Structural and electronic properties of narrow-band-gap semiconductors: InP, InAs, and InSb

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The structural and electronic properties of the narrow-band-gap zinc-blende-structure III-V semiconductors InP, InAs, and InSb are studied with two first-principles schemes: the full-potential linear augmented-plane-wave (FLAPW) method and *ab initio* norm-conserving pseudopotentials. The all-electron equilibrium properties are found to be in excellent agreement with experiment; a comparison between the FLAPW and pseudopotential results emphasizes the role of the shallow "semicore" In 4*d* states for both the structural and electronic properties of these compounds. Our results also show that, within the local-density approximation, InAs and InSb have metallic character, while InP retains its semiconductor properties.

I. INTRODUCTION

Studies of the electronic and structural properties of binary semiconductors have recently received considerable attention, both experimentally and theoretically. However, despite interesting properties related to their narrow energy gaps,[1] the InX^{V} compounds (X^{V}=P, As, and Sb) have been the object of fewer investigations (see, for instance, Refs. 2–7), in comparison to the extensive work performed on other III-V zinc-blende-structure materials like GaAs and AlAs. Among the In compounds, special interest was recently devoted to InP and its behavior under pressure, since[7] the structural phase transition occurs at a pressure close to that of the direct- to indirect-gap transition. Furthermore, the recently achieved[8] epitaxial growth of InAs/InP superlattices has provided good single crystals suitable for accurate experimental measurements and has added new interest to the study of the constituent bulk semiconductors.

In this work, intended as a first step towards a detailed study of their superlattice compounds, we investigate the structural and electronic properties of these semiconductors. We use the full-potential linear augmented-plane-wave[9] (FLAPW), method and the *ab initio* norm-conserving pseudopotential (PS) method.[10] The comparison between the pseudopotential and all-electron results, which will be discussed in detail, indicates the importance of the "semicore" In 4*d* states, which play a role in the electronic structure of these materials similar to that of the Ga 3*d* states in GaAs, and the cation *d* states in the zinc-blende-structure II-VI compounds—as emphasized by several authors.[11–14] Furthermore, and perhaps more important, this study shows that, within the local-density approximation (LDA), InAs and InSb have metallic properties, as a result of the well-known failure of the LDA in the description of the excitation properties of semiconductors. On the other hand, excellent agreement is found with experiment for the equilibrium properties of these materials (especially in the FLAPW study) and good agreement (generally within the experimental resolution) is found for the occupied energy bands. Moreover, the study of the direct energy gap as a function of pressure shows that, although the energy gap itself is severely underestimated, its pressure dependence is correctly described by the LDA.

II. METHOD

The electronic and structural properties of InP, InAs, and InSb have been studied in their zinc-blende structure using the local-density approximation (LDA) to density-functional theory. Two independent first-principles methods have been used, namely the all-electron, full-potential linear augmented-plane-wave (FLAPW) method[9] and the *ab initio* norm-conserving pseudopotential method.[10]

In the FLAPW calculation, plane waves with wave vector $K=|\mathbf{k}+\mathbf{G}|\leq 3.6$ a.u. are used for the expansion of the wave function in the interstitial region, leading to about 280 and 340 basis functions for InP and InSb, respectively. Angular momenta up to $l=8$ are included in the muffin-tin spheres (with radii 2.3 a.u.) for the development of both the wave function and the charge density (and potential). The Hedin-Lundqvist form for the exchange-correlation potential has been used.[15] For the Brillouin-zone sampling, the **k**-point mesh used includes

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ten special points.[16] Valence states, including the In $4d$ states, were treated semirelativistically, while core states were treated fully relativistically and updated at each iteration. Spin-orbit splitting has been included as a perturbation on the semirelativistic calculation.

In the pseudopotential calculation, *ab initio* norm-conserving pseudopotentials as given by Bachelet *et al.*[10] were used in order to describe the electron-ion interaction. The electron-gas data used as input to the LDA are those by Ceperley and Alder[17] as interpolated by Perdew and Zunger.[18] Electronic wave functions were expanded into a plane-wave (PW) basis set. Convergence tests suggested the inclusion of plane waves up to 24 Ry. This corresponds to ~640 and 870 PW's at the equilibrium volume for InP and InSb, respectively. The basis was treated exactly and no use of perturbation theory was made to diagonalize such large matrices. The eigenvalue problem was treated using an efficient block version of Davidson's algorithm.[19] The **k**-point mesh employed for the Brillouin-zone integrations was the same as in the FLAPW calculation.[16]

III. RESULTS

Table I lists the equilibrium lattice constants, bulk moduli (B), and their derivatives (B') for the three materials studied and the corresponding measured values.[20,21] The Murnaghan[22] equation of state was used to fit the total-energy curve to the calculated data. For the lattice parameter, the agreement with experiment found in the FLAPW calculations is excellent; the error is about 0.02%, 0.09%, and 0.2% for InP, InAs, and InSb, respectively. The same was found previously for GaAs, AlAs,[23] and ZnSe.[24] Good agreement is found for the bulk moduli, within 2% for the worst case (InP).

