materials' characterization by spectroscopies and other techniques being now history, the modern interest for these materials is largely fed by possibilities to exfoliate^{2,3} or grow^{4–6} single layers, dope them⁷ or otherwise distort, and bring together with other layered materials into fancy heterostructures or devices.^{8–10}

From the point of view of first-principles studies, history are calculations of electronic structure of a single layer, or of singular polytypes, addressing particular problems or particular experiments. Nowadays as practical schemes to merge the DI with the density functional theory (DFT) do gradually become routine, it seems appropriate to revise the accuracy with which these methods would address the structures and relative stabilities of polytypes. Another point of practical interest which can be addressed by calculations is the variation of band gaps over structurally close materials, that is a clue for tuning the optical properties by structure engineering in the desirable direction. Systematically underestimated in traditional DFT calculations using, say, the local density approximation (LDA) or generalized gradient approximation (GGA), yet available with high accuracy from much more demanding GW calculations, the band gaps seem to be nowadays fairly well reproducible within schemes which require only moderate intervention into the DFT calculation routine. Such

schemes include namely the hybrid functionals, which admix exact exchange into a DFT exchange-correlation (XC) functional, and meta-GGA techniques, which express the XC potential in terms of further parameters than the charge density and its gradient.

In the present work, we offer a comparative analysis of first-principles predictions concerning GaSe and InSe semiconductors along the four axes of comparison: (*i*) critical assessment of different schemes to include the DI into the calculations; (*ii*) comparison of two currently used schemes, – a realization of meta-GGA known as “modified Becke-Johnson” (mBJ) formula for the XC potential¹¹ and the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional,¹² – to obtain band structures and band gaps in good agreement with experiment; (*iii*) comparison of GaSe and InSe as systems structurally and chemically close yet differing in their degree of covalence; (*iv*) for each system – a comparison of stability throughout four polytypes, characterized by delicate differences in their crystal structures.

Moreover, as yet another line of comparison, two different calculation methods, WIEN2k¹³ and VASP,¹⁴ have been used and, in fact, tested against each other on, in part, similar tasks. The satisfactory agreement of results gave us the necessary confidence in the trends discussed.

The work is organized as follows. Section II explains the structures of polytypes, section III sets the context of earlier calculations and important experiments, section IV specifies the methods within the DFT which are of special interest for the present study. Further on, the new results come arranged by topics, with corresponding discussion: Section V deals with optimized crystallographic parameters and performance of different schemes to include the DI; section VI discusses the relative stabilities of polytypes in the context of energy/volume curves; section VII addresses band structures of polytypes obtained with two different approaches and compares the resulting band gaps with experimental data. Section VIII concludes the discussion.

II. CRYSTAL STRUCTURES OF DIFFERENT POLYTYPES

Crystal structures of the four polytypes addressed in the present work have been systematized (for the GaSe compound) by Kuhn *et al.*¹⁵; Likforman and Guittard¹⁶ reported the lattice parameters of γ -InSe. The latter phase being in fact rhombohedral, it is shown, among the other polytypes, in the hexagonal setting in Fig. 1. All polytypes have unit

cells which are similar in projection onto the hexagonal plane, but differ in the number and lateral placement of stacked double layers. This manuscript was accepted by J. Chem. Phys. Click [here](#) to see the version of record. A compact notation to distinguish the polytypes would be to use a/b/c letters to mark three different sites in projecting the atoms onto two-dimensional hexagonal lattice, reserving the uppercase letters for cations and lowercase for anions. Since anions are always in the eclipsing configuration, a two-letter code suffices to pinpoint a double layer, thus extending an (ambiguous) single-letter stacking-sequence labeling used in Ref. 15. The repeated sequence of double layers, included in square brackets, is indicated in Fig. 1 for each polytype. In principle, an infinite number of stacking

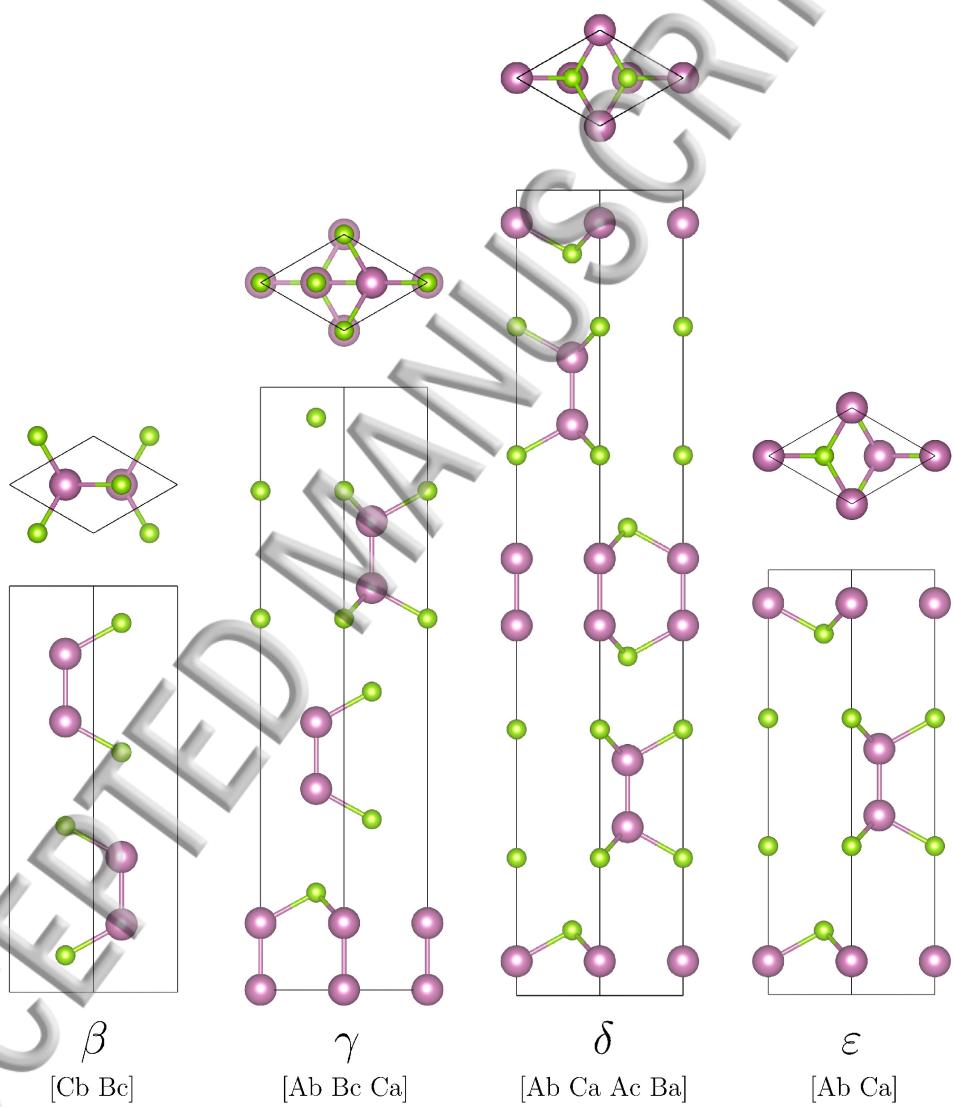


FIG. 1. Side and top view of the unit cells of β , γ , δ and ε polytypes of GaSe or InSe. Large circles: cations, small circles: anions. The stacking notation at the bottom is explained in the text.

TABLE I. Crystal structure definitions for four polytypes of III-VI binaries. The z coordinates are indicated as for GaSe, after Kuhn *et al.*¹⁵

Polytype; stacking order	Space group	Wyckoff positions	$z(\text{Ga})$	$z(\text{Se})$
β [Cb Bc]	$P6_3/mmc$ (194)	4(f)	$\frac{1}{4} - 0.07$	$\frac{3}{4} - 0.16$
		2(g)	0.075	$\frac{1}{2} + 0.15$
ε [Ab Ca]	$P\bar{6}m2$ (187)	2(h)	$\frac{1}{2} + 0.07$	
		2(i)		0.15
γ [Ab Bc Ca]	$R3m$ (160)	3(a)	-0.05; +0.05	$\frac{2}{3} - 0.1; \frac{2}{3} + 0.1$
δ [Ab Ca Ac Ba]	$P6_3mc$ (186)	2(a)	-0.038; +0.039	$\frac{1}{4} - 0.071; \frac{1}{4} + 0.078$
		2(b)	$\frac{1}{4} - 0.038; \frac{1}{4} + 0.038$	$\frac{1}{2} - 0.075; \frac{1}{2} + 0.075$

sequences can be constructed, respecting the simple rule that an anion should never be in the same site with its closest cation, nor with the adjacent-layer anion.

