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Density functional study of the group II phosphide semiconductor compounds under hydrostatic pressure

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Abstract

The full-potential all-electron linearized augmented plane wave plus local orbital (FP-LAPW + lo) method, as implemented in the suite of software WIEN2k, has been used to systematically investigate the structural and electronic properties of the group II phosphide semiconductor compounds M_3P_2 (M = Be, Mg and Ca). The exchange–correlation functional was approximated as a generalized gradient functional introduced by Perdew–Burke–Ernzerhof (GGA96) and Engel–Vosko (EV-GGA). Internal parameters were optimized by relaxing the atomic positions in the force directions using the Hellman–Feynman approach. The structural parameters, bulk modules, cohesive energy, band structures and density of states have been calculated and compared to the available experimental and theoretical results. These compounds are predicted to be semiconductors with the direct band gap of about 1.60, 2.55 and 2.62 eV for Be_3P_2, Mg_3P_2 and Ca_3P_2, respectively. The effects of hydrostatic pressure on the behavior of band parameters such as band gap, valence bandwidths and anti-symmetric gap (the energy gap between two parts of the valence bands) are investigated using both GGA96 and EV-GGA. The contribution of s, p and d orbitals of different atoms to the density of states is discussed in detail.

1. Introduction

The wide band gap semiconductors are currently under intense investigation due to their unusual properties as well as their possible applications in electronic and optoelectronic devices. By alloying them, it is possible to tune the wavelength of emitted light through a wide spectral region and this could offer the opportunity to create a new family of wide band gap semiconductors. Among them nitrogen- and phosphorus-based semiconductor compounds [1–10] and their alloys [1, 11–13] have attracted considerable interest in recent years due to their applications. Alkaline earth metals (Be, Mg, Ca and Sr) are known to form semiconducting compounds with the nitrogen and phosphorus elements of the 15th group in the periodic table. These compounds are crystallized in the body centered cubic structure with the anti-bixbyite phase of the mineral (Mn, Fe)$_2$O$_3$ and space group of T_h^7 (Ia_3-206).

In the present work, our attention is focused on the structural and electronic properties of the group II phosphide semiconductor compounds M_3P_2 (M = Be, Mg and Ca). To the best of our knowledge, the experimental and theoretical reported works on M_3P_2 compounds are as follows: Carvalho *et al* [10] have been concluded that Be_3P_2 micro-crystals are formed in Be-doped phosphorus-based semiconductor compounds grown by chemical beam epitaxy at temperatures higher than 500 °C and high Be concentrations. The similar formation for the Be_3P_2 has been suggested by Panish *et al* [14]. Imai and Watanabe [9] have investigated the electronic structure of Mg_3P_2 by the first-principle pseudo-potential plane wave method. They have obtained a direct band gap of 1.73 eV for this compound. It is noticeable that there are still discussions about the stoichiometric composition of Ca_3P_2 [9], but an experimental work has been reported on the thermodynamic properties [15] of this compound.

These incomplete works and this point that the electronic structures of these compounds have not yet been fully clarified have led to further study of the physical properties of M_3P_2 semiconductor compounds at ambient conditions and hydrostatic pressure. This study can provide a basis for understanding future device concepts and applications.

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Table 1. Four internal parameters (u, x, y, z) in anti-bixbyite cubic structure of M_3P_2 (M = Be, Mg and Ca).

	u (P2)	x (M)	y (M)	z (M)
Be_3P_2	0.994	0.379	0.130	0.374
Mg_3P_2	0.977	0.386	0.146	0.380
Ca_3P_2	0.966	0.389	0.151	0.381

Section 2 gives the details of the computational method and some important parameters. Results and discussion concerning structural and electronic properties and the effect of hydrostatic pressure on the band parameters are in section 3. Concluding remarks are presented at the end of the paper.