In the pseudopotential calculation the equilibrium lattice parameters are systematically underestimated by about 2%. This may be attributed to the contribution of the In $4d$ states, which is neglected in this approach, since similar differences between all-electron and available pseudopotential results were found in GaAs and ZnSe as a result of the contribution of the Ga and Zn $3d$ states (see, for instance, Refs. 23 and 24). In order to test this interpretation, we performed a FLAPW calculation of the equilibrium properties for InP including the In $4d$ states as (self-consistently relaxed) core states, and overlapping exactly the core tails spilling out of the muffin-tin spheres. We obtained $a_0=5.922$ Å, which represents a deviation toward larger values relative to the experimental value and to the value obtained by treating the same states as part of the valence band (see Table I). The bulk modulus B shows a sizable decrease when the $4d$ states are treated as relaxed core states ($B=0.67$ Mb). Better agreement with the experiment is therefore obtained when the In $4d$ states are treated as valence states. Previous pseudopotential calculations of the lattice constants of these materials gave equilibrium lattice constants smaller than the experimental ones and in good agreement with the present pseudopotential results: Zhang and Cohen[5] obtained 5.87, 6.04, and 6.49 Å for InP, InAs, and InSb, respectively; Singh and Varshni[4] obtained 6.34 Å for InSb, and Boguslawski and Baldereschi[25] obtained 5.75 and 5.95 Å for InP and InAs, respectively. On the other hand, the existing (to our knowledge) all-electron calculations of the equilibrium lattice constant are in much better agreement with experiment and with the present FLAPW results. In particular, Gorczyca, Christensen, and Alouani[7] obtained 5.88 Å for InP by use of the LMTO method; other FLAPW calculations (which treated the In $4d$ states as relaxed core states) report 5.918 and 6.084 Å for InP (Ref. 26) and InAs,[27] respectively, which, for InP, are in excellent agreement with our consistent calculation.

The electronic energy eigenvalues at high-symmetry points, calculated at the experimental lattice constants, are listed in Tables II–IV for the occupied and lowest-lying unoccupied states and are compared with the experimental results.[28–30] As a first remark, we notice that InAs and InSb have metallic properties within the LDA, while InP keeps its actual semiconducting character. The failure of the LDA in reproducing the excited properties of these materials is therefore particularly remarkable. When we include the spin-orbit interaction as a perturbation on the scalar-relativistic (SR) results, the direct energy gaps are 0.38, −0.63, and −0.76 eV for InP, InAs, and InSb, respectively, to be compared with the corresponding experimental values, 1.42, 0.42, and 0.24 eV. Our relativistic results are in good agreement with other LDA calculations performed on the same compounds by Cardona and Christensen,[31] using the LMTO method. The correction to the LDA direct energy gaps are about 1.0 eV, changing from material to material by at most ~0.50 eV. This may be interesting in view of the study of the $\mathrm{In}A^{\mathrm{V}}/\mathrm{In}B^{\mathrm{V}}$ ($A^{\mathrm{V}},B^{\mathrm{V}}$=P,As,Sb) superlattices, since it provides an estimate of the accuracy expected for the excitation properties of the superlattices with a simple constant shift of the conduction bands.

When we turn to the valence-band eigenvalues, we see that they are in reasonably good agreement with experiment, generally within the uncertainty of the latter. The total valence-band width, as calculated with the FLAPW method, is slightly smaller than experiment for InAs and

TABLE I. Comparison of calculated pseudopotential (PS) and all-electron FLAPW results for equilibrium lattice parameters and bulk moduli with experiment (from Refs. 20 and 21). Experimental bulk moduli are at room temperature for InP and InAs and at low temperatures for InSb.

	a (Å)	B (Mb)	B'	
InP	5.867	0.71	4.7	FLAPW
	5.74	0.76	4.5	PS
	5.869	0.725		Expt.
InAs	6.063	0.58	5.1	FLAPW
	5.94	0.63	4.7	PS
	6.058	0.579		Expt.
InSb	6.464	0.48	4.5	FLAPW
	6.36	0.48	4.8	PS
	6.479	0.483		Expt.