Space groups and Wyckoff positions with representative z coordinates (corresponding to GaSe after Ref. 15) are given in Table I. The z coordinates in this table are formatted here so as to emphasize the splitting of cation or anion positions from the median planes of the corresponding double layer. We note that this splitting amounts, in all structures, to approximately ± 0.15 for cations and ± 0.3 for anions, in terms of the c parameter per double layer. This reveals a relative robustness of the double layer, the basic structure element differently stacked in different polytypes. There is a misprint in the original Table of Kuhn *et al.*¹⁵ for the ε phase, an anion being attributed to (2h) instead of (2i) position; this is corrected in Table I (consistently with Fig. 1 of Kuhn *et al.*¹⁵ and with the most of structure descriptions since then).

III. PREVIOUS STUDIES

Experimental works in angle-resolved photoemission by Larsen *et al.*¹⁷ and Amokrane *et al.*¹⁸ on InSe, Thiry *et al.*¹⁹ and Plucinski *et al.*²⁰ on GaSe, as well as angle-resolved inverse photoemission by Sporken *et al.*²¹ on both GaSe and InSe provided precious benchmarks for many subsequent calculations of electron band dispersions.

After the initial wave of parameter-dependent calculations on different phases of GaSe and InSe since the end of 1970s,^{1–10} the III-VI semiconductors regained interest since about mid-1990s for *ab initio* studies within the DFT.^{30–34} Of the works done within several last years, Ghalouci *et al.*^{35,36} calculated the equations of state of β - and ε -GaSe³⁵ and InSe³⁶ in comparison with other phases, using the WIEN2k code and the GGA. Ma *et al.*³⁷ provided band structure calculations for GaSe (along with GaS, using the VASP code and GGA) as bulk crystal (lattice parameters optimized) and as a multilayer system. Olguín *et al.*³⁸ relaxed the structure of γ -InSe and ε -GaSe, using the WIEN2k and GGA (applying some additional efforts in the study of band gaps). Rak *et al.*³⁹ simulated, via WIEN2k and VASP calculations, the electronic structure of pure β -GaSe and (within the supercell approach) that containing point defects. Zhang *et al.*⁴⁰ calculated equilibrium structure, elastic and optical properties of ε -GaSe by a pseudopotential planewave (PP-PW) method (CASTEP code). Rybkovskiy *et al.*⁴¹ calculated band structures of β -GaSe, InSe, and GaS in dependence on number of double layers, using another realization of the PP-PW formalism (Quantum Espresso) and several flavors of GGA for comparison, with spin-orbit taken into account. Debbichi *et al.*⁴² optimized crystal structure of β - and γ -InSe using the VASP code (with GGA and the Grimme's correction to simulate DI, see Sec. IV), inspected the effect of inclusion of the spin-orbit interaction on the electron bands, and calculated the band gaps by the GW method.

A number of recent theory works primarily addressed the optical, elastic, or vibrational properties of GaSe and InSe under hydrostatic pressure, or under stress, often in the context of comparison with experimental studies.^{36,37,43–52} Adler *et al.*³¹ reported elastic constants and phonon dispersion in ε -GaSe.

The issue of band gap and its assessment in GW calculations has been addressed by Ferlat *et al.*⁴⁴ for γ -InSe, by Debbichi *et al.*⁴² for β and γ -InSe, by Rybkovskiy *et al.*³⁴ for GaSe, by Ayadi *et al.*¹⁰ for Ga- and In-chalcopyrite bilayers. Olguín *et al.*³⁸ discussed the band structures calculated for γ -InSe and ε -GaSe (using the WIEN2k code with GGA and mBJ) in the context of available GW calculations. Wei An *et al.*⁵³ discussed the band gap, as obtained by different methods for ε -GaSe (and also in β -GaS), offering an overview across other available results and implementations. Notably an excellent agreement has been found between the GW and the mBJ predictions for the band gap and for the band structure in the latter's vicinity.

Despite so many calculations done by state-of-art methods, one can note the following insufficiencies that justify the necessity of our present study. (i) The works usually address the InSe or GaSe compound in one particular phase, or, at most, comparing two structures. Considerable efforts were spent on comparison with “irrelevant” structures (typical for other semiconductors but not for III-VI). Systematic comparisons through several closely competing polytypes, in view of their relative stability or details of their band structures, are missing. (ii) The issues of band gap are usually treated under the angle of how one or another scheme improves its value over the LDA or GGA predictions; the modifications of the band structure as a whole and, in particular, a meaningful analysis of the relative performance of meta-GGA versus hybrid functionals in this sense, are not known to us. (iii) The assessment of DI for the treatment of these layered systems is still rare and, whenever done (e.g., Ref. 41 and 42) is *ad hoc* and not systematic.

IV. CALCULATION METHODS, PARAMETERS CONTROLLING THE ACCURACY, AND XC FLAVORS

A. WIEN2k and VASP; general setup

Two different computer codes, WIEN2k¹³ and VASP,¹⁴ with – in part – overlapping possibilities, have been used. WIEN2k is an all-electron code that employs large basis set of plane waves augmented to numerical functions within atomic spheres; its accuracy is controlled by cutoff parameters for basis function and charge density expansions, for which we used the values **RKMAX** = 9.0 and **GMAX** = 14.0, correspondingly. The VASP code,^{14,54,55} while not being an all-electron one but using the projected augmented-wave (PAW) scheme^{56,57} for treating the core states, has proven its high accuracy and convenience of use in a huge number of recent applications to quite different systems.⁵⁸ The use of VASP for reliable probing of total-energy preferences between polytypes imposes setting of some calculation parameters to values different from the standard (default) ones. The **PREC** tag, responsible for certain cutoffs, has to be set to the “Accurate” level; **ENCUT** (the planewave cutoff for the basis functions) was set to 500 eV; **EDIFF** (the convergence criterion for stopping the electronic relaxation) has to be reduced to **1E-8** (from the default value of **1E-4**), and the criterion of the smallness of forces on atomic relaxation has to be set not higher than **EDIFFG**.

= -0.01 (in eV/Å), otherwise the structure relaxation results are too unstable.



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A calculation parameter important for both WIEN2k and VASP, that affects the stability (numerical noise) of total energy results, is the density of the \mathbf{k} mesh used for the Brillouin zone integration. The integration as such was performed by the tetrahedron method^{59,60} in WIEN2k and by Monkhorst-Pack sampling⁶¹ in VASP. Either way, for reliable discrimination of polytypes (by their total energies), it is essential to enhance the \mathbf{k} -mesh density until the total energy *differences* get stabilized to the accuracy needed for a meaningful comparison of polytypes, i.e., within \approx 0.2 meV per formula unit. For this, one had to go at least up to \sim 16 divisions along the in-plane (long) reciprocal lattice vectors of hexagonal lattices, in order to stabilize, at least qualitatively, the relative placement of energy/volume curves of different polytypes. Concerning the choice of XC flavor, we proceed at the GGA level, with the parametrization after Perdew–Burke–Ernzerhof (PBE),^{62,63} and further on with the latter's modification for “solids and surfaces” (PBEsol).⁶⁴

A comparison of band structures calculated with WIEN2k and VASP (for β -GaSe) can be found in Fig. 4.5 of the Srour’s thesis.⁶⁵ The bands are indistinguishable for visual assessment even as the corresponding calculations have been done for not identical XC schemes and, correspondingly, for slightly different optimized crystal structures.

A deficiency of our calculation setup is the omission of spin-orbit interaction. It was included in the pioneering *ab initio* work on InSe by Gomes da Costa,³⁰ as well as in some recent calculations.^{41,42,53} The effect of spin-orbit coupling on the band structure, that can be seen in Fig. 4 of Debbichi *et al.*⁴² or in Fig. 7-8 of Ghaloui *et al.*,³⁶ is small yet appreciable, especially in lifting some degeneracies. As these effects will likely pronounce in the similar way throughout polytypes, we do not expect the qualitative trends concerning the latters’ relative stability to be affected. As for the estimations of absolute band gap values, a slight correction following the inclusion of spin-orbit coupling is quite plausible.

B. Inclusion of dispersion interactions

The last decade has witnessed tremendous effort in the development of various correction methods to account for the DI missing in conventional Kohn-Sham DFT calculations. One can single out two types of approaches. The first one applies specific non-local correlation functional that approximately accounts for DI, in the spirit of that originally developed by

Dion *et al.*⁶⁶ and improved in subsequent works.^{67,68} The other group of methods encompasses additive correction schemes, in which dispersion energy is included on top of “conventional” DFT results; a number of such schemes are included in the VASP package.^{69–73}

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We note that there is no implicit electron potential, band structures etc. associated to these schemes, but just the total energy (elaborated, in some cases, to yield corresponding forces). Consequently, the properties affected concern just the equilibrium geometry.