2. Computational methodology

Density functional theory (DFT) [16, 17] calculations have been carried out using the scalar relativistic FP-LAPW + lo method, as implemented in the all-electron WIEN2k code [18]. The GGA96 [19], which is based on exchange–correlation energy optimization, is utilized to optimize the internal parameters and to calculate the total energy. The Engel–Vosko [20] generalized gradient approximation (EV-GGA), which optimizes the exchange–correlation potential, and also GGA96, are used for band structure calculations. In the FP-LAPW + lo approach the wavefunction, charge density and potential are differently expanded in two regions of the unit cell. Inside the non-overlapping spheres of radius R_{MT} around each atom, the spherical harmonic expansion is used and in the remaining space of the unit cell the plane wave basis set is chosen. The values of 2.3, 1.9 and 1.7 au for Ca, Mg and Be atoms respectively and 2.1 au for P have been chosen for the muffin-tin radii. The maximum l value for the wavefunction expansion inside the atomic spheres is confined to $l_{max} = 10$. The parameter $R_{MT}K_{max} = 7.5$, where R_{MT} is the smallest muffin-tin radius and K_{max} is the truncation for the modulus of the reciprocal lattice vector, was used for the plane wave expansion of the wave functions in the interstitial region (this corresponds to a kinetic energy cutoff of 20.77 Ryd). Reciprocal space integration in the first Brillouin zone has been performed on a grid of 216 k points. Convergence of total energies with respect to the number of k points and K_{max} has been thoroughly checked. Convergence criteria for the energy and charge difference were 0.01 mRyd and 0.0001 respectively.

The cohesive energy is defined as the total energy of isolated atoms minus the energy of the formula unit in the solid. In order to obtain an accurate value for the cohesive energy, the energy calculations for isolated atoms and crystal must be performed at the same level of accuracy. To fulfill such a requirement, the energy of an isolated atom was computed by considering a large cell (FCC structure) containing just one atom. The size of this cube was chosen sufficiently large so that the energy convergence with respect to the size of the cube was less than 0.001 Ryd. The corresponding sides were obtained as 17, 17, 19 and 21 au respectively for N, Be, Mg and Ca atoms. However, to ensure that the atomic energies are well converged, the parameter for determining the size of the basis set, $R_{MT}K_{max}$, was gradually increased until the change in the atomic energies was less than ~1 mRyd.

Table 2. Lattice parameters, bulk modulus (B), its pressure derivative (B') and cohesive energy per formula unit obtained using FP-LAPW + lo calculations within GGA96 for M_3P_2 compounds. Results of others are included for comparison.

	Lattice parameters	B (GPa)	B'	E_{coh} (Ryd per formula unit)
Be_3P_2:				
Present work	19.262	99.087	3.60	1.6941
EXP[a]	19.181			
EXP[b]	19.181			
Mg_3P_2:				
Present work	22.813	58.922	3.38	1.3634
EXP[b]	22.696			
Calc[c]	22.734			
Ca_3P_2:				
Present work	25.372	41.882	3.78	1.6113

[a] Reference [10].

[b] Reference [21].

[c] Reference [9].

3. Results and discussion

3.1. Total energy calculations

The M_3P_2 compounds, at ambient conditions, crystallize in the cubic anti-bixbyite phase of the mineral $(Mn, Fe)_2O_3$ compounds in body centered space group Ia_3 (206) with 40 atoms per primitive cell. In this structure, the metal atoms are in tetrahedral sites of a cubic close packed array of P atoms. The metal atoms are in general positions, 48e of Ia_3 (x, y, z; etc) and there are two kinds of P atoms. P1 is in position 8b (1/4, 1/4, 1/4; etc) and P2 is in position 24d (u, 0, 1/4; etc) [21].

The available experimental lattice constants are used as the starting point to perform the structural calculations. As no calculated or experimental values for internal parameters of these compounds have yet been reported in the literature, at first their rough values are selected from similar compounds such as Be_3N_2 and Mg_3N_2. These parameters have been optimized by relaxing the atomic positions in the force direction using molecular dynamic methods. Then the optimized internal parameters are used to calculate the total energy for several lattice volumes, and by fitting the results with the Murnaghan equation of state [22] the equilibrium lattice parameter for each compound has been calculated. Finally, using the new optimized lattice parameters, once again the more accurate values of internal parameters are re-calculated. The obtained results for internal parameters are reported in table 1. In table 2, the calculated equilibrium lattice constants, cohesive energy per formula unit, bulk modulus and its pressure derivative for all compounds are presented and compared with available experimental or theoretical data. Our calculated lattice parameters for the Be_3P_2 and Mg_3P_2 are in good agreement with the available experimental and theoretical values. The small overestimation of about 0.42% and 0.52% with regard to the experimental data for Be_3P_2 and Mg_3P_2 respectively confirms the exact calculations by