TABLE II. Electronic energy levels for InP calculated at the experimental lattice constant. Experimental values are from Ref. 28 unless otherwise indicated. SR and R stand for semirelativistic and fully relativistic, respectively. CA and HL refer to the use of the Ceperley-Alder and Hedin-Lundqvist forms for the exchange-correlation potential, respectively.

	FLAPW (SR,HL)	FLAPW (SR,CA)	FLAPW (R,HL)	PS (SR,CA)	Expt. (XPS)
Γ_{1c}	0.42	0.42	0.38	0.98	1.42[a]
Γ_{15}	0.0	0.0	0.0	0.0	0.0
			−0.12		
Γ_1	−11.56	−11.57	−11.60	−11.16	−11.0(4)
Γ_{12}	−14.37	−14.38			−16.80(15)
Γ_{15}	−14.52	−14.55			
X_{1c}	1.64	1.63	1.60	1.68	
X_5	−2.37	−2.38	−2.36	−2.12	−2.0(2)
			−2.46		
X_3	−5.93	−5.93	−5.97	−5.59	−5.9(2)
X_1	−9.16	−9.16	−9.20	−9.14	−8.9(3)
L_{1c}	1.27	1.27	1.23	1.60	
L_3	−1.01	−1.01	−0.98	−0.85	−1.0(3)
			−1.11		
L_1	−5.86	−5.87	−5.90	−5.54	−5.9(2)
L_1	−9.84	−9.84	−9.87	−9.73	−10.0(3)

[a]References 29 and 30.

InSb [in InSb better agreement is found with the ultraviolet-photoemission-spectroscopy (UPS) results] and larger for InP. This last result is somehow surprising, since the bottom of the valence band is formed by the tightly bound anion *s*-bonding states, whose binding energy is expected to be underestimated by the LDA. For InSb, we notice that the inclusion of spin-orbit coupling is necessary in order to obtain good agreement with experiment. The spin-orbit splittings are 0.12, 0.36, and 0.76 eV for InP, InAs, and InSb, respectively, growing with the atomic number of the anion, as expected. Good agreement is found with the corresponding experimental values[32] 0.11, 0.38, and 0.82 eV.

While the valence states are reasonably described by the LDA, as expected the semicore In 4*d* states are too shallow, compared to experiment, by about 2.5 eV. It is

TABLE III. Electronic energy levels for InAs at the experimental lattice constant. Experimental values from Ref. 28 unless otherwise indicated. Symbols are as in Table II.

	FLAPW (SR,HL)	FLAPW (SR,CA)	FLAPW (R,HL)	PS (SR,CA)	Expt. (XPS)
Γ_{1c}	−0.51	−0.51	−0.63	−0.03	0.42[a]
Γ_{15}	0.0	0.0	0.0	0.0	0.0
			−0.36		
Γ_1	−11.93	−11.93	−12.06	−11.54	−12.3(4)
Γ_{12}	−14.41	−14.44			−17.09(15)
Γ_{15}	−14.54	−14.57			
X_{1c}	1.45	1.46	1.33	1.60	
X_5	−2.35	−2.35	−2.47	−2.13	−2.4(3)
			−2.48		
X_3	−5.96	−5.96	−6.08	−5.66	−6.3(2)
X_1	−9.95	−9.95	−10.07	−9.89	−9.8(3)
L_1	0.75	0.75	0.63	1.04	
L_3	−1.01	−1.01	−1.00	−0.88	−0.9(3)
			−1.26		
L_1	−5.86	−5.86	−5.98	−5.57	−6.3(2)
L_1	−10.48	−10.49	−10.60	−10.36	−10.6(3)

[a]Reference 30.

TABLE IV. Electronic energy levels for InSb at the experimental lattice constant. Experimental values from Ref. 28 unless otherwise indicated. Symbols are as in Table II.