In the DFT+D2 approach of Grimme,⁷⁴ the dispersion energy results from summing up the two-atom interactions, which scale with interatomic distances R_{ij} as $\sim(-R_{ij}^{-6})$ and are moreover enveloped by a (smeared step-like) *damping function* to prevent spurious over-bonding at small distances. The related parametrization is phenomenological and element-related. The DFT+D3 approach by Grimme *et al.*⁷⁵ adds an interaction term proportional to $\sim R_{ij}^{-8}$ and suggests a different choice of the damping function than that in Ref. 74. The scheme marked as DFT+D3-BJ corresponds to a subsequent suggestion by Grimme *et al.*⁷⁶ to modify (yet again) the damping function of DFT+D3, following the reasoning by Johnson and Becke.⁷⁷ Tkatchenko and Scheffler (TS, Ref. 78) proposed a way to calculate the weighting parameters of $\sim R_{ij}^{-6}$ interactions “on the fly”, taking into account the modifications of the atoms’ static polarizabilities in a given chemical environment. An ambiguity which may herewith arise in separating the combined charge density into atom-related contributions is technically removed using the Hirshfeld atomic partitioning⁷⁹ and notably, as elaborated by Bučko *et al.*,^{70,71} the “Iterative Hirshfeld partitioning”, earlier proposed by Bultinck *et al.*,⁸⁰ on top of the TS approach. The resulting scheme, henceforth referred to as DFT+TS/HI, was tested to accurately describe the dispersion interactions in both covalent and ionic systems.^{70,71}

A bunch of additive schemes, dubbed MBD for “many-body dispersion”, bypass the refinement of phenomenological parameters and go directly for the results expected from the behavior of polarizability functions, making use e.g. of the adiabatic-connection fluctuation-dissipation theorem – see Refs. 81, 82 for details. In a nutshell, the long-range part of the electron correlation energy, missing in conventional DFT schemes, is recovered via inclusion of (long-range) dipole-dipole interactions between (short-range-screened) atomic polarizabilities, the latter being represented by those as for quantum harmonic oscillators. The practical implementation and corresponding tests (within the VASP code) are described by Bučko *et al.*⁷² An attempt to generalize atomic-related polarizability over the case of variable elec-

tron number (and hence ionicity), discussed by Gould *et al.*,⁷³ led to a demonstration that the polarizability is piecewise linear in the electron number, and resulted in corresponding refinement of the MBD scheme. The technical details related to realization and tests within VASP of this scheme labeled MBD/FI (for Fractional Ions) are given in Ref. 73. Note that practical calculations with VASP using the MBD and MBD/FI schemes require, for maintaining the necessary stability of results, to use much more dense \mathbf{k} -mesh (e.g., $32 \times 32 \times 8$ in our case) than usual.^{72,73}

Among a large number of recent articles dealing with the assessment of practical schemes in include the DI, we single out a recent analysis by Tawfiq *et al.*⁸³ specifically concerning layered materials, to which we'll refer in the Discussion.

C. Hybrid functional (HSE06)

The hybrid XC functionals replace some part of the DFT exchange energy by the exact exchange from a Hartree-Fock (HF) calculation; this typically has a favorable effect on the accuracy in prediction of equilibrium geometries; moreover the band gap (underestimated in conventional DFT, overestimated in HF calculations) becomes closer to reality. In the present work, we applied the Heyd-Scuseria-Ernzerhof (HSE) version of a hybrid XC functional,^{12,84} as implemented in the VASP code with modifications of the screening parameters explained in Ref. 85 and casted under the label ‘HSE06’. These calculations being relatively time-consuming, we did not perform full structure relaxation within this scheme, but refer to HSE band structures, calculated for PBEsol optimized geometry, for discussion on band gaps and comparison with the mBJ.

D. Modified Becke – Johnson XC potential

A technically simple scheme specifically aimed at “improving” electron bands and band gaps via using a particular meta-GGA XC potential have been introduced by Tran and Blaha¹¹ under the name “modified Becke – Johnson” (mBJ), in the development of the latter authors’ idea⁸⁶ to explicitly use the gradient of the kinetic energy density to imitate the characteristic shell structure of exchange potential in atoms and hence (implicitly) a discontinuity of the total energy variation with the electron number, a crucial element in a

correct assessment of the band gap. The implementation in WIEN2k and related extensive tests were described by Koenig *et al.*⁴⁷ This manuscript was accepted by J. Chem. Phys. Click [here](#) to see the version of record. We note that mBJ is not a stand-alone total energy functional but just a suggestion for XC potential, that leads to electron bands but not to total energy / forces. Corresponding calculations have been performed for the PBEsol optimized geometry, and comparison done with the HSE band structures.

V. OPTIMIZED CRYSTAL STRUCTURES OF DIFFERENT POLYTYPES

The lattice parameters as optimized in our calculations, using different XC potentials, are indicated in Fig. 2 and Fig. 3, in comparison with earlier calculation results and experiments. The c parameter, for an easy comparison, is normalized per one double layer unit (i.e., divided by two for β and ε phases, by three for γ , by four in case of the δ phase). One can conclude that the standard PBE scheme systematically overestimates the in-plane a parameter (by $\sim 2.7\%$, as compared with experiment), and especially the c parameter (by $\sim 13\%$), that can be primarily traced to the overestimated interlayer distance. This deficiency is cured by applying (essentially, any) scheme for inclusion of the DI in combination with the PBE. At first sight, the performance of PBE+D2 seems to be excellent in GaSe, in comparison with available experimental data; however, the same scheme yields a too short (by $\sim 2\%$) a parameter for InSe.

Similar observations (that PBE gives a wrong c parameter but the equilibrium geometry can be fixed by the use of PBE+D2) have been done in a recent work by Rybkovskiy *et al.*,⁴¹ however, without specifying the numerical error nor indicating to which extent this applies to the three materials studied (GaS, GaSe, InSe).

Alternatively and pragmatically, the PBEsol XC scheme seems to perform reasonably well without any additional inclusion of the DI. On the contrary, the combination of PBEsol with the D3 and moreover the BJ schemes tends to overbind too much, resulting in underestimation of both a and c (by $\sim 1\text{--}2\%$; the corresponding data are not included in Fig. 2,3, but can be found in Fig. 4.1 of the Srour's thesis.⁶⁵ Rybkovskiy *et al.*⁴¹ report that PBEsol improves the in-plane distances, in comparison to PBE, but still overestimates the interlayer separation (without further elaborating).

Whereas PBE+D2 turns out to be not sufficiently reliable (at least for InSe), more sophisticated schemes of including the DI do comfortingly yield more accurate prediction of

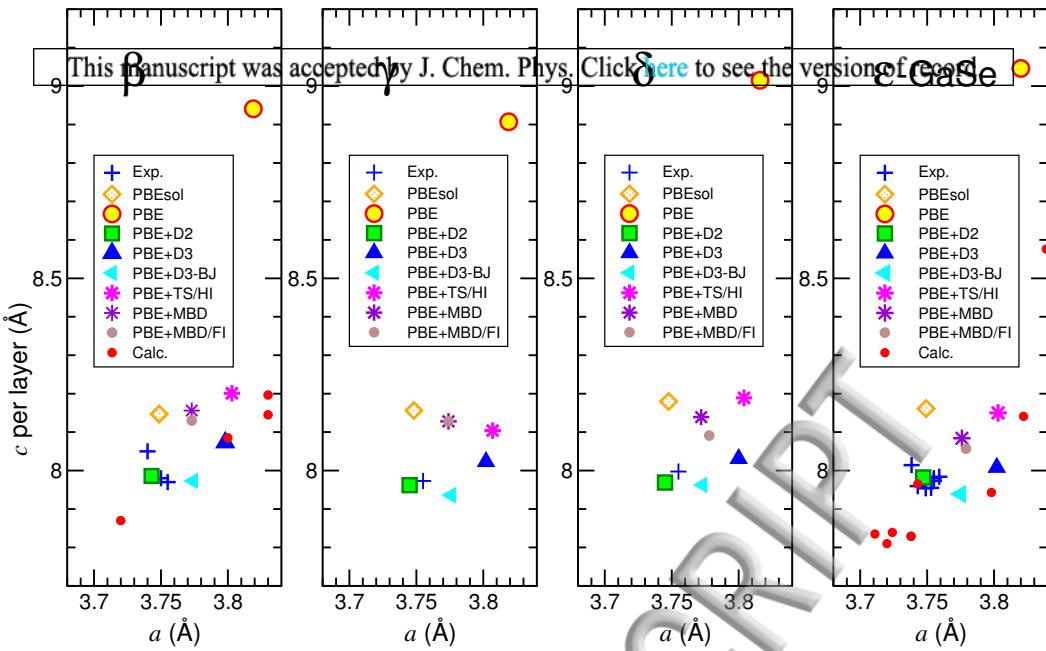


FIG. 2. Lattice parameters in β , γ , δ and ε phases of GaSe from the present calculations using the VASP code and from earlier studies. The experimental data are indicated by blue crosses, the results of previous calculations – by red dots. Details of Exp. and Calc. values are given in the Supplementary Material. The schemes of inclusion the dispersion interactions on top of PBE are explained in Sec. IV B.

