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Abstract. The wave functions of boron, aluminium and gallium phosphides have been calculated at both the Hartree–Fock and local density approximation levels using the *ab initio* linear combination of atomic orbitals method implemented in the program CRYSTAL. The Mulliken populations, bandstructure, electron charge densities, and structure factors are evaluated and compared.

The chemical bonds are mainly covalent, as revealed by the difference electron charge-density maps obtained by subtracting from the total densities the superposition of the spherical atomic densities. A charge-density accumulation between the nearest neighbours slightly shifted towards the phosphorus appears in the AlP and GaP compounds, whereas an opposite charge transfer from phosphorus to boron is observed in boron phosphide from the Mulliken population analysis.

1. Introduction

In solid-state physics, quantum mechanical calculations provided, a few years ago, an *ab initio* approach to several ground-state properties, such as Mulliken populations, valence bandstructure, and charge distribution, which characterize the nature of chemical bonds. A periodic Hartree–Fock (HF) linear combination of atomic orbitals (LCAO) computational scheme [1] was proposed, and implemented in the general-purpose computer program CRYSTAL [2, 3] for the study of crystal compounds. Within this program, correlation effects are taken into account at two levels of sophistication: (i) to correct *a posteriori* the HF energy and energy-dependent quantities through correlation-only electron density functionals (DF) [4]; and (ii) to improve the calculation of the electronic density by solving at each stage of the self-consistent-field (SCF) process the HF and Kohn–Sham (KS) equations [5]. In a recent paper [6], this last method in the local-density approximation (LDA) was used to calculate the Compton profiles of hexagonal boron nitride with an excellent degree of accuracy when compared with experiment [7].

In the present work, this *ab initio* LCAO periodic approach has been applied both at the HF and DF-LDA levels to the BP, AlP, and GaP series. This choice has been suggested for the following reasons: (i) the systems are simple and have highly symmetric structures, so very accurate computational conditions and extended basis sets could be used; (ii) the presence of cations belonging to three different periods of the periodic table allows the analysis of the influence of size and polarizability on the electron charge distribution and scattering properties; and (iii) in the III–V semiconductor group, the series of phosphide

compounds has not been yet investigated so much because these compounds have high melting points and are very unstable under humid conditions, which makes growing single crystals difficult. In these conditions, the interest of a theoretical study, made in order to establish the nature of their chemical bond and to compare physical properties, becomes evident.

BP, AlP, and GaP are cubic with the zinc-blende structure and the non-centrosymmetric group $F\bar{4}3m$. This structure is the same as for GaAs, InSb, or cubic BN, which are among the most well known and thoroughly investigated compounds of the III–V semiconductor family because of their technological importance.

The plan of the paper is as follows. In section 2, the computational details and all-electron basis sets are provided. Section 3 reports a few physical properties of these compounds and compares these data with the HF results already published. In section 4, the electronic structure of BP, AlP, and GaP is investigated by calculating the Mulliken populations, electron charge density, bandstructure, and structure factors. The effect of correlation, as obtained at the LDA level, is briefly discussed. Conclusions are drawn in section 5.

2. Computational details and basis sets

The Hartree–Fock method has already been described and applied to the study of the two compounds BP and AlP [8]. In this work, the calculations are performed using the density functional scheme as described in reference [5]. The main features are briefly reported here. DFT in the local density approximation has been introduced into the SCF process, resolving at each stage the Kohn–Sham (KS) equations instead of the HF equations. Exchange and correlation have been treated by DFT using in the KS monoelectronic operator an exchange–correlation potential. In the LCAO method, this potential is represented in a basis set of gaussian atomic orbitals. The Perdew–Zunger parametrization of the Ceperley and Alder free-electron-gas potential has been used. With the computer program developed in reference [5], it is possible to study the electronic structure at the HF or KS level using the same computational conditions. The evaluation of the Coulomb and exchange series is carried out by adopting the following values [1] of the truncation tolerances: $ITOL_1 = ITOL_2 = ITOL_3 = 5$, $ITOL_4 = 6$, $ITOL_5 = 12$. These values indicate that two-centre integrals are disregarded or neglected [1] whenever the overlap is smaller than 10^{-ITOL}. A shrinking factor value of $IS = 8$ of the reciprocal-lattice vectors is used; its value determines the number (43) of k-points in the irreducible part of the first Brillouin zone where the Fock matrix is diagonalized. The values of these parameters, ITOL and IS, are a good compromise between reasonable computational times and sufficient accuracy of the total energy.