	FLAPW (SR,HL)	FLAPW (SR,CA)	FLAPW (R,HL)	PS (SR,CA)	Expt. (XPS)	Expt. (UPS)
Γ_{1c}	−0.47	−0.47	−0.74	−0.01	0.24[a]	
Γ_{15}	0.0	0.0	0.0	0.0	0.0	0.0
			−0.76			
Γ_1	−10.83	−10.85	−11.11	−10.46	−11.7(3)[b]	−11.2[c]
Γ_{12}	−14.64	−14.59			−17.29(15)[b]	−17.49[c]
Γ_{15}	−14.73	−14.68				−17.31[c]
X_{1c}	1.28	1.30	1.04	1.32		
X_5	−2.28	−2.30	−2.48	−2.11	−2.4(4)[b]	
			−2.65			
X_3	−6.01	−6.03	−6.29	−5.76	−6.4(2)[b]	−6.5[c]
X_1	−8.88	−8.89	−9.15	−8.69	−9.5(2)[b]	−9.0[c]
L_{1c}	0.39	0.39	0.13	0.63		
L_3	−1.04	−1.03	−1.06	−0.91	−1.4(3)[b]	−1.05[c]
			−1.54			
L_1	−5.70	−5.71	−5.98	−5.45	−6.4(2)[b]	−6.5[c]
L_1	−9.48	−9.49	−9.75	−9.23	−10.5(3)[b]	

[a]Reference 30.
[b]Reference 28 (XPS).
[c]Reference 28 (UPS).

interesting, however, to compare the chemical shift of these states with experiment. The center of the In 4*d* band is 0.33 eV higher in InSb than in InAs, and a further 0.12-eV shift is observed upon going to InP (spin-orbit splitting on the valence-band maximum was included in this calculation). Experimentally, the same shifts are 0.20 and 0.29 eV, respectively [using the same x-ray-photoelectron-spectroscopy (XPS) measurements[28]]. The agreement is only qualitative. It should be noticed, however, that these differences are much smaller than the spin-orbit splitting of the In 4*d* states, ~0.85 eV (Ref. 28) (our calculations give 0.86 eV), and comparable with the scattering of the existing experimental data.[28] Agreement within ~0.2 eV between the LDA and experiment for the chemical shifts was also found[33] previously for GaAs and AlAs. We observe that the width of the In 4*d* band increases in going from InSb (0.09 eV in the SR calculation) to InP (0.15 eV), as a consequence of the lattice-constant decrease.

We now turn to a comparison of the all-electron and pseudopotential (PS) results. In order for the comparison to be fully consistent, we have calculated the electronic structure of these materials using the FLAPW method and the same Ceperley-Alder[17] form used in the pseudopotential calculation. The corresponding results, listed in Tables II–V, show marginal differences with respect to the Hedin-Lundqvist calculations. In all three materials, the direct energy gap is consistently larger in the PS calculation, while the valence-band width (VBW) is smaller. However, if we calculate the difference between the anion *s* (bonding) Γ_1 level (bottom of the valence band) and the In *s* (antibonding) level, the FLAPW and PS results agree to within $\lesssim 0.1$ eV, which proves the consistency of these completely independent results. This means that the valence-band maximum (VBM) Γ_{15} is higher in the FLAPW results, by 0.56, 0.48, and 0.46 eV for InP, InAs, and InSb, respectively, as a consequence of the orthogonality repulsion between the VBM Γ_{15} (mostly due to the anion *p*-bonding states) and the Γ_{15} component of the shallow In 4*d* states, neglected in the pseudopotential approach. On the other hand, the mixing with In *d* states is symmetry forbidden for the Γ_1 *s*-bonding states and the Γ_{1c} *s*-antibonding state. The VBM therefore moves relative to these levels. This effect has been discussed by several authors[11–14] for GaAs and for the II-VI compound semiconductors, where, since the cation *d* states are more shallow and usually lie above the anion *s* band, it is expected to be more important. This (*p*-*d*) orthogonality effect is made apparent by an analysis of the angular-momentum decomposition of the charge density into atomic sites. In InSb, for example, the VBM states contain (inside muffin-tin spheres with radius 2.3 a.u.) 3%

TABLE V. Angular-momentum-projected decomposition of the charge density inside atomic spheres ($R = 2.3$ a.u.) for InP, InAs, and InSb.

		s	*p*	*d*	Total
InP	In	0.61	0.47	9.64	10.73
	P	1.37	2.20	0.05	3.63
InAs	In	0.63	0.44	9.63	10.72
	As	1.37	1.88	0.03	3.29
InSb	In	0.64	0.44	9.62	10.72
	Sb	1.10	1.24	0.02	2.38

In *d*-like charge, to be compared with 8% In *p*-like charge. As a counterpart of this hybridization, the Γ_{15} component of the In 4*d* states has 0.4% Sb *p* character. In order to better compare the pseudopotential and all-electron results, we plot in Fig. 1 the energy bands calculated (semirelativistically) with the two methods for InP (the energy zero has been set to the VBM, for consistency with the tables). The two band structures are seen to be in good agreement apart from the *p*-*d* orthogonality-induced shift just mentioned. (Note that this shift appears with the opposite sign in Fig. 1 due to the energy zero chosen.) This shift is not, however, uniform over the Brillouin zone, being weighted by the anion *p* character and, therefore, by the *s*-*p* mixing. In particular, while symmetry forbidden at Γ, this mixing is apparent at the zone boundary (e.g., at L).

