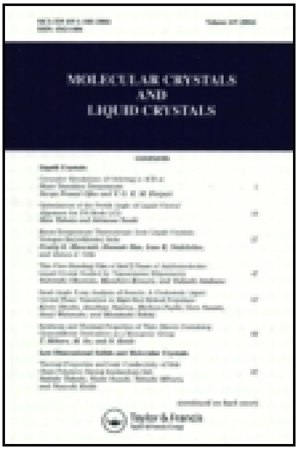

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Intercalation Compounds of Graphyne

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Intercalation Compounds of Graphyne

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We report the band structures of first stage potassium intercalated graphyne using the optimized geometries. The calculation was carried out using the full-potential linear-combination-of-atomic-orbitals method. The optimized distance between two graphyne layers sandwiching the intercalate layer is shorter than typical graphite intercalation compounds. These intercalation compounds are metallic. The character of the band around the Fermi level at Γ point is $C2p_z$. The band with the character of K4*s* lies about 2.4 eV higher than the Fermi level at Γ point for the compound intercalating one potassium in a unit cell, while that lies about 0.89 eV higher than the Fermi level at Γ point for intercalating two potassium in a unit cell. Further we refer the amount of charge transfer between potassium and carbon atoms.

Keywords: graphyne; carbon allotrope; intercalation compound; band calculation

INTRODUCTION

Graphyne was proposed as one of the carbon allotropes which has high possibility of synthesis[1]. Graphyne was named in connection with graphite and acetylenic composition, that is, this is composed of planar layers cotaining both hexagonal rings and acetylenic linkages. Then graphyne consists of layers containing *sp* and sp^2 carbons. The planar structure is shown in Fig.1. Graphyne is predicted to have a low formation energy and high thermal stability, though its formation energy is higher than for graphite. Graphyne is also predicted to be a semiconductor while it will have similar mechanical properties as graphite. Further nonlinear optical properties characteristic to conjugated polymers are

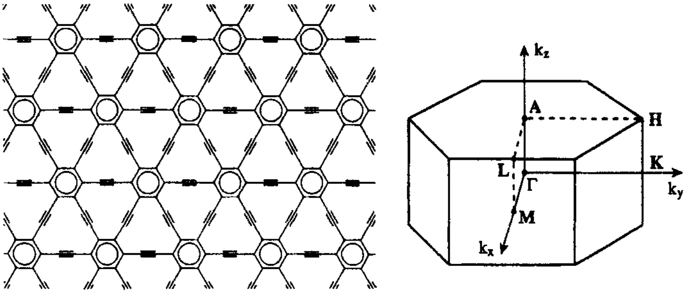

FIGURE 1 Planar structure for graphyne. The Brillouin zone is shown with high symmetry points for a hexagonal structure.

expected. It is very interesting and promising for the formation of intercalation compounds since graphyne is a layered compound.

We have already calculated and reported the optimized geometry and the electronic structure for two-dimensional graphyne[2]. The optimized lattice length is 6.86 Å, and the binding energy is 7.95 eV/atom. We have also found graphyne is a semiconductor with the band gap 0.55 eV at M point. We have obtained preliminary results of the optimized geometries and the electronic structures for three dimensional graphyne. The band structure of three dimensional graphyne is metallic or semiconducting. It depend on how to put one layer upon another layer. We are now calculating precisely the three-dimensional graphyne. In this paper we report the electronic structures of potassium intercalation into graphyne. We dealt with three cases for possible occupation sites of potassium.

As a result the interplanar spacing of adjacent carbon layers in the stage-1 intercalated graphyne is considerably shorter than stage-1 graphite. Although we expected the possibility of intrasheet compounds for potassium intercalation, potassium atoms set in the graphyne layer are not stable in energetics. It turned out that potassium atoms come to stay at the middle between graphyne layers. These potassium-graphyne intercalation compounds are metallic. The electronic structures are also shown.