All-electron basis sets have been adopted in this work. They have already been described by Orlando *et al* [8] for BP and AlP. They are of the 6-21*G type where a d-like polarization function was added. For GaP, the P basis set is the same as for BP or AlP. For Ga, the basis set adopted is the one used by Pandey *et al* [9] in the study of gallium nitride GaN; it is of the (6.4.111/41)G type with two d-type shells. As in the BP and Al cases, the exponent α of the outer shell of the Ga and P basis sets was only optimized at the HF level for the experimental geometry. The values obtained are $\alpha_{sp}(Ga) = 0.203$, $\alpha_d(Ga) = 0.658$, $\alpha_{sp}(P) = 0.126$, and $\alpha_d(P) = 0.45$. These basis sets lead us to use 32, 36, and 49 atomic orbitals in the BP, AlP, and GaP unit cells, respectively.

Table 1. The energy per unit cell E (au), lattice parameter a (Å), binding energy BE (au), and bulk modulus B (GPa) calculated at the LDA level. The values obtained at the HF level are given in parentheses while the experimental data are in bold type.

	E	a	BE	B
GaP	−2261.9535[a]	5.372[a]	0.245[a]	98[a]
	(−2263.9831)[a]	(5.541)[a]	(0.180)[a]	(99)[a]
	—	(5.560)[b]	(0.154)[b]	(95)[b]
		5.450[c]	**0.268**[d,b]	**91**[c]
AlP	−581.5674[a]	5.463[a]	0.283[a]	87[a]
	(−582.7375)[e]	(5.553)[e]	(0.201)[e]	(92)[e]
		5.451[d]	**0.317**[f,e]	**86**[g]
BP	−364.7362[a]	4.526[a]	0.358[a]	166[a]
	(−365.4380)[e]	(4.598)[e]	(0.237)[e]	(170)[e]
		4.538[d]	**0.383**[h]	**173**[h]
				190[i]

[a]This work.
[b]Reference [10].
[c]Reference [16].
[d]Reference [11].
[e]Reference [8].
[f]Reference [13].
[g]Reference [15].
[h]Reference [12].
[i]Reference [14].

Table 2. Electronic distributions corresponding to a Mulliken population analysis calculated at the LDA level. Total charges on the A (B, Al, Ga) and P atoms, and A–P overlap populations of the nearest neighbours. The values obtained at the HF level are given in parentheses. All of the charges are in units of e (the charge on the electron).

	BP	AlP	GaP
A	5.40	13.12	30.09
	(5.23)	(12.52)	(29.80)
P	14.60	14.88	15.91
	(14.77)	(15.48)	(16.20)
A–P	0.63	0.60	0.53
	(0.72)	(0.65)	(0.52)

3. Results and discussion

3.1. Physical properties

Table 1 reports the equilibrium data calculated at the LDA level and compares them with those previously obtained at the HF level using either an all-electron basis set (BP, AlP [8]) or an electron core pseudopotential (GaP [10]). For comparison, experimental results are also given. Our data result from a best fit with the Murnaghan equation of state [17] built up with 10–12 points, in the range $V_0(1 \pm 0.1)$ (V_0 is the experimentally derived volume of the unit cell).