In order to compare the ionicity of these compounds, we list in Table V the angular-momentum decomposition of the valence charge density inside the muffin-tin spheres. The In atoms are remarkably similar in the three compounds, while larger differences are observed in the anion charges: the P spheres contain about 0.32 electrons more than the As spheres, as a result of the different ionicity and their different atomic sizes; a larger difference is observed between As and Sb. As another way of showing the ionicity differences between these materials, we plot in Fig. 2 the contour map of the charge density—as obtained in the FLAPW calculation—for the Γ_{15} states at the VBM for InP, InAs, and InSb [Figs. 2(a), 2(b), and 2(c), respectively]. The valence states are mainly due to the anion *p* states and show the hybridization with In *d* orbitals previously pointed out. The ionicity differences going from InP to InSb result in a greater localization of the electronic charge distribution around P and an enhanced sphericity as compared to the heavier anions. Particularly important is the difference between InP and the remaining two compounds; this is consistent with the calculated energy gap of InP (0.42 eV) being much larger than those of both InAs (-0.51 eV) and InSb (-0.47 eV). We have to point out here that, due to the lattice-constant difference, the difference between

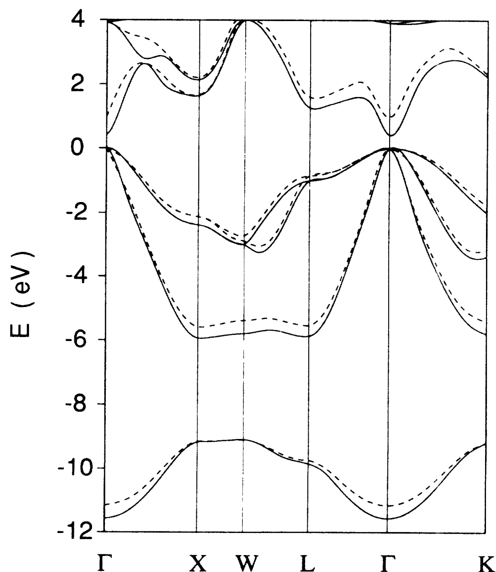

FIG. 1. Self-consistent band structure of InP at the experimental equilibrium lattice constant. Solid (dashed) lines refer to the FLAPW (PS) calculation.