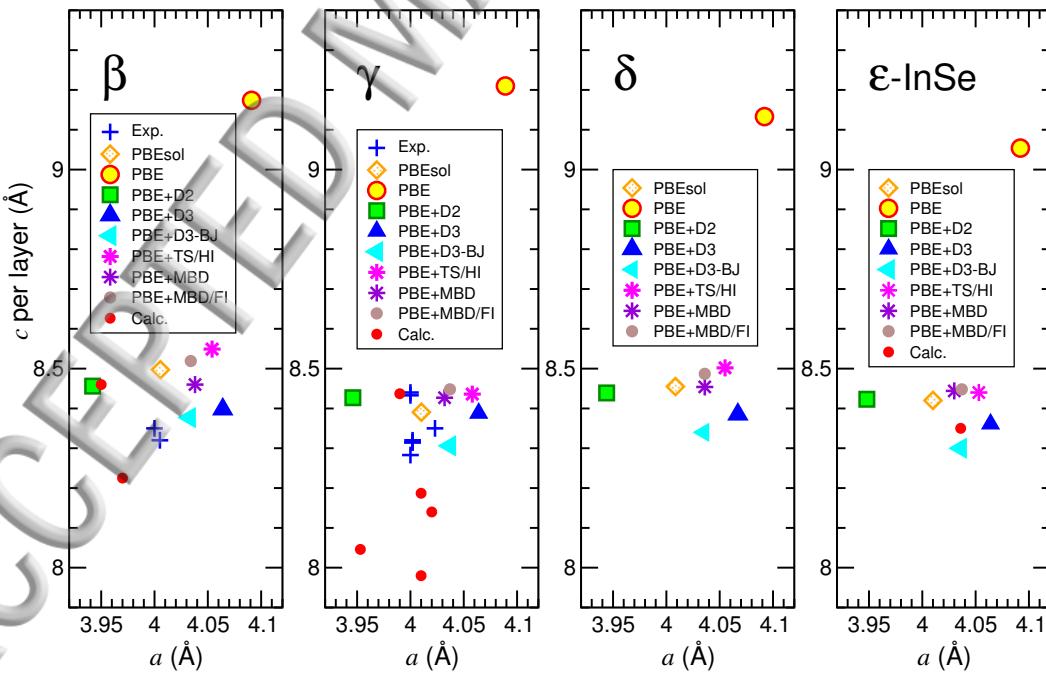


FIG. 3. Similar to Fig. 2, for different phases of InSe.

the lattice parameters. Even as experimental lattice parameters are available for some phases only (β , ϵ -GaSe and δ , γ -InSe), the stability of a and reduced c throughout polytypes seems plausible. In this perspective, an accurate (and consistent) performance of PBE+D3-BJ, arguably the best among “phenomenological” schemes, and more sophisticated TS/HI and MBD approaches seem reassuring. One can note not much difference in the MBD results with and without “fractional ions” modification, for an apparent reason that our materials do not possess a strongly ionic character. We’ll come to the differences in the energy / volume curves yielded by different dispersion schemes in the next section.

The details of the crystal structure, optimized throughout phases with ultimate \mathbf{k} -mesh of $(24 \times 24 \times 6)$, are given in Tab. II and III (from PBEsol calculations only). The internal coordinates are expressed in such way as to facilitate their comparison throughout polytypes; namely, the values in the numerator (e.g., $\simeq 0.15$ for Ga, $\simeq 0.29280$ for Se) everywhere play a role of deviation from the median plane of a double layer, in units of “reduced” c parameter (e.g., $\simeq 8.2$ Å for GaSe). Note that in γ and δ phases, the median planes of double layers are not fixed by symmetry, and an arbitrary rigid shift of all the z coordinates can be applied. Our z scale were in these cases gauged so as to “equilibrate” positive and negative deviations for all the ions. With this, the γ phase (of both GaSe and InSe) maintains its double layers practically mirror symmetric with respect to the median plane. For the δ phase, on the contrary, the (+) and (-) coordinates within either (a) or (b) positions are *not* symmetric, meaning that each double layer is polarized up or down; however, there is an approximate criss-cross symmetry between (a) and (b) positions, so that the (a^+) distance from the median plane nearly equals that for (b^-), and vice versa, for a given atom species. This means that the up / down polarizations of consecutive double layers are alternating throughout the stacking. Apart from this systematic “flaw”, the coordinates remain remarkably stable over the polytypes; the variations throughout the phases of InSe ($\lesssim 1.2\%$ over c values, $\lesssim 0.7\%$ over cation-cation distances) are just minutely more pronounced than in the case of GaSe ($\lesssim 0.4\%$ and $\lesssim 0.1\%$, correspondingly).

Obviously, the accuracy in absolute values suggested by Tables II, III exceeds by far the credibility of contemporary first-principles schemes; nevertheless, the systematic errors are likely to be common for different polytypes, so that the qualitative trends should presumably hold. More instructive than just the equilibrium geometries are the energy profiles around the corresponding minima, discussed in the following section.

TABLE II. Optimized crystal structure parameters for different phases of GaSe, after VASP. This manuscript was accepted by J. Chem. Phys. Click [here](#) to see the version of record.

calculation with PBEsol. z -coordinates are formatted such that they reveal the distances from the double-layer median planes; see text for details.

Poly-type	a (Å)	c (Å)	Wyckoff position	$z_{(\text{Ga})}$	$z_{(\text{Se})}$
β	3.7487	2×8.1469	(f)	$\frac{1}{4} - (0.14925)/2$	$\frac{3}{4} - (0.29336)/2$
γ	3.7482	3×8.1563	(a ⁺)	$(0.14905)/3$	$\frac{2}{3} + (0.29285)/3$
			(a ⁻)	$-(0.14901)/3$	$\frac{2}{3} - (0.29290)/3$
δ	3.7477	4×8.1795	(a ⁺)	$(0.14781)/4$	$\frac{1}{4} + (0.29298)/4$
			(a ⁻)	$-(0.14914)/4$	$\frac{1}{4} - (0.29162)/4$
			(b ⁺)	$\frac{1}{4} + (0.14928)/4$	$\frac{1}{2} + (0.29134)/4$
			(b ⁻)	$\frac{1}{4} - (0.14882)/4$	$\frac{1}{2} - (0.29265)/4$
ε	3.7492	2×8.1610	(g)	$(0.14897)/2$	$\frac{1}{2} + (0.29278)/2$
			(h)	$\frac{1}{2} + (0.14898)/2$	
			(i)		$(0.29280)/2$

TABLE III. Similar to Table II, for InSe.

Poly-type	a (Å)	c (Å)	Wyckoff position	$z_{(\text{In})}$	$z_{(\text{Se})}$
β	4.0055	2×8.4972	(f)	$\frac{1}{4} - (0.16394)/2$	$\frac{3}{4} - (0.31429)/2$
γ	4.0102	3×8.3906	(a ⁺)	$(0.16553)/3$	$\frac{2}{3} + (0.31796)/3$
			(a ⁻)	$-(0.16552)/3$	$\frac{2}{3} - (0.31798)/3$
δ	4.0085	4×8.4550	(a ⁺)	$(0.16549)/4$	$\frac{1}{4} + (0.31437)/4$
			(a ⁻)	$-(0.16286)/4$	$\frac{1}{4} - (0.31696)/4$
			(b ⁺)	$\frac{1}{4} + (0.16290)/4$	$\frac{1}{2} + (0.31691)/4$
			(b ⁻)	$\frac{1}{4} - (0.16552)/4$	$\frac{1}{2} - (0.31433)/4$
ε	4.0100	2×8.4201	(g)	$(0.16492)/2$	$\frac{1}{2} + (0.31680)/2$
			(h)	$\frac{1}{2} + (0.16488)/2$	
			(i)		$(0.31686)/2$

VI. EQUATIONS OF STATE AND RELATIVE STABILITY OF POLYTYPES

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The energy / volume $E(V)$ curves for different polytypes have been earlier studied in Ref. 89, using the PBEsol XC potential and the WIEN2k vs VASP calculation methods in comparison. In addition to a nominal result of which phase has lower energy at equilibrium, the curve as a whole indicates how the relative stability of phases would be shifted by (positive or negative) pressure. Since the $E(V)$ curves for different polytypes are (near the respective minima) close within 1 meV per double unit (i.e., 4 atoms – see Fig. 2 and 3 of Ref. 89), a reliable (noise-free) resolving them required an utmost care in controlling the numerical accuracy (in terms of \mathbf{k} -mesh, see Fig. 1 of Ref. 89, and planewave cutoffs). In the present study, we focus at the effects of including the DI, in the form of a simple Grimme D2 scheme, the Grimme D3 scheme with Becke-Johnson dumping function, and with more sophisticated MBD, the latter three on top of the PBE XC potential; the results are depicted in Fig. 4. Every point in the curves corresponds to a full relaxation of a , c and internal coordinates for a given trial volume. Fitting to the Murnaghan equation of state yields the bulk moduli, shown in Table IV and discussed further on.