It is well known that the HF calculations overestimate the lattice parameters. This result is confirmed for the series of phosphide compounds, since the mean overestimation is 1.6% with respect to the experimental data. LDA calculations significantly improve the

agreement with experiment, which becomes very good except for GaP where the lattice parameter is 1.4% smaller than the experimental one. When the HF results are corrected 'a posteriori' with the correlation-only functional [18], the lattice parameter of GaP is improved ($a_0 = 5.461$ Å) but the bulk modulus deteriorates ($B = 110$ GPa). In these conditions, the previous discrepancy seems due, in great part, to the gallium belonging to a higher row of the periodic table than boron or aluminium. Comparison of LDA and HF calculations shows that electron correlation accounts for about 30% of the binding energy of these solids. Finally, the bulk modulus is very slightly improved by the LDA calculations with respect to the HF calculations, since the mean error is 6% with respect to experiment, while the HF calculations lead to an error of about 7%.

3.2. Electronic structure

3.2.1. Mulliken population analysis and electron charge densities.   It must be remembered that Mulliken populations are, to a large degree, arbitrary since the overlap population distribution between two atoms is arbitrarily set as 50% attributable to each of them. However, Mulliken populations are useful for providing the net charge on atoms qualitatively, and for obtaining an indication of the character of the chemical bond. Table 2 reports the charges (in units of *e*) on each atom A (B, Al, Ga) and P, and the overlap populations calculated at the LDA and HF (in parentheses) levels for comparison.

The large overlap populations given in table 2 indicate a predominantly covalent character of the chemical bond accompanied by a small charge transfer from one atom to the other, as shown by the net charge on the atoms. These two features also indicate that the ionicity increases on going from BP to AlP and to GaP, i.e. when the cation goes down from the first to the third row of the periodic table. Other features should be noted. The BP and AlP charge transfer is reversed at the LDA level, and boron and aluminium are negatively charged. Similar conclusions have already been established from HF calculations [8]. The electronic correlation effect taken into account at the LDA level makes these compounds slightly less ionic; this result confirms previous observations about ionic and semi-ionic compounds [5], and seems to be a general rule. The Mulliken populations given in table 2 show that the LDA calculations do not quantitatively alter the characteristics of the bond with respect to the HF calculations. For this reason, the total electron charge density (ECHD) already reported from HF calculations [8] is not given here. Only the LDA difference ECHD maps obtained from the difference between the total ECHD maps and the superposition of the electron charge density of the free atoms localized at the crystal sites are projected onto the (110) plane of the structure. These difference maps allow us to discuss more accurately the small differences characterizing each compound. Figures 1(a), 1(b) and 1(c) give the difference ECHD maps calculated at the LDA level corresponding to BP, AlP, and GaP, respectively. It can be noted that these maps are very similar to those calculated by Orlando *et al* [8] for BP and AlP at the HF level. Generally speaking, figure 1 shows the typical features of the covalently bonded semiconductors. The bond charge is large and located close to halfway between the two nearest atoms. However, important differences appear. In fact, we note that with respect to silicon—a fully covalent semiconductor for which the isoelectronic curves are symmetric [19]—the bond charge is slightly disturbed by the electron charge transfer from one atom to another (a semi-covalent bond). In AlP and GaP, the saddle point is located closer to the phosphorus site, with a larger displacement in GaP than in AlP. In contrast, in BP the saddle point is in the middle of the B–P bond. The location of positive isodensity curves around the B nucleus can be due on the one hand to the large attraction of this nucleus characterized by its small radius,

