Ab initio electronic structure of superionic conductor Li$_3$P

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Lithium phosphide (Li$_3$P) has recently been introduced as a good lithium ion conductor. Results of ab initio Hartree–Fock calculations for the electronic structure and the optimized lattice parameters for the hexagonal P6/mmm space group are reported. The total energy, band structure, density of states and charge densities are obtained. The results demonstrate how the band structure of the insulator Li$_3$P can be derived from the band structure of its metallic constituent Li$_2$P and Li monolayers. The metal-insulator transition occurs if the inter-plane distance falls below 4.24 Å.

Most of experimental [1,2] and theoretical [3–6] efforts in lithium ion conductors for applications in solid-state lithium batteries have been focussed on lithium nitride (Li$_3$N). Recently, lithium phosphide (Li$_3$P) has been shown as a good lithium ion conductor, stable up to 2.2 V. In this paper we report the first ab initio Hartree–Fock calculation for Li$_3$P obtaining the lattice parameters, cohesive energy, band structure and density of states.

The crystal structure of Li$_3$P belongs to the hexagonal P6/mmm space group and is shown in fig. 1. In this figure, Li$_2$P layers alternate with pure Li lay-

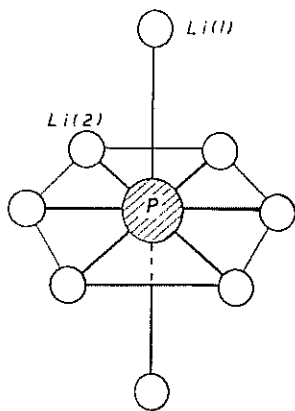Fig. 1. Hexagonal P6/mmm structure of Li$_3$P. The in-plane Li(2)–P distance is $a/\sqrt{3}$, the perpendicular Li(1)–P distance is $c/2$.

ers along the c direction. The Li atoms in the pure Li and Li$_2$P layers are hereafter referred to as Li(1) and Li(2) atoms respectively. The in-plane Li(2)–P distance is $a/\sqrt{3}$ and the perpendicular Li(1)–P distance is $c/2$.

The all-electron linear combination of atomic orbitals Hartree–Fock calculations are performed employing the CRYSTAL 88 program [7]. A recent monograph describes the details of the program and its application to wide variety of metallic and nonmetallic systems [8]. A series of calculations was performed to obtain a basis set of a total of 22 contracted Gaussian atomic orbitals for P representing 5s, 4p and 2d functions. These functions represent a triple zeta valence basis with a set of polarization functions. For Li, a core-like atomic orbital is supplemented by an outer sp shell and an additional s function giving a total of 3s and 1p functions. More details can be found elsewhere [9]. We note here that our use of extended and highly polarizable basis sets in the calculations reduces the risk of predetermining the character of the solution, e.g., the amount of charge-transfer from lithium to the anion and, consequently, the ionic or partially covalent character of Li–P bonds.

The only experimental study [10] on the preparation and characterization of Li$_3$P reports the lattice parameters, $c = 7.59$ Å and $a = 4.271$ Å. In this configuration, a total energy per unit cell of -363.0339 hartree is obtained. However, very dif-