We note that the volume axes in Fig. 4 are consistent throughout the four panels shown for each compound. In order to give meaning to the energy values, we express in each case the total energy (per formula unit) of the relative bulk phase relative to that of the fictitious two-atom “molecule”, calculated (obviously taking spin polarisation into account) in a large enough empty box, at the equilibrium interatomic distance according to the calculation scheme in question. In this way, the *a priori* large (and irrelevant) variations of the total energy values between different schemes can be eliminated. The remaining energy differences amount to small (within $-0.1/+0.2$ eV) fluctuations around the value of ≈ -3.4 eV, for both GaSe and InSe – see Fig. 5.⁹⁰ The bunches of energy curves corresponding to different calculation schemes are placed along the common energy axis; we note that, by the sophistication of the method used to include the DI, the PBE+D2 is *a priori* overcomed by PBE+D3BJ, and the latter, in its turn, by PBE+MBD. It is noteworthy that the PBE+MBD curves are the closest to PBEsol prediction in what regards both the equilibrium volume *and* the depth of the energy well.

Tawfik *et al.* in their recent work⁸³ emphasized the importance, and simultaneously a

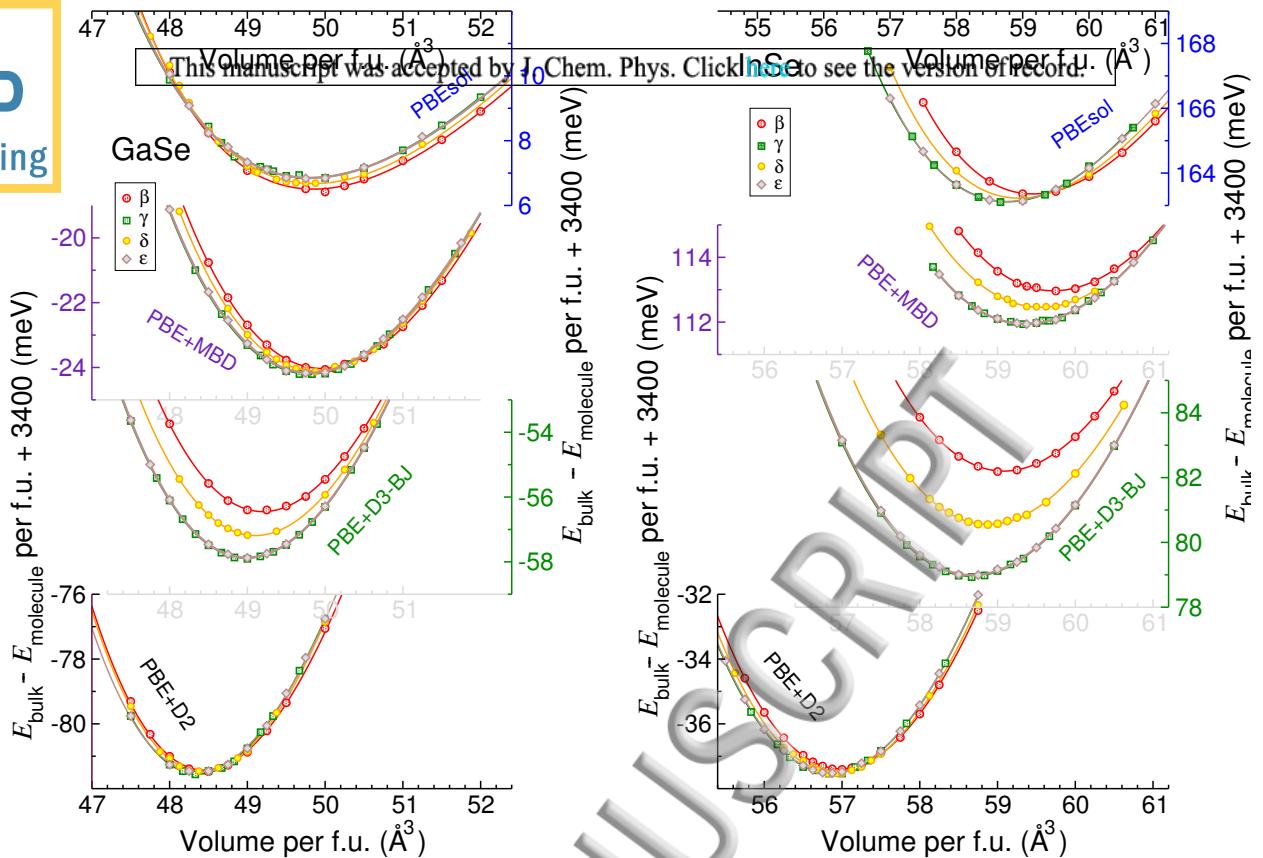


FIG. 4. Energy / volume curves for four polytypes of GaSe (left panel) and InSe (right panel), as calculated with PBESol (upper plot), with dispersion interaction included according to the D2 Grimme scheme on top of PBE (lower plot), according to the D3 Grimme scheme with Becke-Johnson cutoff function (third plot from the top), and with many-body dispersion interaction included on top of PBE (second plot from the top of each panel). The energies shown are the differences of total energies of corresponding bulk system (per formula unit) and that of the isolated fictitious two-atom “molecule”, calculated within the corresponding scheme. Note that the volume axis and the energy scale are common throughout the panels; large empty intervals along the energy axis are cut out. Symbols indicate total energies after full structure relaxation for a given volume; the lines are the Murnaghan fit through these data. See text for discussion.

relative difficulty, for a reliable scheme to be chosen to account for the DI to achieve *both* the equilibrium structure *and* the binding energy with sufficient accuracy. Being short of credible experimental benchmarks to judge about the binding energy within the accuracy needed, we present in Fig. 5 the “scatterplot” of the energy difference vs c lattice constant,

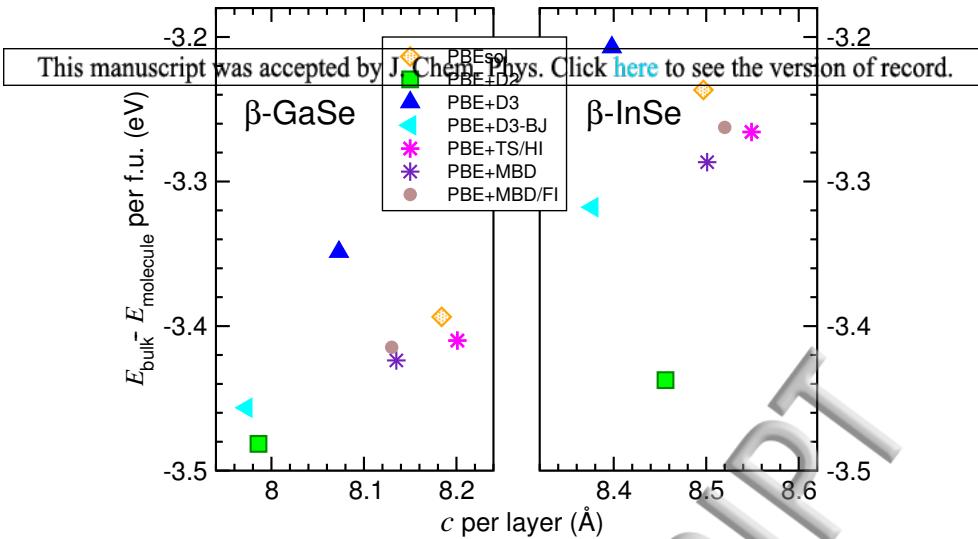


FIG. 5. Relation between the energy difference (per formula unit) and the equilibrium c -parameter (per double layer) as predicted by different calculation schemes to take the DI into account (cf. Fig. 2, 3).

inspired by the inset to Fig. 1 of Ref. 83. Apart from giving an idea of the magnitude of scattering in these two parameters, Fig. 5 helps to conclude that predictions from the more sophisticated schemes to include the DI fall reassuringly close.

Two observations can be done concerning the general impression of Fig. 4: (i) For both compounds and all the calculation schemes, the $E(V)$ curves for γ and ε polytypes stay practically degenerate, within the meaningful accuracy; (ii) this merged (γ , ε) curve is in all cases the most distinct from that for the β polytype, the δ curve taking its position cleanly in between. This can be understood from the differences in the double-layer packing, or, specifically, how the next layer is placed on top of the previous one. The β phase is characterized by a “double lock” whereby the next-layer anion sits on top of the current-layer cation and vice versa (in the eclipsed configuration), this schema going on in both senses (the [Bc Cb] packing, see Fig. 1). In γ and ε , the next-layer cation is placed on top of the current-layer anion; however, the next double layer is pivoted and the reverse cation-anion “lock” across the interlayer gap is missing. The γ [Ca Ab Bc] and the ε [Ca Ab] phases differ only in what concerns the packing beyond the nearest-neighboring double layer. Under this angle, the δ phase is indeed intermediate: out of its four double layers, two and the next two are pairwisely in “double lock”, with pivoted “loose locks” in between. (This also

explains the above discussed asymmetry / alternating polarization of double layers in the δ phase). A conclusion from this analysis is that, since all other imaginable polytypes cannot be but various combinations of “double locked” and “loosely locked” double layers, their relative $E(V)$ curves are very likely to fall between the limits drawn by β and (γ or ε) ones.