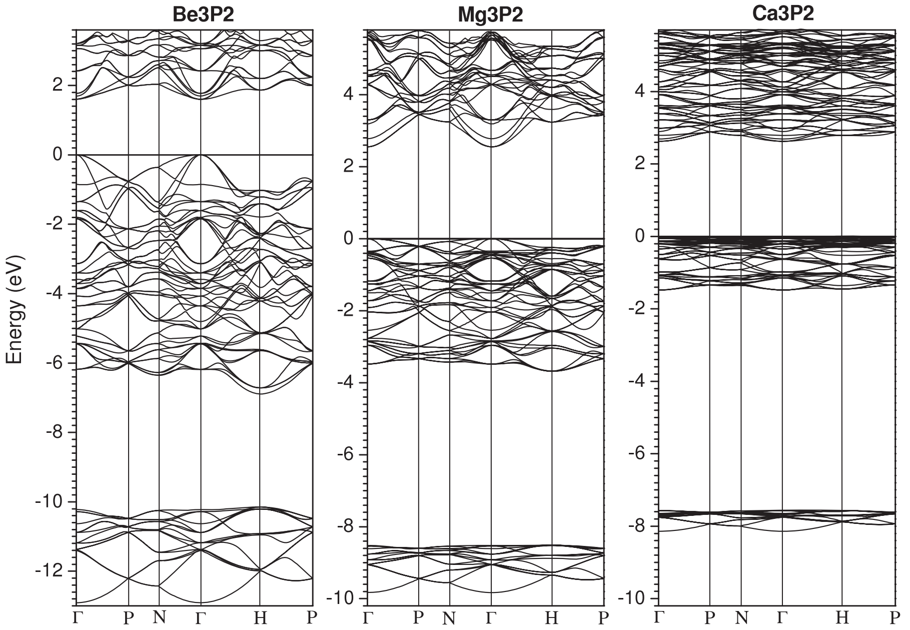

Figure 1. Band structures of M_3P_2 compounds obtained by EV-GGA at the equilibrium lattice parameter calculated by GGA96. The direct band gaps are about 1.60, 2.55 and 2.62 eV for Be_3P_2, Mg_3P_2 and Ca_3P_2, respectively, at the Γ point.

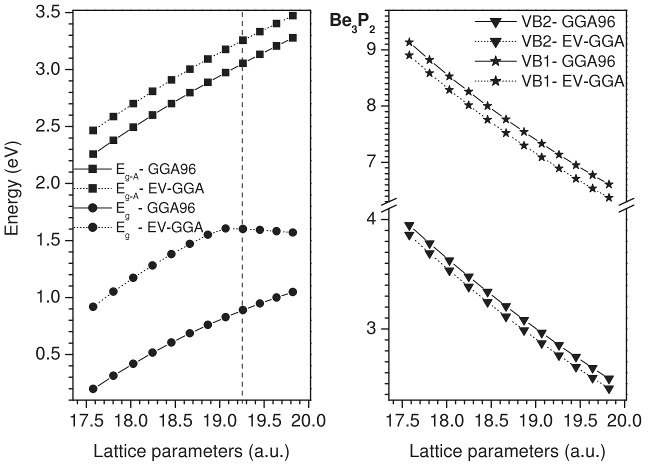

Figure 2. The behavior of the band gaps (E_g), valence bandwidths and anti-symmetric gap, E_{g-A}, for Be_3P_2 using both GGA96 and EV-GGA methods at different lattice parameters. The dashed line indicates the zero pressure point (theoretical equilibrium lattice constant).