ferent results are obtained when we relax the configuration to minimize the total energy with respect to the lattice parameters a and c. The calculated lattice parameters, $a=4.45$ Å and $c=4.80$ Å, in this relaxed configuration are significantly different than the ones obtained from the diffraction study. The minimum total energy is now found to be -363.1470 hartree. The c/a ratio is 1.08 as compared to the re-
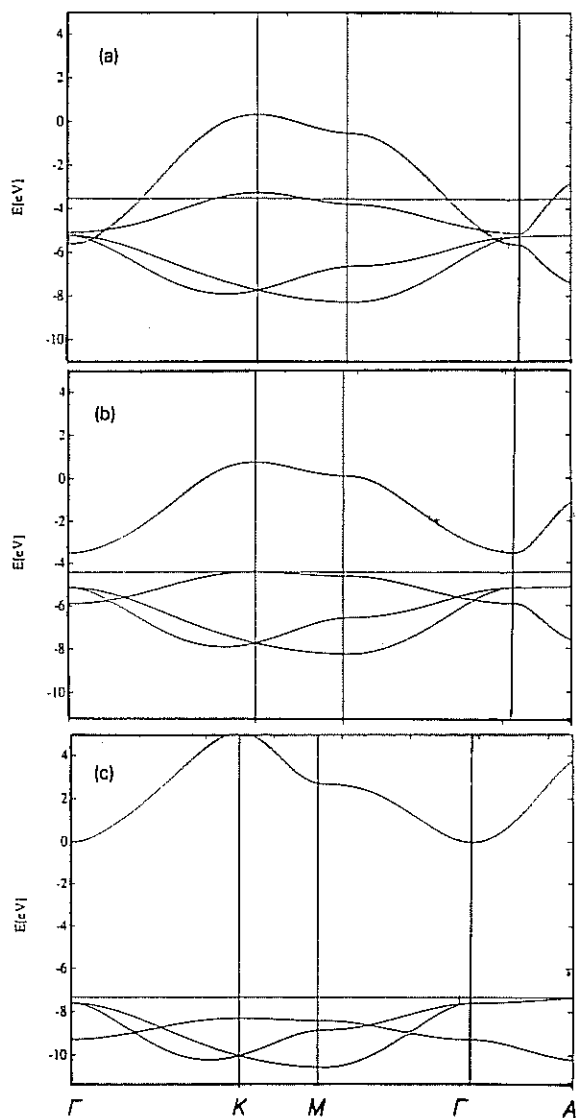
Table 1

Total energy, lattice parameter, band gap, charge distribution and the lowest non-zero multipole moments of Li_3P. The corresponding values for Li_3N are taken from refs. [4] and [9].

	Li_3P	Li_3N [a]
Lattice parameter, a	4.45 Å	3.65 Å
c	4.80 Å	3.87 Å
c/a	1.08 Å	1.06 Å
Total energy/unit cell	-363.1470 [b]	-76.8924 [b]
HF cohesive energy	6.65 eV	5.30 eV
HF band gap	7.25 eV	7.80 eV
Correlated band gap [a]	1.4 eV	1.8 eV
Charge – P	16.67 N	10.10
Li(1)	2.10	2.00
Li(2)	2.11	1.95
Dipole moment – P	0.87	0.29
Li(1)	0.13	-0.38
Li(2)	-0.11	-0.33
Quadrupole moment – P	-63.19	-36.50
Li(1)	-1.82	-2.08
Li(2)	-0.36	0.53
(Li) 1s core-level split	0.10 eV	0.35 eV

[a] For Li_3N, both calculated and experimental lattice parameters are about the same (ref. [4]).

[b] In hartrees.

ported one of 1.777. We note here that an excellent agreement [4] between the calculated and experimental values of the lattice parameters for Li_3N indicates the reliability of the method in predicting geometries. Since Li_3P also exists in the monoclinic phase, we suspect that this discrepancy is due to polycrystalline samples containing the polyphases of Li_3P.

In the equilibrium configuration, the HF cohesive energy is 6.65 eV and the minimum (indirect) energy gap between Γ and A points (fig. 2c) is found to be 7.25 eV, 0.6 eV smaller than the gap calculated for Li_3N. The three overlapping uppermost valence bands are essentially associated with the 3p state of phosphorus. The phosphorus 3s band has almost no dispersion and lies about 9 eV below the 3p bands. The lowest conduction band has mainly lithium 2s character. If one estimates correlation contribution in the same way [4,11] as for Li_3N, the cohesive energy becomes 12.5 eV. Comparison of the band structure, charge distribution and lowest non-zero multipole moments in table 1 shows that both electronic and ionic structures of Li_3P in this configuration are similar to the one obtained for Li_3N.

Fig. 2. Band structure of Li_3P for (a) $c=9.0$ Å, $a=4.271$ Å; (b) $c=8.09$ Å, $a=4.271$ Å, and (c) for the equilibrium values $c=4.80$ Å, $a=4.45$ Å.