Addressing the issue of energy preference of different polytypes, one can note that the situation (for both compounds and all calculation methods) is not such that one of the above “limiting” curves would fully encompass the other and definitely win.⁹¹ Rather, the curves are crossing not far from their respective minima, so that the equilibrium in favor of one or the other phase is likely to be shifted under a moderate effect of pressure. In all cases, the β phase would eventually win at large enough volume (hence negative pressure), and γ / ε – under positive pressure, from small enough volume downwards. As it turns out from the results of PBEsol calculations, GaSe definitely prefers the β phase at the ambient conditions, and needs the pressure of $\simeq 0.6$ GPa (judging by the common tangent, to be drawn on the left, where the curves cross) to be pushed into the γ or ε phase. InSe, on the contrary, tends for γ / ε phase at zero pressure, but a small expansion (negative pressure of -0.1 GPa) would make the β phase competitive. We note in this relation that rhombohedral (γ) was, indeed, early enough identified as *the* structure of single-crystal InSe,¹⁶ whereby even earlier reports (by Semiletov, in 1958) of detecting a hexagonal two-layer phase were attributed in Ref. 16 to “very peculiar conditions” (by evaporation in vacuum) of preparing the thin-film samples in question.

The $E(V)$ profiles calculated in PBE+D2 are markedly contracted (see the increased values of the bulk moduli in Table IV), to the point that different polytypes become almost indistinguishable in the scale of Fig. 4. This holds for both GaSe and InSe. An explanation could be that the D2 scheme, only sensitive to interatomic distances but not to details of the short-range arrangement of atoms, is too crude to make distinction between the polytypes. The shift of the curve to smaller volumes with simultaneous increase of its stiffness due to inclusion of the D2 correction is generally known (see, e.g., Fig. 1 of Ref. 69).

The PBE+MBD calculation, sensitive to the charge density distribution, recovers the discrimination between polytypes, to a different extent in GaSe and InSe. In InSe, the sequence of phases is roughly the same as after the PBEsol calculation (the γ or ε phases are dominating at ambient conditions and up to appreciable negative pressure); the stiffness is slightly larger than that estimated by PBEsol. In GaSe, the ground-state phase at ambient

TABLE IV. Calculated values of the bulk modulus B_0 and its pressure derivative B' for GaSe and InSe in comparison with available experimental and calculation results. This manuscript was accepted by J. Chem. Phys. Click [here](#) to see the version of record.

InSe in comparison with available experimental and calculation results. The span of values for B_0 covers different polytypes. B_R , B_V stand for the Reuss average (lower bound) and Voigt average (upper bound) of the bulk modulus estimated from the elastic constants – see text for detail.

Method	GaSe		InSe	
	B_0 (GPa)	B'	B_0 (GPa)	B'
PBEsol	11.1 – 12.1	21 – 31	15.0 – 15.6	23 – 25
PBE+D2	32.7 – 33.7	10 – 14	31.0 – 31.5	5 – 10
PBE+D3-BJ	26.2 – 26.7	11 – 12	25.0 – 25.2	10
PBE+MBD	20.4 – 21.3	13 – 16	20.9 – 21.6	12 – 16
expt. volume (pressure) fit	34(2) ^a	6.4(5) ^a		
$B_R \dots B_V$ (from expt. elastic constants)	$\left\{ \begin{array}{l} 27.7 \dots 38.5^b \\ 28.6 \dots 38.8^c \end{array} \right.$		34.6 … 39.6 ^b	
calc. energy (volume) fit (two choices of B')			$\left\{ \begin{array}{l} 29^d \\ 34^d \end{array} \right.$	
$B_R \dots B_V$ (from calc. elastic constants)	$\left\{ \begin{array}{l} 28.4 \dots 38.4^e \\ 28.3 \dots 38.2^f \end{array} \right.$			

^aRef. 46; ^bRef. 92; ^cRef. 93; ^dRef. 52; ^eRef. 31; ^fRef. 33.

pressure, by very small margin, according to PBE-MBD calculation would be γ or ε ; the preference of the β phase can be restored by negative pressure of -0.2 GPa.

The PBE+D3-BJ scheme produces the largest discrimination between polytypes, whereby the γ and ε phases have at all volumes lower energy than δ than β , and this for both GaSe and InSe compounds.

The calculated values of the bulk moduli B_0 in Table IV offer another interesting benchmark concerning the performance of different calculation schemes. We see that PBEsol, PBE+D2, PBE+D3-BJ and PBE+MBD yield four groups of B_0 values ($\simeq 11$ – 15 GPa, $\simeq 25$ – 27 GPa, $\simeq 32$ GPa and $\simeq 21$ GPa, respectively), whereby the differences between polytypes within each group are comparable with technical errors of fitting (depending on the range chosen, etc.). According to PBEsol calculation, GaSe comes out somehow softer than InSe; however, each of two other calculation schemes yields very close (within $\simeq 6\%$)

values of B_0 for GaSe and InSe. The experimental estimations of the bulk moduli of the two crystals, ~~in view of the scattering of the data reported, look indeed quite identical.~~ This manuscript was accepted by J. Chem. Phys. Click [here](#) to see the version of record. In addition to (rarely) reported face values of bulk modulus B_0 along with its pressure derivative B' , some previous works listed the elastic constants, from which the Reuss average and the Voigt average⁹⁴ can be extracted, known to be correspondingly the lower and the upper bound for B_0 .

Interestingly, the earlier *ab initio* estimations of bulk moduli^{31,33,52} shown in Table IV are quite close to experiment. These calculations have been done with the LDA and hence result in slight overbinding (that somehow compensates for the missing DI) and in a corresponding hardening of the $E(V)$ profile to almost exemplary values (albeit for a wrong reason).

VII. mBJ- AND HSE-CORRECTED BAND STRUCTURES AND BAND GAPS

A. Band foldings in different polytypes

Energy bands (which are the origin of the total energies and the hence derived differences between polytypes) are basically formed by interactions within the double layer, then get replicated and distorted according to how the number of units varies throughout the polytypes. Fig. 2 of Rybkovskiy *et al.*³⁴ is an instructive example of realistic DFT band structure calculated for an isolated double layer of GaSe, with its seven valence bands (counting upwards from $\text{Ga}4s^2$, at about 7 eV below the valence band top, followed by $\text{Ga}4p$ and $\text{Se}4p^4$). The closest approximation to it in our case is the band structure of γ -GaSe, with one double-layer unit per rhombohedral primitive cell.⁹⁵ In the following figures, the \mathbf{k} -path is uniformly chosen in the hexagonal setting throughout all the polytypes; the γ -GaSe would therefore exhibit three times more bands in the hexagonal setting than in the rhombohedral one (see the discussion below). We skip discussion of GGA bands as not particularly relevant and go directly for the systematic analysis of “corrected” band structures (within mBJ and HSE) which would also enable us to discuss the band gaps in comparison with experimental data.