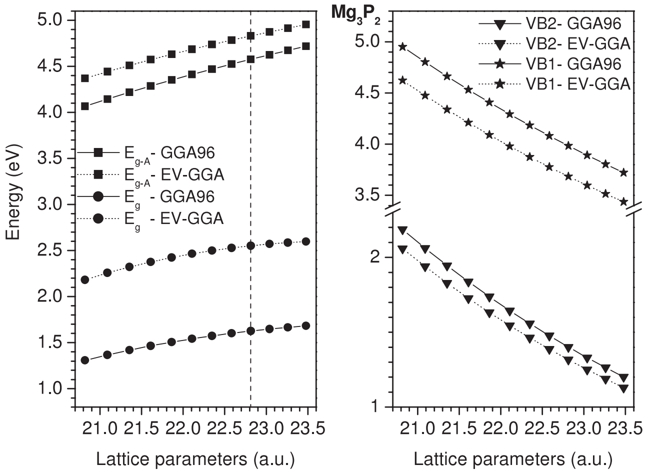

Figure 3. The variations of the band gaps (E_g) valence bandwidths and anti-symmetric gap, E_{g-A}, with respect to lattice parameters, for magnesium phosphide using both GGA96 and EV-GGA methods. The dashed line shows the zero pressure point (theoretical equilibrium lattice constant).

the FP-LAPW + lo method. To our knowledge no structural calculation has been reported for the Ca_3P_2 compound in the literature, hence our results can be considered as a prediction.

The inter-atomic distances, calculated using the optimized internal parameters and equilibrium lattice constants, are reported in table 3. It can be concluded that the smaller the average bond length the larger the bulk modulus, consistent with the semi-empirical Cohen's equation [23]. This may also be due to the fact that the electronegativities of Be, Mg and Ca are about 1.5, 1.3 and 1.0 respectively. So with growing atomic number of cations in M_3P_2 compounds the M–P bonds will be more ionic and less rigid.

Table 3. Inter-atomic distances in three phosphide compounds, M_3P_2 (M = Be, Mg and Ca).

	M–P1	M–P2
Be_3P_2	2.196	2.181, 2.195, 2.226
Mg_3P_2	2.596	2.545, 2.597, 2.645
Ca_3P_2	2.886	2.867, 2.881, 2.910

3.2. Electronic properties

In calculating the self-consistent band structure within DFT, both LDA and GGA usually underestimate the energy gap. This is mainly because they have simple forms that are not

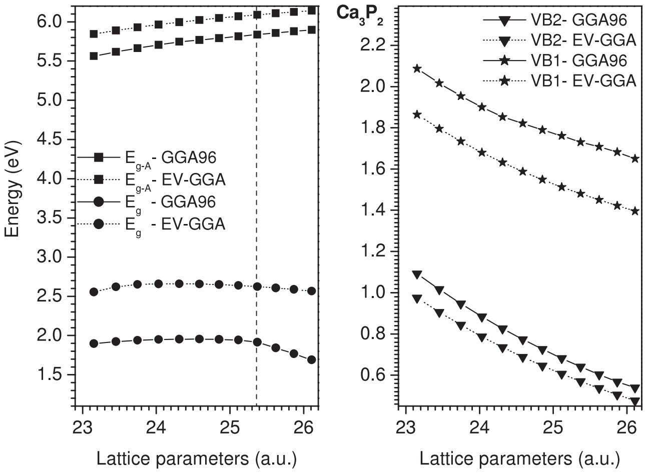

Figure 4. The behavior of the band gap (E_g) valence bandwidths and anti-symmetric gap, E_{g-A}, with respect to pressure on the unit cell, for Ca_3P_2 using both GGA96 and EV-GGA methods. The dashed line marks zero pressure (theoretical equilibrium lattice constant).

sufficiently flexible to reproduce accurately both the exchange–correlation energy and its charge derivative. Engel and Vosko [20], by considering this shortcoming, constructed a new functional form of exchange–correlation potential (EV-GGA) and were able to better reproduce the exchange potential at the expense of less agreement in exchange energy. The EV-GGA has been applied to several solids and compared with other GGA-based calculations [2, 3, 24, 25]. It has been concluded that EV-GGA usually improves the band gap and some other properties that mainly depend on the accuracy of the exchange–correlation potential, while for calculating the properties that are based on total energy calculations, such as equilibrium lattice parameter and bulk modulus, GGA96 is more appropriate. Hence, in the present work, first the equilibrium lattice constant and internal parameters are calculated by GGA96, and subsequently the results are applied to calculate the band structure of M_3P_2 compounds along high symmetry directions by EV-GGA and GGA96. The obtained band structures of M_3N_2 compounds at the theoretical equilibrium lattice constant are presented in figure 1.