To gain additional insight into the binding and electronic structure of Li$_3$P, we now consider its stability and band structure relative to the separated Li$_2$P and Li monolayer constituents. At infinite separation, Li$_2$P (with a partially filled P-3p$_z$ band) and Li (with a partially filled Li-2s band) form metallic layers as shown in fig. 3. The Fermi energy of Li$_2$P is at -3.5 eV and that of Li is at -1.8 eV. As we bring these metallic layers close together, we find that it is now energetically favorable to transfer some of the Li charge (from the Li layer) to P (in the Li$_2$P layer) by occupying the P-3p$_z$ band. At $c = 9.0$ Å, (fig. 2a) the system is still metallic, with the Li-2s and P-3p$_z$ bands barely overlapping. For $c = 8.1$ Å, (fig. 2b) the Li-2s band is completely pushed above the Fermi energy and a band gap opens. Here most of the valence electron of Li is transferred to the P atom. At the equilibrium configuration, the system
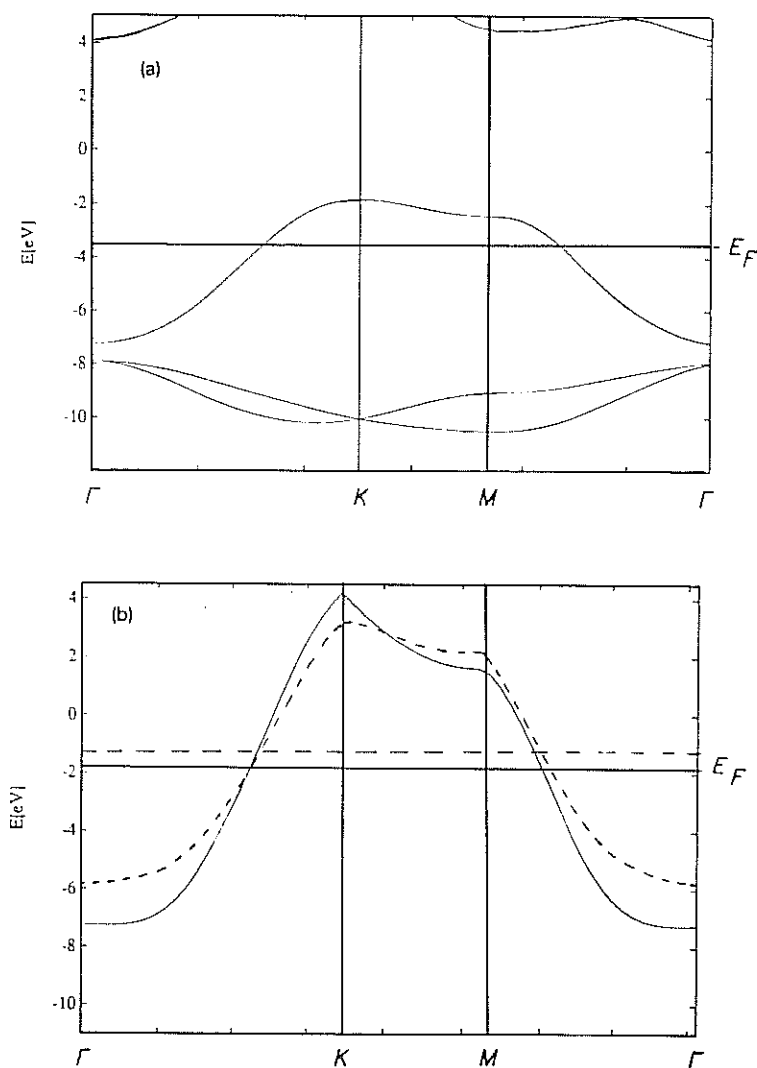

Fig. 3. (a) Band structure of a hexagonal Li$_2$P monolayer for the equilibrium lattice constant $a = 4.389$ Å; (b) band structure of a hexagonal Li monolayer for the equilibrium lattice constant $a = 3.194$ Å. The dashed line shows the band structure if a is expanded to 4.271 Å.

is largely ionic in character, with a significant gain in energy of 4.17 eV/cell representing almost two-thirds of the total (Li$_3$P) energy/cell of 6.65 eV. The main contribution to the cohesive energy of Li$_3$P is therefore predicted to be due to the interaction between its constituent layers.

A similar study has been performed for lithium arsenide (Li$_3$As). The same discrepancy between the proposed experimental and theoretical geometry was discovered. The energy minimum for Li$_3$As is found for the same $c/a = 1.08$ ratio as obtained for Li$_3$P, with $a = 4.60$ Å and $c = 4.96$ Å.

In summary, ab initio electronic structure calculations obtain markedly different lattice parameters and less anisotropic electronic structure for Li$_3$P and Li$_3$As than reported from the diffraction study. The band structure for Li$_3$P is almost identical to the one calculated for Li$_3$N and its evolution can be understood in terms of the interaction between the constituent layers which are metallic at infinite separation.

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