CALCULATION METHOD

The calculation was carried out by the first principles full-potential linear-combination-of-atomic-orbitals method[3]. We used the local-spin-density approximation based on the density-functional theory[4], and for the exchange-correlation potential we used Ceperley and Alder results[5]. In calculation of getting the optimized potential we chose to use 13 k points in the Brillouin zone by the good-lattice-point method. We examined the results for several cases by use of 89 k points, which were generated in the same method. There was little amount of difference in both results.

RESULTS AND DISCUSSION

The graphyne and intercalate layers are arranged in an A α A stacking sequence, where A refers to the graphyne layers and α to the intercalate layer. We dealt with the following cases as shown in Fig. 2. We denote the in-plane distance between the centers of adjacent hexagons by a. The K-K in-plane distances are a, $a/\sqrt{3}$, and a for (a), (b), and (c), respectively.

(a) $C_{12}K$: Potassium atoms are placed in every other position above the center of a 12 carbon ring in the middle of adjacent carbon layers, that is, one potassium atom is intercalated into a unit cell.

(b) C_6K: Potassium atoms are placed in every position above the center of a 12 carbon ring in the middle of adjacent carbon layers, that is, two potassium atoms are intercalated into a unit cell.

(c) $C_{12}K$: Potassium atoms are placed in every position above the center of a

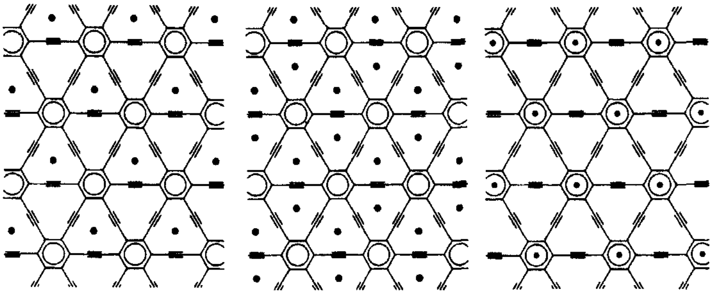
(a) (b) (c)

FIGURE 2 In-plane structures of potassium intercalated graphyne. Black dots represent potassium atoms.

carbon hexagon in the middle of adjacent carbon layers, that is, one potassium atom is intercalated into a unit cell.

First we performed the optimization of geometry by maximizing the binding energy. Furthermore we calculated the heat of formation of three compounds relative to undoped graphyne and solid potassium. The optimized lattice lengths *a* (= the in-plane distance between the centers of adjacent hexagons), *c*, and the heats of formation are given in Table I. The heat of formation for a typical graphite intercalation compound C_8K (graphite - K)[6] are also given for comparison.

The lattice length *a* is just about the same length of three dimensional graphyne (= 6.86 Å). The lattice length *c*, that is, the distance between two graphyne layers sandwiching the intercalate layer is remarkably shorter than those of typical graphite intercalation compounds. For the purpose of examining our calculation we applied our method to graphite and graphite intercalation compounds. As a result the lattice length parallel to the layers does not differ from experimental value. But the lattice length perpendicular to the layers is about six percent shorter than the experimental value. Therefore, it would be reasonable that each lattice length *c* which is given in Table I should be put six percent correction. The length between adjacent layers is very short after correction.

TABLE I Optimized lattice lengths *a*, *c*, and the heats of formation.

	a (Å)	*c* (Å)	heat of formation (cal/mol)
(a) $C_{12}K$	6.90	4.45	5.01×10^4
(b) C_6K	6.90	4.30	8.52×10^4
(c) $C_{12}K$	6.90	4.83	1.69×10^4
C_8K (graphite - K)[6]			2.85×10^4

As seen in TABLE I the heats of formation of the compounds (a) and (b) are higher than that of C_8K (graphite - K). Therefore the compounds (a) and (b) are considered stable, while the compound (c) is considerably less stable comparing with C_8K (graphite - K). Thus, graphyne is very promising as an intercalation compound. We expected intrasheet compounds (c=0) for potassium atom intercalation. But such a phase that potassium atoms set in the graphyne layer is found unstable in energetics.