The valence bands for all cases are separated into two sub-bands that are labeled starting from the top as VB1 and VB2. The widths of these sub-bands are progressively decreased and the anti-symmetric gap (E_{g-A}: the energy gap between two parts of the valence bands) between them is increased from Be_3P_2 to Ca_3P_2 compounds. The Γ–Γ band gap, E_g, values are obtained as 0.889 and 1.60 for Be_3P_2, 1.63 and 2.55 for Mg_3P_2 and 1.91 and 2.62 for Ca_3P_2 using GGA96 and EV-GGA respectively at the theoretical equilibrium lattice constant.

To study the response of the band structure with respect to the hydrostatic pressure, the electronic calculations are performed at different lattice parameters using both EV-GGA and GGA96. The corresponding pressures are changed from

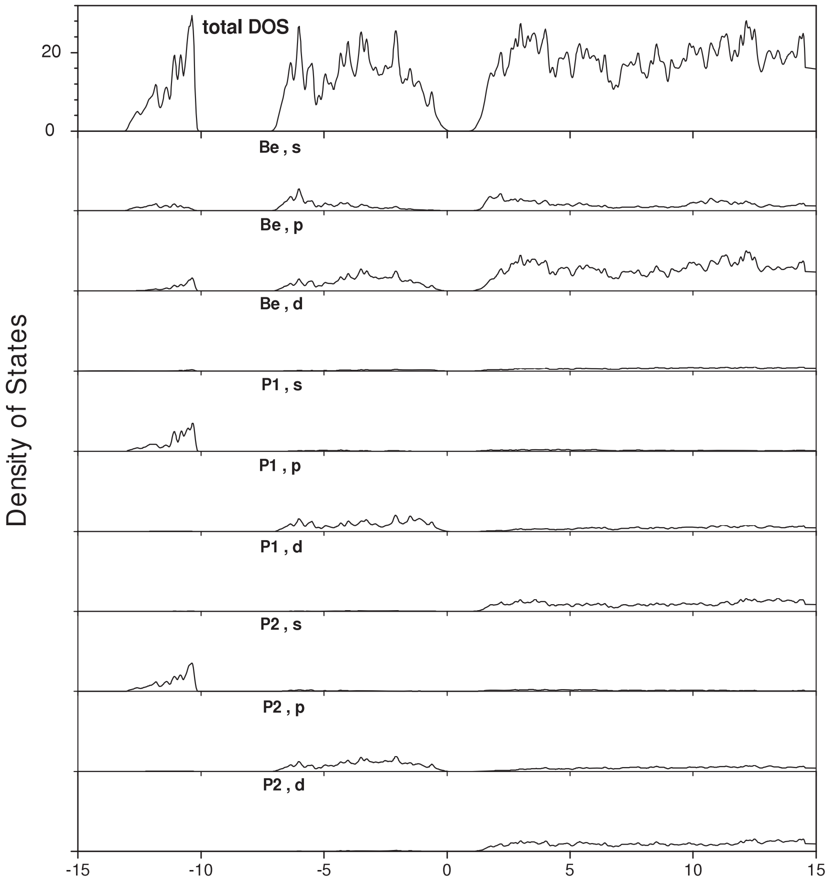

Figure 5. Total and partial density of states for s, p and d orbitals of Be_3P_2 compound using GGA96 at equilibrium lattice constant.