and show on the other hand the diffuse character of the p orbitals of P coming close to the B nucleus without p core electrons. These results confirm the Mulliken population analysis which shows a significant electron charge transfer from P to B and from Ga to P in BP and GaP, respectively. They present, on the other hand, an apparent discrepancy for AlP, where the difference ECHD maps indicate a very small charge transfer from Al to P, while the Mulliken data indicate a transfer in the opposite direction.
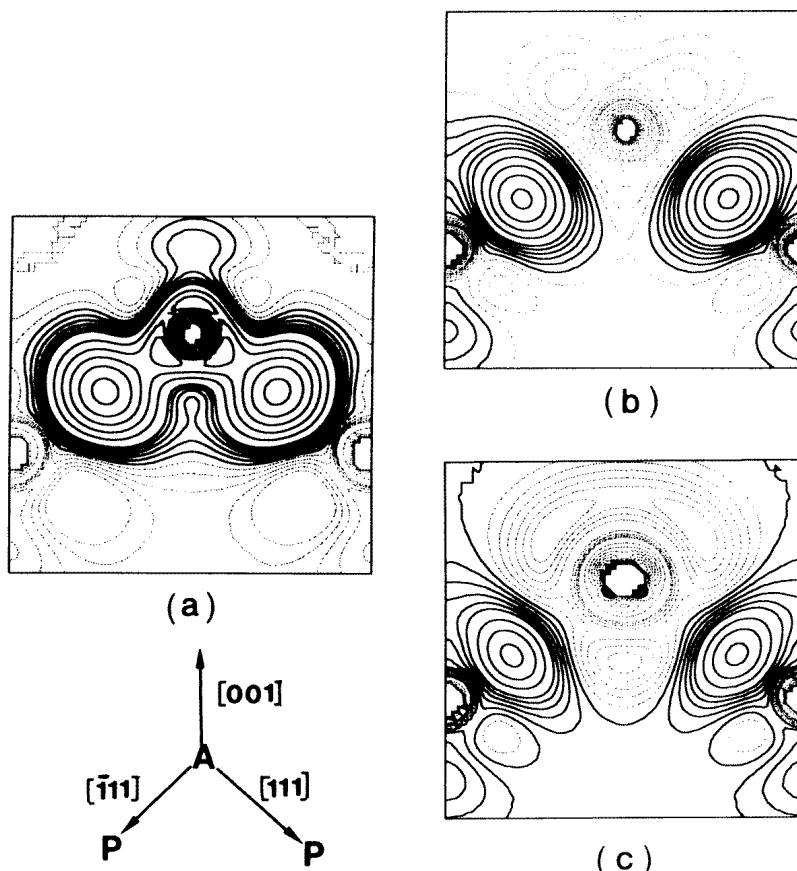
Figure 1. Difference electron charge-density maps projected onto the plane (110). The step width between two positive contours (full lines) is $0.005e$ Å^{-3}. The dotted lines correspond to the negative contours; the step width is 0.02 for BP (a), 0.005 for AlP (b), and 0.01 for GaP (c).

3.2.2. Structure factors. The x-ray structure factors $F_o(s)$ are calculated from the Fourier transformation of the static electron density in the direction of the scattering vector (s). The structure factors of 19 reflections belonging to the region of small values of $(\sin\theta)/\lambda$ are given in table 3. In this table, the HF results—which are similar to the LDA ones up to the third figure—are not reported for reasons of clarity.

To discuss the deformation of the electron cloud around the atoms, it is useful to compare these structure factors with those calculated in the independent-atom model $(F_o^{IAM}(s))$ developed by likening the crystal to a superposition of free atoms. For the zinc-blende-type

Table 3. Static structure factors F_o calculated at the LDA level and with the IAM model (F_o^{IAM}). The F_o-values in parentheses are the experimental data of reference [21] corrected for the anomalous dispersion and for the temperature effect.