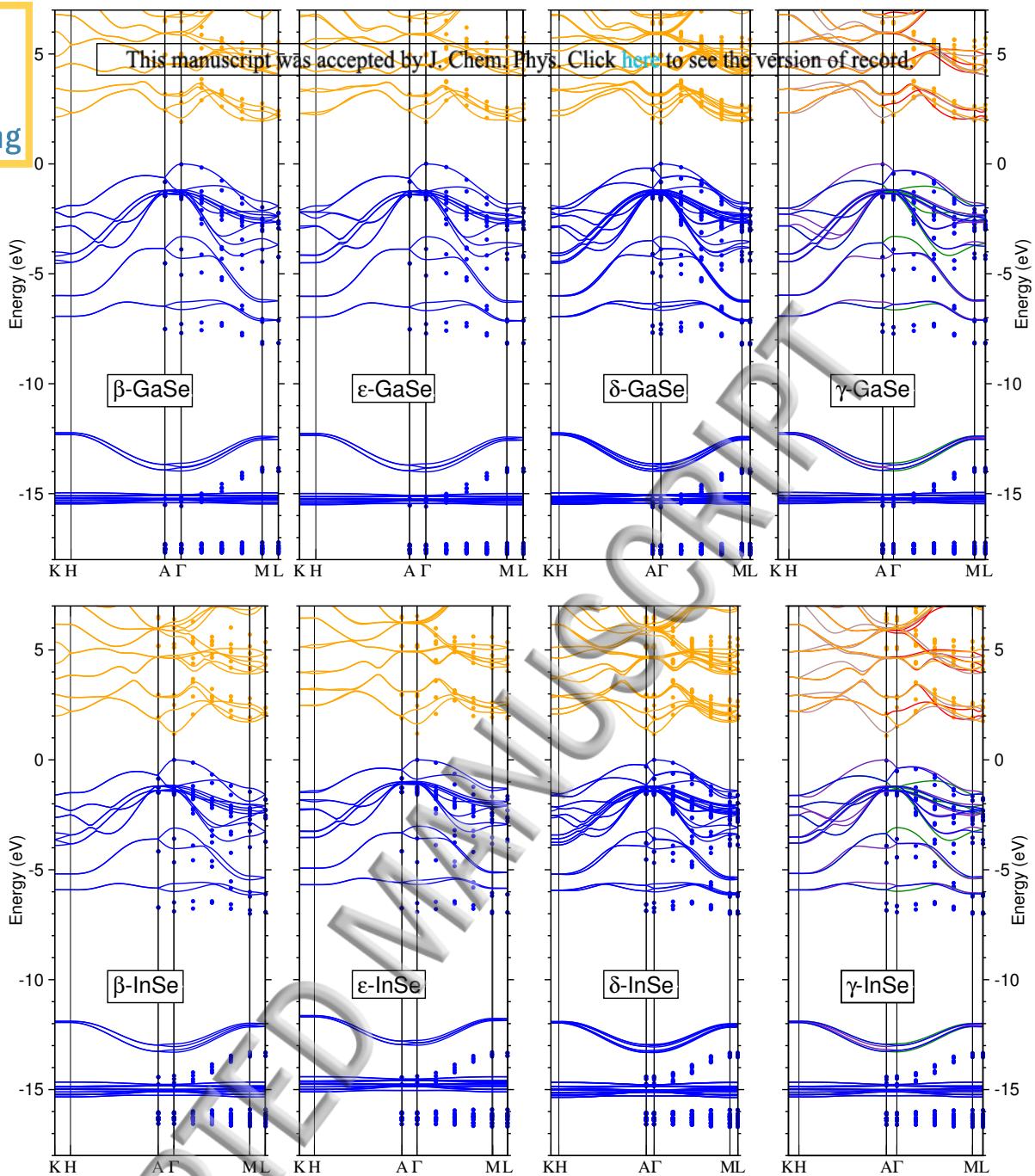


FIG. 6. Band structures of GaSe (upper row) and InSe (lower row) polytypes calculated by WIEN2k with mBJ (lines) and by VASP with HSE06 (dots). Occupied bands are drawn in blue, vacant bands – in yellow; for the γ polytypes, an additional color coding is used – see text for discussion. Zero energy is set at the conduction band top. A , H and L points are on top of respectively Γ , K and M .

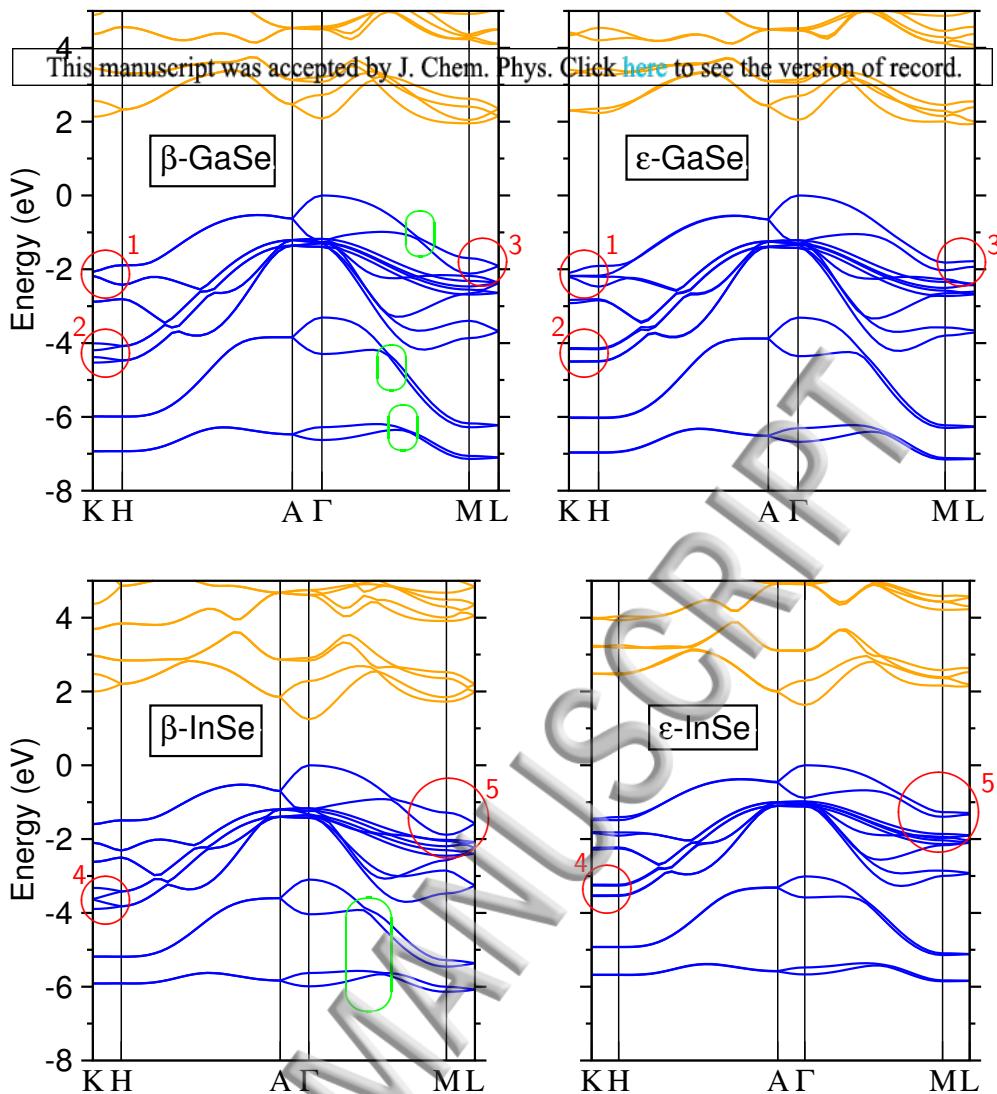


FIG. 7. Blow-up of the mBJ bands of Fig. 6 for β and ε phases of GaSe (upper row) and InSe (lower row). Red numbered circles and green ovals indicate the elements addressed in the text.

B. mBJ band structures; differences between polytypes

The band structures calculated with mBJ are shown in Fig. 6. Some fragments which merit attention and to which the reference is made in the text are enlarged and marked by numbered red circles in Fig. 7.

The comparison of β and ε phases, which have the same number of bands and basically similar dispersions, reveals differences in band splittings and degeneracies in some symmetry points, or along some symmetry lines. Since the structural difference between β and ε is in the stacking of otherwise identical layers, the differences in the band dispersion come about

at the BZ boundary, along $K - H$ and $M - L$, and affect the bands of predominantly Se4p character. This manuscript was accepted by J. Chem. Phys. Click [here](#) to see the version of record. The two upper occupied bands in the β phase proceed as doubly degenerate ones along $K \rightarrow H$ (and further on towards A), whereas the degeneracy is lifted in their counterparts of the ε phase (label 1 in Fig. 7). In the “adjacent part” of the BZ boundary, along $M \rightarrow L$, the said two upper bands converge towards degeneracy, whereas in the ε phase they proceed almost parallel (label 3; also label 5 in case of InSe). An opposite pattern of splitting comes about for a pair of lower placed bands (in the range $-4 / -5$ eV in GaSe and $-3 / -4$ eV in InSe) which proceed as double degenerate ones along $H - K$ in ε but markedly split from H towards K in the β phase (label 2 for GaSe and label 4 for InSe in Fig. 7).

Generally, many bands remain doubly degenerate on the upper (flat) BZ boundary, e.g., along $H - A$, but get split on going inside ($A - \Gamma$), and the degeneracy is lifted in the basal ($\Gamma - M$) plane. It is noteworthy how some of these split bands go side by side in ε phase but undergo a crossing in the β phase. Such crossings are marked in Fig. 7 by green ovals.

Large band dispersions along $\Gamma - A$ reveal the interaction between the double layers. On passing from two to four double layers, the BZ is halved and the $A - H$ path is backfolded onto $\Gamma - K$ etc., doubling the number of bands. This becomes obvious from comparing the band structures of the (four double layers) δ phase with those of (two-layers) β or ε . In case of the γ polytype, the situation is more delicate. The primitive cell is rhombohedral; plotting the band structure in the hexagonal setting amounts to superposing three band structures calculated along three \mathbf{k} paths, the original one and the two displaced by $\pm 1/3$ of the BZ height. Such band structures are marked in the right-hand side panels of Fig. 6 by different colors, separately for occupied and unoccupied bands.⁹⁶ The most spectacular consequence from the fact that the γ phase possesses an odd number of double layers is that, due to a forth-back-forth folding of bands, the valence-band top and the conduction-band bottom occur not in Γ but in A .

As is well seen from the GaSe band structures in Fig. 6, the local minimum of the conduction band in M competes with that in Γ for being the global one. Should this happen, the band gap would become indirect, since the valence band top remains always in Γ . The band gap values for direct and indirect gaps are given in Table V, to be discussed below. For InSe, the band gap is direct for all polytypes.