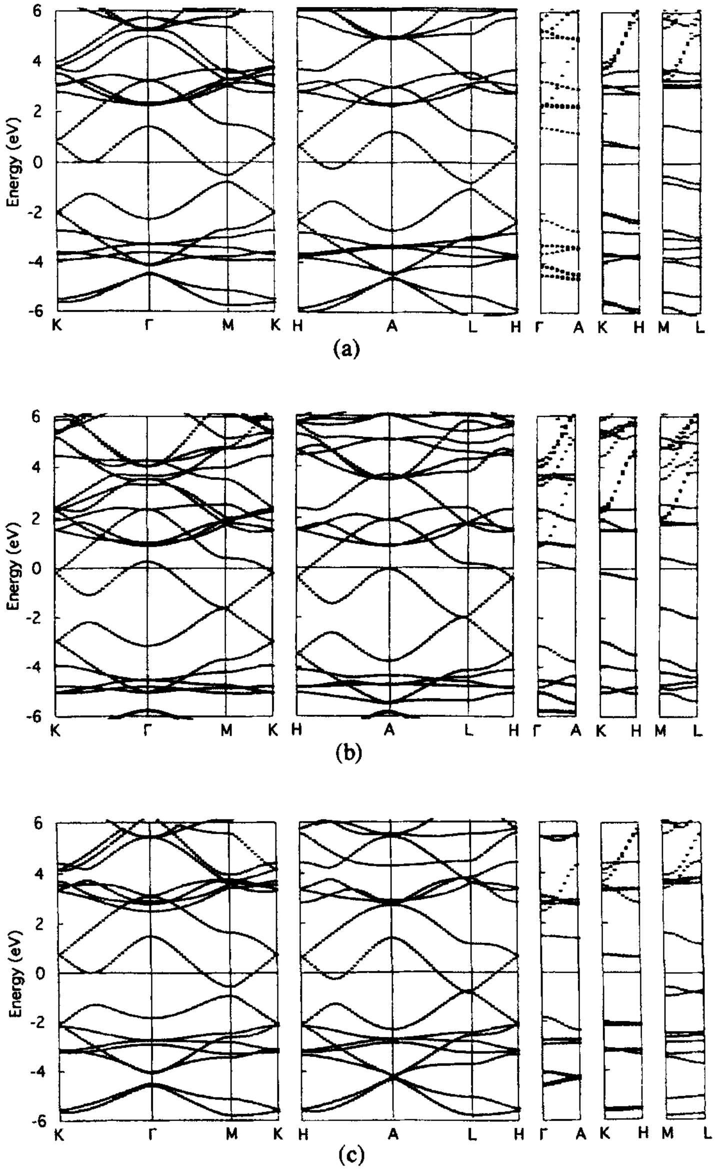

FIGURE 3 Electronic structures of potassium intercalated graphyne.

TABLE II The difference which was subtracted the charge of a neutral atom from the optimized charge of its atom.

	A type carbon (1/atom)	B type carbon (1/atom)	Intercalant potassium (1/atom)
(a) $C_{12}K$	+0.02	-0.09	+0.45
(b) C_6K	+0.03	-0.19	+0.53
(c) $C_{12}K$	-0.23	+0.14	+0.51

Next we show the electronic structures of potassium intercalated graphyne in Fig. 3. The intercalation compounds are metallic. The character of the band around the Fermi level at Γ point is C2p_z, and the bands with the character of K4*s* lie about 2.2 eV, 0.89 eV and 2.5 ev higher than the Fermi level at Γ point for the cases of (a), (b) and (c), respectively.

Now we present the estimation of the amount of the charge transfer between intercalant and graphyne layer. Carbon atoms are classified into two types by the situation. We call each of six carbons which compose a hexagonal bond the A type carbon, and each of six carbons which compose an acetylenic bond the B type carbon. We give the difference which was subtracted the charge of a neutral atom from the optimized charge of its atom in Table II. Positive sign represents that the atom is positive ion. In the case of (a) and (b) A type carbons are slightly ionized with positive charge, and B type carbons are given electrons from intercalant potassium. The charge transfer of the case of (c) is different from that of the cases of (a) and (b) in the sign of the charge. This is because that A type carbon is situated almost middle between the intercalant potassium and B type carbon as seen in Fig. 1.

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