	BP		AlP		GaP		
	F_o	F_o^{IAM}	F_o	F_o^{IAM}	F_o		F_o^{IAM}
111	11.14	10.91	15.33	15.06	28.94	(28.83)	28.77
200	7.28	7.39	1.49	1.30	14.68	(14.40)	14.79
220	10.32	10.38	17.40	17.53	31.86	(32.19)	32.04
222	5.97	6.00	0.72	0.71	12.48	(12.79)	12.53
311	7.92	8.07	11.39	11.58	22.76	(22.92)	23.00
331	7.05	7.02	10.16	10.14	19.73	(19.43)	19.77
333	6.19	6.22	9.04	9.08	17.32	(17.24)	17.44
400	8.69	8.79	14.85	14.58	26.95	(26.19)	27.16
420	5.19	5.21	0.76	0.80	10.46	(10.48)	10.50
422	7.80	7.81	13.31	13.34	23.79	(23.86)	23.91
440	6.99	7.01	11.99	12.01	21.32	(21.01)	21.41
442	4.00	4.02	1.07	1.06	7.81		7.88
444	5.70	5.73	9.91	9.95	17.69		17.76
600	4.00	4.02	1.06	1.06	7.80		7.88
622	3.54	3.55	1.13	1.12	6.97		7.06
640	3.17	3.17	1.15	1.14	6.36		6.44
644	2.59	2.59	1.10	1.11	5.54		5.61
662	2.38	2.37	1.06	1.06	5.27		5.32
666	1.80	1.79	0.85	0.87	4.65		4.68

structure, the expressions for the structure factors are given by

$$F_o^{IAM}(s) = 4[f_{o,A}(s) + f_{o,P}(s)] \qquad \text{for } h+k+l = 4n$$
$$F_o^{IAM}(s) = 4[f_{o,A}(s) - if_{o,P}(s)] \qquad \text{for } h+k+l = 4n+1$$
$$F_o^{IAM}(s) = 4[f_{o,A}(s) - f_{o,P}(s)] \qquad \text{for } h+k+l = 4n+2$$
$$F_o^{IAM}(s) = 4[f_{o,A}(s) + if_{o,P}(s)] \qquad \text{for } h+k+l = 4n-1$$

where $f_{o,A}(s)$ and $f_{o,P}(s)$ are the atomic (A and P) scattering factors given by the *International Tables for Crystallography*, ITC [39], and h, k, l are the Miller indices. We have verified that the values of $f_o(s)$ are basis set independent, by comparison of the ITC values of $f_o(s)$ with those calculated using the present basis sets reoptimized for each free atom. First of all, before discussing the connection between the values of $F_o(s)$ and the nature of the chemical bonds, it is necessary to compare our structure factors to the available experimental data. To our knowledge, no recent experimental data measured on single crystals exist, but there are recent experimental data on powdered BP [20] and GaP [21] samples, which are reported in parentheses in table 3, after corrections to zero temperature and for anomalous dispersion. The agreement factor R defined as

$$R = \sum_{hkl} |F_o - F_{o,exp}| \bigg/ \sum_{hkl} F_{o,exp}$$

is 1.2% for GaP, showing that the agreement is very satisfactory. In the case of GaP, a theoretical study made by Wang and Klein [22] leads to $F_o(s)$ values (not given in table 3, for clarity) which are practically identical to ours, since the R-factor is only 0.2%. In the light of these values and of those recently obtained for cubic boron nitride (cBN) [23] which belongs to the same series, it is possible to discuss the results of table 3. Except for

Table 4. The phosphorus valence band calculated at the LDA level. $E(s)$ and $E(p)$ are the energies (in au) of the bottom of the phosphorus valence s and p bands respectively, while $\delta E(s)$ and $\delta E(p)$ are the corresponding bandwidths (in eV). The last six lines report the populations of the s and p valence shells of the A and P atoms for the phosphorus p valence band. The values obtained at the HF level are given in parentheses.

	BP	AlP	GaP
$E(s)$	−0.69	−0.61	−0.62
	(−0.98)	(−0.87)	(−0.88)
$\delta E(s)$	5.2	2.5	3.1
	(7.2)	(3.4)	(4.0)
$E(p)$	−0.46	−0.40	−0.41
	(−0.65)	(−0.55)	(−0.56)
$\delta E(p)$	9.1	5.7	6.7
	(13.0)	(7.8)	(9.0)
$p(P)$	2.81	3.22	3.91
	(3.03)	(3.78)	(4.29)
$s(A)$	0.65	0.85	0.71
	(0.55)	(0.66)	(0.55)
$p(A)$	2.09	1.57	1.07
	(1.97)	(1.27)	(0.95)

that for the 111 reflection, the F_o-values are smaller than the corresponding F_o^{IAM}-values for BP and GaP, while the differences $F_o - F_o^{IAM}$ are either positive or negative in AlP. In this last case, where the atoms belong to the same row of the periodic table, the atomic scattering factors are close, and the difference $F_o - F_o^{IAM}$ is much more sensitive to the deformation of the electron cloud in the crystal.