All these observations are not necessarily specific to mBJ, but we mention them since we

consider the mBJ band structure reasonably accurate in the absence of superior quality (say, GW) calculations. Moreover we'd like to emphasize that the preferences in total energies between polytypes are not accidental but may, in principle, be traced down to particular features in the band dispersions.

C. HSE band structures

The hybrid-functional calculations has become another broadly accepted way to “improve” the underestimated band gaps, along with the band structure as a whole, as compared to conventional DFT calculation. Band structures calculated with HSE06 along (in part) the same \mathbf{k} path as that applied above for mBJ are shown in Fig. 6 as blue (for occupied states) and yellow (for vacant states) dots. We can confirm that all the above observations concerning the band splittings in β vs ε phases (red circles in Fig. 7) remain valid for HSE calculations. The remarks concerning the band crossings are not conclusive here, due to a sparseness of the \mathbf{k} grid. The quantitative differences in the band gap values are discussed in the following.

D. General observations from comparing the mBJ and HSE band structures

Whereas the need for reliable band gap predictions remains probably the major motivation behind using these schemes, one should not overlook that in the process the whole band structure gets somehow, and differently, modified, as compared to conventional DFT predictions. This reveals the fact that differently localized states are differently affected by the two formalisms. The HSE inherits from the Hartree-Fock the tendency to place occupied (e.g., semicore) states too low. Taking the valence band top for zero energy, we find (in β -GaSe) the bottom of the Se4p-related valence band at ~ -6.2 eV with mBJ (roughly the same as with PBEsol, see Fig. 4.3 of Ref. 65) but at ~ -7 eV with HSE; the Ga4s-related flat band that spans ~ -7 to -6 eV in PBEsol and mBJ shifts by ~ 1 eV downwards with HSE; the Se4s-related bands that span ~ -14 to -12.5 eV plunges down by ~ 1.5 eV, and the bunch of flat Ga3d at ~ -15.2 eV are found more than 2 eV deeper in a HSE calculation than in mBJ. Interestingly, in InSe the plunging of these semicore bands is less spectacular; notably the In4d is deepened (in HSE, as compared to mBJ) by ~ 1.5 eV only, apparently

due to a weaker localization of these states as compared to Ga3d. One can note that the mBJ calculation predicts the gap between the two lowest bunches of bands included in the figures, i.e., the Se4s and the cation-*d*, smaller in GaSe than in InSe, whereas this is the other way around with HSE. It could be instructive to resort to electron spectroscopy studies, which we failed to find in earlier publications, for a critical assessment of the semicore bands' placement according to mBJ and HSE formalisms.

E. Band gap character and magnitude

The calculated band gap values in comparison with available experimental data are summarized in Table V. Compared to PBEsol, both HSE and mBJ schemes augment the gap by ≈ 1 eV in GaSe and ≈ 0.9 eV in InSe, setting the values quite close to experimental data. Looking more attentively, for GaSe the experiment reports an indirect gap (without specifying its nature) to be slightly smaller than the direct one, for both the β and the (γ or ϵ , not clearly identified) polytypes. The mBJ calculation yields an astonishing agreement with these subtle details, assuming the indirect gap between Γ and M , and the polytype likely matching the (γ or ϵ) experimental study being the γ . In fact, the indirect $\Gamma - M$ gap ($A - M$ in γ polytype) is shorter than the direct one in all four polytypes probed in calculations. The HSE predictions for the band gap lay close (within several % to both the experiments and the mBJ results), however, the direct gap comes out shorter than the indirect one in all polytypes of GaSe. For InSe, the band gap seems to be direct according to both the experiment (presumably done on the γ phase) and the HSE calculations; the absolute gap value is within %13 of deviation from experiment after the HSE calculation and within 7% after the mBJ calculation. These observations do not yet necessarily infer that the mBJ is generally more reliable than the HSE; one should take into account that the augmentation of the band gap with respect to the GGA value occurs due to different mechanisms in mBJ and in HSE formalisms, so that the whole band structure is affected. Anyway, mBJ offers a very reasonable accuracy for a calculation cost much more attractive than that related to HSE.

TABLE V. Calculated band gap values (in eV) for different polytypes of GaSe and InSe in comparison with experiments and available GW calculations. Details of Exp. and Calc. values are given in the Supplementary Material.

Method	gap nature	polytypes			
		$\beta(2H)$	$\gamma(3R)$	$\varepsilon(2H)$	$\delta(4H)$
GaSe					
PBESol	(direct):	0.934 [†]	0.924 [§]	0.745 [†]	0.853 [†]
mBJ	(direct):	2.092 [†]	2.113 [§]	1.889 [†]	2.010 [†]
HSE	(direct):	1.928 [†]	1.931 [§]	1.881 [†]	1.856 [†]
mBJ	(indirect):	1.949 [‡]	1.963 [¶]	1.786 [‡]	1.886 [‡]
HSE	(indirect):	2.219 [‡]	1.971 [¶]	1.976 [‡]	2.014 [‡]
Exp.	(direct):	2.169 ^a		2.120 ^a ; 2.0196 ^b	
Exp.	(indirect):	2.117 ^a		2.065 ^a ; 2.010 ^b	
Exp.	(direct)				2.020 ^c
Exp.	(indirect)				1.995 ^c
Exp.	(exciton peaks):	2.050 ^d		2.004 ^d	2.026 ^d
Calc. GW	(direct)			2.34 ^e ; 1.75 ^f ; 2.11 ^g	
InSe					
PBESol	(direct):	0.304 [†]	0.240 [§]	0.731 [†]	0.607 [†]
mBJ	(direct):	1.232 [†]	1.204 [§]	1.697 [†]	1.493 [†]
HSE	(direct):	1.172 [†]	1.132 [§]	1.198 [†]	1.151 [†]
HSE	(indirect):	2.107 [‡]		1.874 [‡]	1.881 [‡]
Exp.	(direct):		1.29 ^h ; 1.24 ⁱ		
Calc. GW ^j	(direct):	1.1 [†]	1.3 [§]		

Gap nature: [†] $\Gamma - \Gamma$, [‡] $\Gamma - M$, [§] $A - A$, [¶] $A - M$; experimental data: ^aRef. 97, ^bRef. 98, ^cRef. 99,

^dRef. 100, ^eRef. 34, ^fRef. 51, ^gRef. 53, ^hRef. 101, ⁱRef. 43, ^jRef. 42. In the experimental

works^{97,98} cited for GaSe, the distinction between γ and ε phases was not done.

VII. CONCLUSION

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Summarizing, for GaSe and InSe layered semiconductors we studied the performance, within the general context of the DFT, of several prescriptions, now in broad use, for XC potentials, aiming to obtain reasonable description of the band structures and in particular the band gaps. In parallel, the performance of these schemes was studied in what concerns the accurate prediction of the ground-state properties (equilibrium lattice parameters and – implicitly – elastic properties). This latter task was tackled by considering, in particular, modifications of the DFT total energy aimed at grasping, either via additive corrections (the Grimme's, or more flexible schemes), or via realistic polarization models (MBD scheme), the effect of dispersion interactions. The tests have been done on layered GaSe and InSe semiconductors, which have a virtue of being historically well studied, but not so much at the level of fine differences between their available polytypes.

We find that among the schemes routinely employed at the level of modern DFT calculations in view of obtaining reasonable band gaps, namely, mBJ meta-GGA and hybrid HSE functional, both yield the gap values in good quantitative agreement (within several %) with experiment and with GW results. We do not find a conclusive evidence in favor of one of the schemes to give systematically better results than the other. Moreover the predictions on whether the optical gap is direct or indirect may differ, according to two schemes, in view of somehow different details of band dispersions and a close competition between placing the conduction-band minimum at the BZ axis (Γ , A) or periphery (M , L). We point out a noticeable difference (up to ~ 1 eV) between mBJ and HSE schemes in the placement of semicore states (Ga 3d and 4s; In 4d and 5s), presumably related to the latter's localization degree. It would be instructive to compare these predictions with the findings from photoemission spectroscopy, of which we could not find any (within the energy range of interest and sufficient energy resolution) for the systems in question.

Our other finding concerns the predictions of the equilibrium structures, and the comparison of corresponding total energies. It turns out that whereas the conventional DFT schemes, e.g., GGA-PBE, largely overestimate the a and especially the c parameter (hence the interlayer vdW gap), a considerable improvement (to within 1% of the experimental values) is achieved by using either PBEsol, or Grimme D2 / D3 / (Becke-Johnson) corrections to PBE. The discrimination of total energy / volume curves between polytypes,

already quite delicate as assessed in PBEsol calculations, becomes nearly impossible on inclusion of Grimme corrections (in PBE-D2 calculations), presumably due to enhanced sensitivity of such models to interatomic distances between contributing atoms and not to genuine short-range order and charge density distribution. However, the calculations done with first-principles many-body dispersion scheme do largely recover the discernibility of polytypes.

SUPPLEMENTARY MATERIAL

See supplementary material for the bibliography sources, numerical values, and explanations concerning the experimental and calculation data on lattice parameters (Fig. 2, 3) and band gaps (Table V).

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