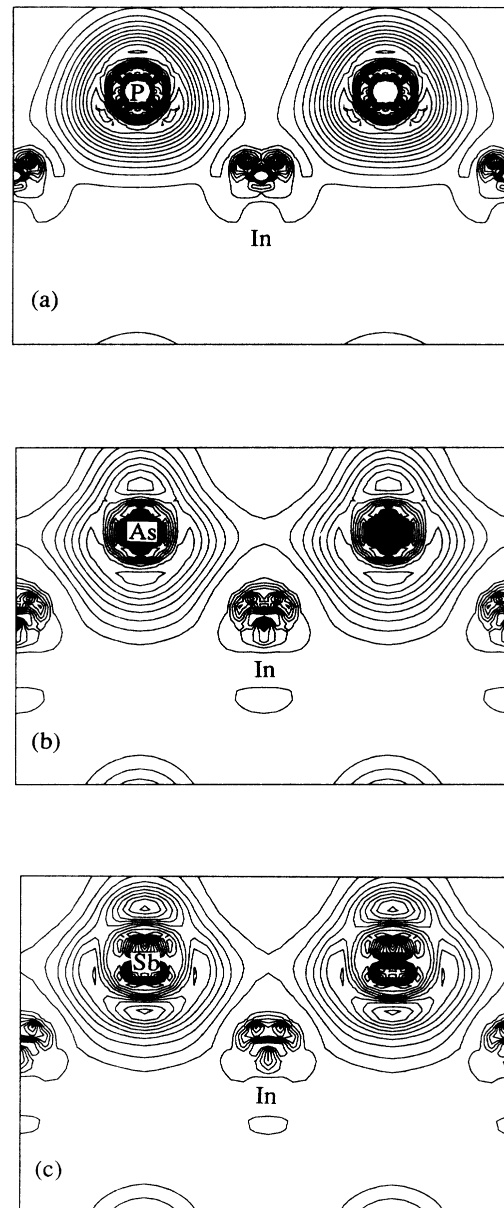

FIG. 2. Charge-density contour plots for the Γ_{15} states in (a) InP, (b) InAs, and (c) InSb. Contours are given on a linear scale and successive contours differ by $3e$/(unit-cell). The lowest charge-density contour shown refers to the $3e$/(unit-cell) level.

TABLE VI. Calculated and experimental values for the coefficients b,α,β.

		b	α (10^{-6} eV bar^{-1})	β (10^{-12} eV bar^{-2})
InP	FLAPW	−5.19	7.8	−19.6
	PS	−7.14	10.4	−21.3
	Expt.[a]	−6.35±0.05	8.4±0.2	−18.3
InAs	FLAPW	−5.24	9.2	−28.2
	PS	−6.44	11.6	−27.0
	Expt.[b]		10.0	
InSb	FLAPW	−5.77	12.3	−41.4
	PS	−6.95	15.9	−45.9
	Expt.[b]		15.0	

[a]Reference 34.
[b]Reference 35.

InAs and InSb does not show up significantly in Fig. 2. In fact, the use of equal spheres for As and Sb implies larger relative interstitial contribution to the total charge in InSb than in InAs. Any alternative choice of sphere radii (e.g., touching spheres) would always imply a degree of arbitrariness, and therefore comparison between muffin-tin-projected charges are only indicative.

We also studied how the gap dependence with pressure is represented by both FLAPW and PS calculations. In particular, we studied the behavior of the gap as a function of the pressure (p) assuming a quadratic dependence[34] ($E_g=E_0+\alpha p+\beta p^2$) and, also, as a function of the lattice-constant relative variation ($\Delta a/a_0$) [in this case the relation[33] is $E_g=E_0+3b(\Delta a/a_0)$]. In order to obtain the pressure values, we used the Murnaghan[22] equation of state and the values for B_0 and B' as obtained, respectively, by the two theoretical calculations. Our calculated results for the α,β,b coefficients, compared with the available experimental values,[34,35] are shown in Table VI. Both calculations agree reasonably well with the experimental values given for InP, where very accurate measurements are available also for the quadratic coefficient for E_g versus p. We notice a larger value for the deformation potential ($b=\frac{1}{3}dE_0/da$) given by the PS calculation, which is consistent with other calculated results listed in Ref. 34. The sublinear variation of E_g with pressure, mainly due to the nonlinearity of the bulk modulus at high pressures, is well represented by both methods (the agreement is within the experimental error), in contrast with what was found for the ZnSe case.[24,36] In this latter case, in fact, the existing pseudopotential calculations did not correctly recover the sign of the quadratic term; this seems to lead to the conclusion that, whereas the LDA does describe the quadratic behavior reasonably well, a suitable treatment of the cation d states is more crucial for the II-VI compounds rather than the III-V compounds. Despite the underestimate of the band gap, the LDA seems to correctly reproduce the pressure dependence of the gap itself—in agreement with that found by previous calculations (see, for example, Refs. 24, 36, and 37). This result may indicate that the pressure dependence of the self-energy correction may be small and appears to agree with recent quasiparticle calculations, within the GW approximation, of pressure coefficients of the band gap in silicon.[38] A study of the FLAPW results obtained for the other two compounds (InAs, and InSb) shows that the linear coefficient of E_g versus $\Delta a/a_0$ decreases upon going from InP to InSb as the compound ionicity decreases, a tendency that has also observed for several other compounds.[34] The same trend is not observed in the PS calculations.

IV. CONCLUSIONS

We calculated the structural and electronic properties of the binary compound semiconductors InX^{V}, with X^{V}=P, As, and Sb. The equilibrium properties are in excellent agreement with the experimental results when calculated with the FLAPW method. The smaller lattice parameters obtained with the pseudopotential approach emphasize the role of the shallow In 4d semicore states in determining the structural properties of these compounds.

While the occupied bands are in good agreement with the experimental results, the well-known failure of the LDA in determining the excited properties of semiconductors results in a metallic character for InAs and InSb. By contrast, the pressure dependence of energy gaps compares favorably with the existing experiment.

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