As for cBN, the deviation of the differences $F_o - F_o^{IAM}$ from zero is large for the 111, 200, 220, 311, and 400 reflections. The difference associated with the 111 reflection is the largest one, and is positive for each compound. It represents 2% (BP), 1.8% (AlP), and 0.6% (GaP) of the F_o-value, and can reach 8% in cBN. It contains the contribution of both atoms and expresses the deformation of their electron clouds along the [111] direction. It is correlated in part with the covalency of the A–P bond. The 200 reflection is controlled only by the charge transfer from one atom to the other. Since it belongs to the group of weak reflections ($h + k + l = 4n + 2$), $F_o - F_o^{IAM}$ is more significant and accurate for AlP and cBN than for BP or GaP. It is to be noticed that this difference is similar to that for AlP and cBN, and corresponds in the two cases to about 12% of the F_o-value. This result indicates a similar charge transfer from the 'cations' B or Al towards the 'anions' N or P respectively, as confirmed by the difference ECHD maps, but which is contrary in the AlP case to the result from the Mulliken populations. In the same group, the 222 reflection describes the anisotropy of the bond charge. In AlP, $F_o(222)$ is much smaller than that corresponding to cBN: a larger proximity of the atoms in the cBN cell probably lies at the origin of this difference. In the group of strong reflections ($h + k + l = 4n$), all of the amplitude differences $F_o - F_o^{IAM}$ are negative, except that associated with the 400 reflection of AlP. As in cBN, these negative values and those corresponding to the 311 reflection are explained by the monopole deformation of atomic wave functions in comparison with the free state. In this series, including also cBN, the results are very homogeneous; therefore the behaviour of the 400 reflection is surprising, and it would require further analysis confirming the calculation of the structure factors of AlN and AlAs before one could ascertain whether it is attributable to the role of aluminium in the charge distribution.
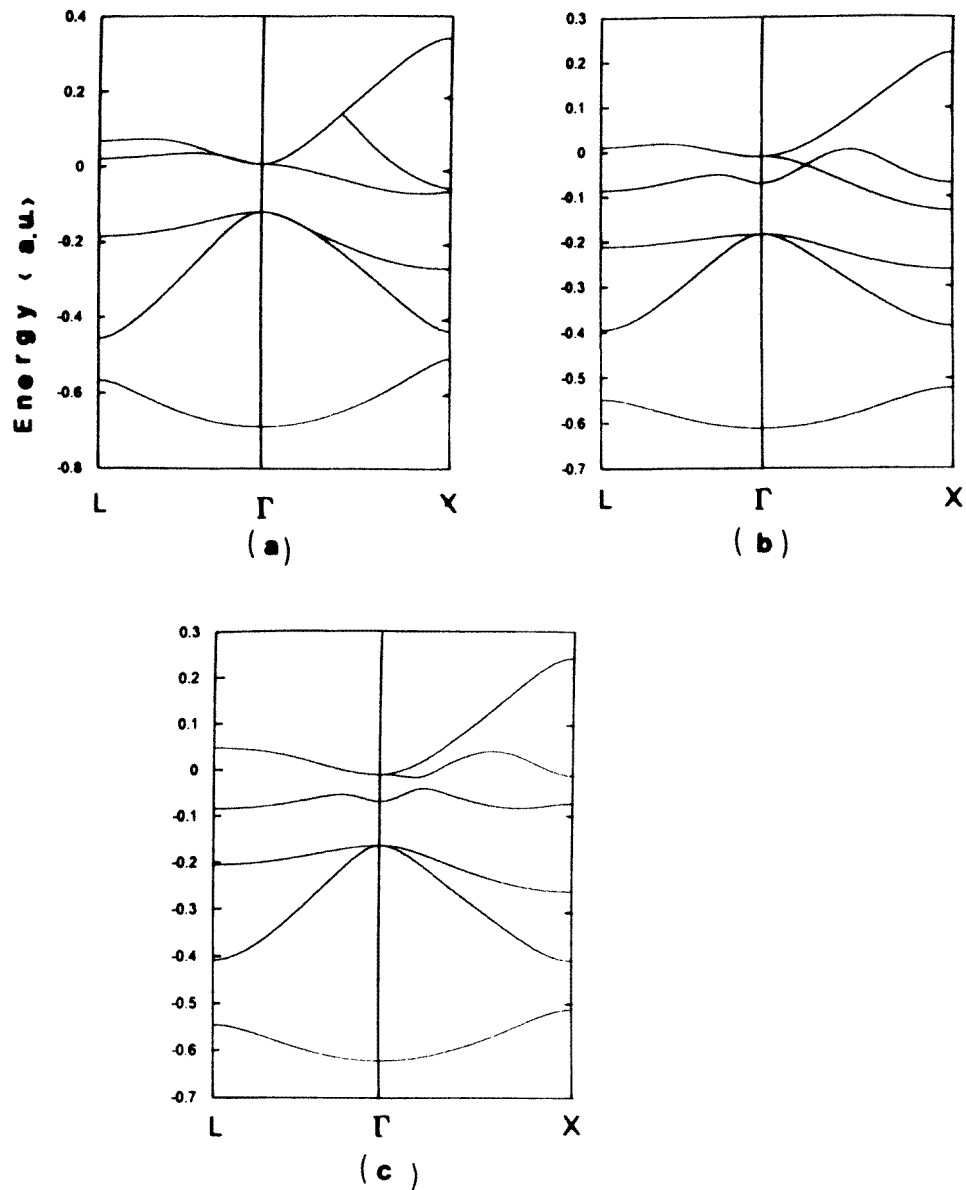
Figure 2. Electronic bandstructures along the path L–Γ–X: the valence and lower conduction bands corresponding to BP (a), AlP (b), and GaP (c).