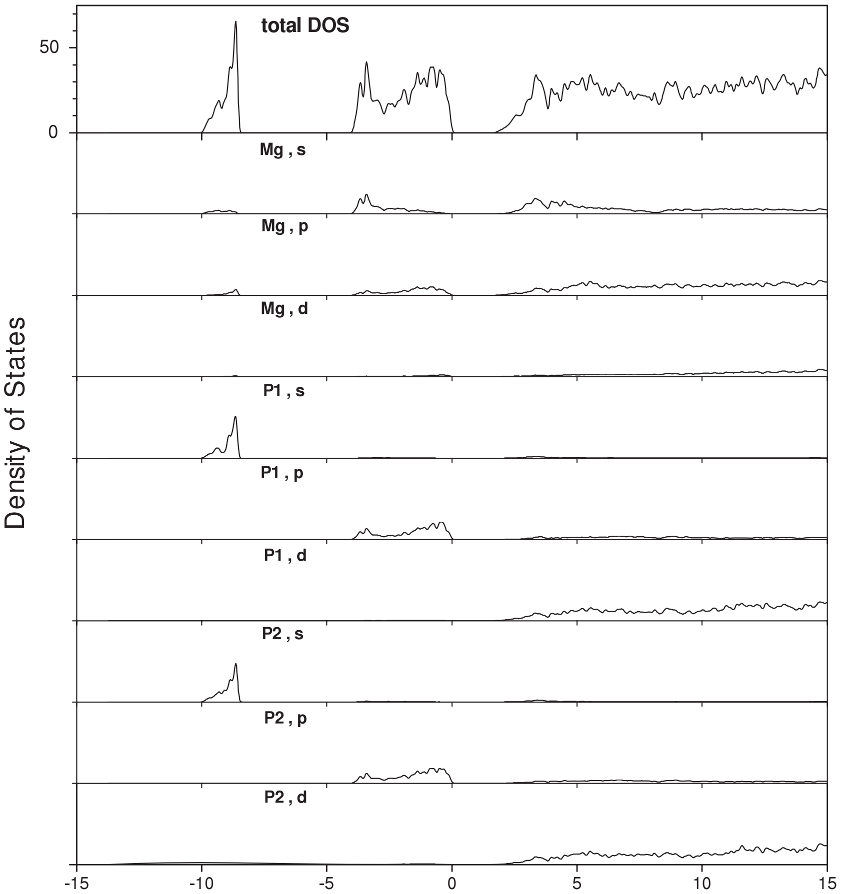

Figure 6. Total and partial density of states for s, p and d orbitals of magnesium phosphide using GGA96 at zero pressure.

-7.34 up to $+46.39, -4.41$ up to $+26.63$ and -3.08 up to $+20.19$ GPa for Be_3P_2, Mg_3P_2 and Ca_3P_2 respectively. The effects of hydrostatic pressure on the band gap, valence bandwidths and anti-symmetric gap using both GGA96 and EV-GGA are shown in figures 2–4. It is clearly seen for all cases that by applying positive pressure on the system the band gaps remain along Γ–Γ but the values for both GGA96 and EV-GGA monotonically decrease. Similar behavior is observed for the anti-symmetric gaps. This means that by reducing the lattice parameter the system is closer to the metal–insulator transition.

Although GGA96 and EV-GGA predict different values for the band gap, the behaviors of the gaps with respect to positive pressure are rather similar using these two approximations. It is evident from figures 2–4 that the monotonic slope of the E_g curves is decreased from Be_3P_2 to Ca_3P_2 at positive pressures. This behavior is consistent with the bulk modulus values of these compounds. At negative pressure the trend is different for GGA96 and EV-GGA. This may be due to the fact that the EV-GGA approach overestimates the lattice parameters and underestimates the bulk modulus with respect to the GGA96 [2]. By reducing the lattice parameter, the valence bandwidths are increased in all compounds. This behavior is rooted in the fact that the smaller the average bond length the greater the hybridization between different orbitals.

To further study the electronic structure of these compounds, the total (whole cell contribution) and angular momentum decomposed (partial) densities of states (DOSs) are computed at the equilibrium lattice constant by the tetrahedral method [26] using GGA96. The corresponding results are plotted in figures 5–7. The fundamental points to note from the DOS calculations are as follows.