3.2.3. The bandstructure and density of states.   Among the electronic properties of these compounds, the bandstructure is certainly that which has been the most investigated. Several papers can be cited where the bandstructure is reported, and where calculated and experimental values of the gaps are compared for BP [12, 24–26], AlP [25–27], and GaP [26, 29–33]. When compared with the experimental gaps, it is well known that the theoretical ones obtained by the LCAO-HF and LCAO-LDA methods are overestimated and underestimated, respectively. In this work, we have limited our calculations to the ground-

state properties, i.e. to the location, bandwidth, and density of states of the phosphorus valence band. The bandstructure calculated at the LDA level for the three compounds along the L–Γ–X pathway of the first Brillouin zone is represented in figures 2(a)–2(c). Table 4 gives the energy of the bottom of the s and p phosphorus valence bands and the associated bandwidth. The density of states of the p phosphorus valence band is also analysed in the s and p orbitals of A atoms and p orbitals of the P atom. LDA and HF (in parentheses) values allow us to quantify the electron correlation effect. The examination of this table leads to the same general conclusions as when the HF or LDA results are considered. However, significant differences between these two approaches must be underlined

(i) With respect to the HF calculations, LDA destabilizes the bottom of each phosphorus band and decreases the corresponding bandwidth. These variations are very similar in AlP and GaP but significantly higher in BP

(ii) LDA strengthens the covalency of the chemical bonds since the participation of the B, Al, and Ga orbitals in the population of the p phosphorus valence band becomes larger.

In the light of the values of the projected DOSs, it is clear that the degree of covalency of the A–P chemical bond increases from GaP to AlP and to BP since the participation of the p orbitals of the A atom in the p phosphorus valence band varies from 18% to 26% and to 35%. This result confirms the conclusion obtained from the difference electron charge densities reported in figures 1. It must be noted that the bottom of the phosphorus valence bands is located at energy levels which are very close for the three compounds, but the bandwidths are different. For a given compound, the bandwidth of the p phosphorus valence band, depends especially on the distance between the nearest-neighbouring phosphorus atoms (see, for example, the proposed correlation in the oxide compounds [34]). Comparison of the values calculated for AlP and GaP which are characterized by the same value of the lattice parameter seems to indicate that stronger ionicity of the GaP bond is a feature which contributes to the increasing of the corresponding bandwidth. In BP, which is the most covalent compound of the series, the large bandwidth is mostly caused by the smaller P–P distance.

3.2.4. The character of the chemical bonds. The data presented so far allow us to analyse the nature of the bonds in these phosphide compounds according to classical chemical concepts such as ionicity and covalency. While these concepts are not very well founded, they are undoubtedly useful for classifying compounds into different categories with different chemical and physical properties. With respect to MgO [35] and silicon [36], which exhibit fully ionic and covalent characters, respectively, as shown by the same method, the compounds BP, AlP, and GaP differ greatly. For MgO, the Mulliken charges have the formal values ±2, the isodensity curves in the ECHD maps are spherical and well located around the nuclei, and the bandstructure is made up of pure levels and bands well separated from each other—the topmost valence band being essentially characterized by p oxygen character. In contrast, in silicon the overlap population is large (0.59*e* with a STO-3G basis set), and the ECHD maps show a large diffuse bond charge perpendicular to the Si–Si bond with a saddle point located in the middle of the bond. With these results as a reference, the ones calculated for BP, AlP, and GaP indicate that these compounds are mainly covalently bonded, with a slight disturbance arising from an electron charge transfer towards the P atom (a semi-covalent bond). Considering the low degree of ionicity of the bond, and correlating this ionicity with the magnitude of the electron charge transfer (the Mulliken population and displacement of the saddle point in the ECHD maps towards the P atom) and of the participation of the p orbitals of the B, Al, and Ga atoms in the p phosphorus valence

band, our results suggest the following ionicity order: GaP > AlP > BP. BP is nearly covalent. These conclusions confirm perfectly the sign and the order of the ionicity scale (f) as calculated by Philips [37] (f(BP) = 0.006, f(AlP) = 0.307, and f(GaP) = 0.327) but present a reverse ordering of AlP and GaP for the ionicity calculated by Christensen *et al* [38] (f(BP) = 0.001, f(AlP) = 0.421, and f(GaP) = 0.361).

4. Conclusions

New LCAO calculations have been made at the LDA level in order to explain and compare the electronic structures of boron, aluminium and gallium phosphides. With respect to the HF results, they show that the electron correlation effect improves the quality of the calculation of the physical properties of these compounds, and significantly increases the degree of covalency of the chemical bond. The values of the structure factors which depend to a large extent on core electrons are the same when calculated from the LDA and from HF approaches. Electron charge-density maps and structure factors associated with the 111, 200, and 222 reflections, particularly sensitive to the states of the valence electrons in the crystal, support the general feature that the chemical bond in BP, AlP, and GaP is mainly covalent, but slightly perturbed by an electron charge transfer from one atom to the other (a semi-covalent bond). The electron deformation maps are qualitatively similar to those for silicon insofar as they show a bond charge build-up elongated perpendicularly to the bond axis, but with the important difference that the deformation bonding charge is shifted towards the anion site (phosphorus in AlP and GaP). In BP where the saddle point is located at the mid-point of the bond length, the Mulliken population analysis indicates that the charge transfer goes from P towards B. The bandstructures, and especially the analysis of the DOSs projected onto the p phosphorus valence band, show that the p orbitals of B, Al, and Ga participate strongly in the population of this band. The degree of semi-covalency character of the chemical bond increases through the series (Ga, Al, BP)—that is, when the cation goes up from the third to the first row of the periodic table.

Acknowledgment

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