Finally, the overall total DOSs for all cases are very similar to each other; the valence bands are split in two groups, a narrow sub-band located deep in the lower energy range and a wider one near the Fermi level. The s orbitals of the P atoms have the major contribution to the lower valence sub-band with a width that decreases by growing the atomic number of M. This means that, from Be_3P_2 to Ca_3P_2, the electrons located in this group are more localized and have less influence on the conduction bands. The upper valence sub-band for all compounds is mainly dominated by the phosphorus 3p states and with less contribution from the s and p orbitals of M atoms. It is evident from DOS plots that the p orbitals of P atoms hybridize with the s and p states of M atoms in VB1, while the s orbitals of P atoms have insignificant overlap with other orbitals.

4. Conclusion

The FP-LAPW + lo method has been used to systematically study the zero temperature structural and electronic properties

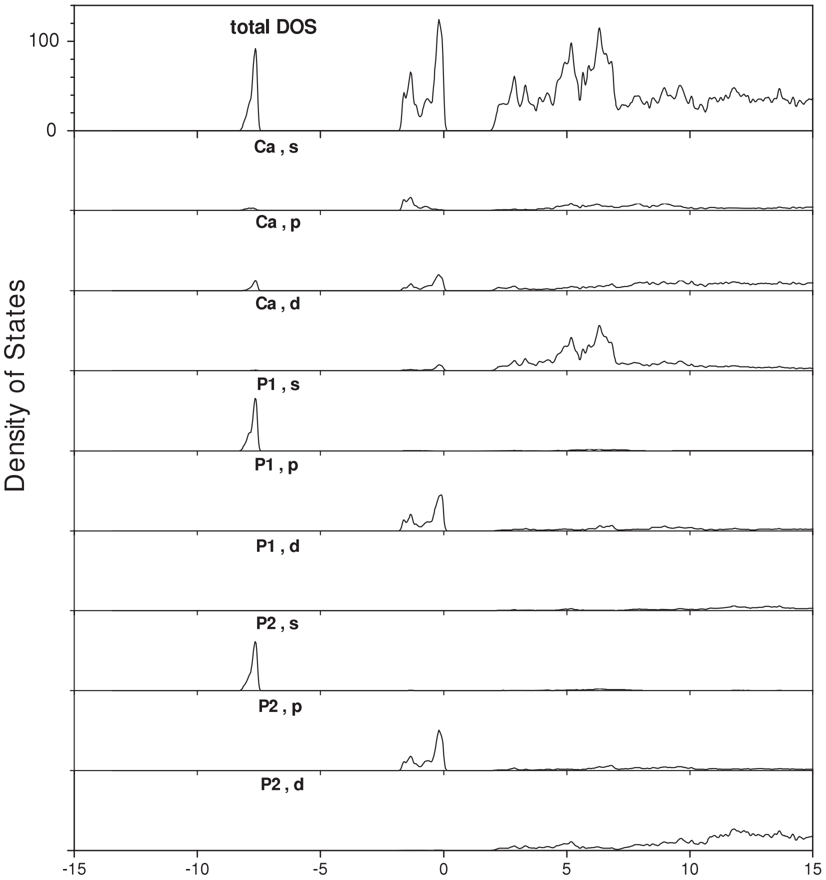

Figure 7. Total and angular momentum decomposed density of states for s, p and d orbitals of Ca_3P_2 compound using GGA96 at ambient conditions.

of M_3P_2 (M = Be, Mg and Ca) semiconductor compounds. To our knowledge no perfect data in the electronic and structural properties of M_3P_2 compounds have been reported so far, hence our results can serve as a prediction for future study. The obtained lattice parameters are in good agreement with the known experimental data. The direct band gap values at zero pressure are predicted as 1.60, 2.55 and 2.62 eV for Be_3P_2, Mg_3P_2 and Ca_3P_2 respectively. The overlapping of phosphorus p orbitals with the s and p states of M atoms in the lower valence bands is remarkable but the s orbitals of P atoms have insignificant hybridization with other orbitals.

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