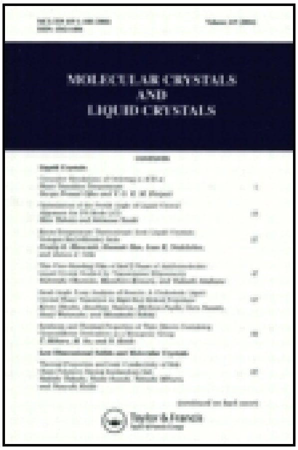

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First-Principles Studies on Pd Intercalated Graphite

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Based on first-principles calculations, structure optimization of Pd intercalated graphite is performed and the equilibrium values for lattice constants are obtained, in agreement with experimental values. In graphite the carbon atoms within the basal plane are bound together by strong covalent σ-bonds, while atoms in adjacent layers are weakly bound by Van der Waals bonds, results in semimetal. Being intercalated with Pd, due to Pd-4d and C-2p hybridizations, partial charge transfers occur from Pd to C, which increase the density of states at Fermi level and make the compound metallic-like; the heat of formation is found to be 2.45eV for per Pd atom intercalation.

Keywords: graphite intercalation compound; first-principles

INTRODUCTION

It is well known that carbon has very flexible bonding features: sp^3 hybrid orbitals form strong σ bonding, while sp^2, sp^1 hybridizations form σ and π bondings. Therefore, carbon can exhibit very rich structures: diamond, graphite, fullerenes, carbon nanotubes, amorphous carbon, porous carbon and graphite intercalation compounds (GIC). These carbon-based materials can display various unique properties: from insulator to superconductor. In hexagonal graphite, the c/a axial ratio is 2.726 which gives rise to highly anisotropic electronic properties, and it is easy to intercalate foreign atoms to form intercalation compounds, which have many interesting properties[1] and many possible technological applications[2]. Usually alkali metal atoms or alkaline earth-metal atoms or molecules (e.g.Li, K, Rb, Cs, Ba, $AlCl_3$) are intercalated into the graphite. However, with the advent of flexible and precise experimental techniques, other atoms can also be intercalated into graphite. Recently, Pd atoms are intercalated by one of the authors[3], the high-resolution electron microscopy revealed that the structure has C-Pd1-C-Pd2-C...stacking, Pd atoms reside above the center of hexagonal carbon bonding, carbon atoms show the stacking sequence AAAA... There are 16 carbon atoms and 2 Pd atoms in the unit cell with lattice constant a=4.92Å and c=7.8Å. The purpose of this paper is to study this new graphite intercalation compound by using first-principles theory. The main problems we concern about are following: (1) the stability of structure; (2) how much energy is needed to intercalate Pd atom ? (3) how much charge is transferred between Pd and graphite? and (4) how the electronic structure is changed with Pd intercalation?

THEORETICAL METHOD

Ab initio methods based on density-functional theory (DFT) are well established tools to study structures and properties of materials. Especially the plane-wave basis and pseudopotential method combined with DFT has provided a simple framework whose accuracy and predictive power have been convincingly demonstrated in large variety of systems, because this method has following advantages: (1) the treatment of nonspherical charge densities and potentials is straightforward (no shape approximations); (2) the calculation of Hellmann-Feynman forces is greatly simplified so that extensive geometry optimization is possible; and (3) the basis is spatially unbiased with no preference for a particular arrangement of atoms. However, in the Pd intercalated graphite, Pd has 4d electrons, carbon has the tightly bound 2p valence wave functions, which are sharply peaked due to the lack of corresponding core states for cancellation. As a result, in the conventional norm-conserving pseudopotential scheme, a relatively hard pseudopotential has to be generated and a relatively large number of plane-wave basis functions are required in calculations. Therefore, in our calculations, we used more powerful *ab initio* ultrasoft pseudopotential scheme with plane-wave basis (Vienna *Ab initio* Simulation Program (VASP)) [4-5], in which the finite-temperature local-density functional theory developed by Mermin[6] is used, and variational quantity is the electronic free energy. Finite-temperature leads to broadening of the one-electron levels that is very helpful to improve the convergence of Brillouin-zone integrations. The electron-ion interaction is described by a fully nonlocal optimized ultrasoft pseudopotentials[7,8], which has been extensively tested for transition metals[9] as well as the first-row elements[8]. The minimization of the free energy over the degrees of freedom of electron densities is performed using the conjugate-gradient iterative minimization technique[10]. 300 eV has been used as cut-off energy in the plane-wave expansion of the pseudo-wavefunctions, which is large enough to obtain a good convergence, and the exchange-correlation energy of valence electrons is adopted the form of Ceperly and Alder [11] as parameterized by Perdew and Zunger [12]. The Brillouin zone (BZ) integrations are done by Monkhost-Pack special irreducible k-points(IRKP) method[13], in which 150 IRKP's are used.

The energy convergence criterion is 0.0001eV.

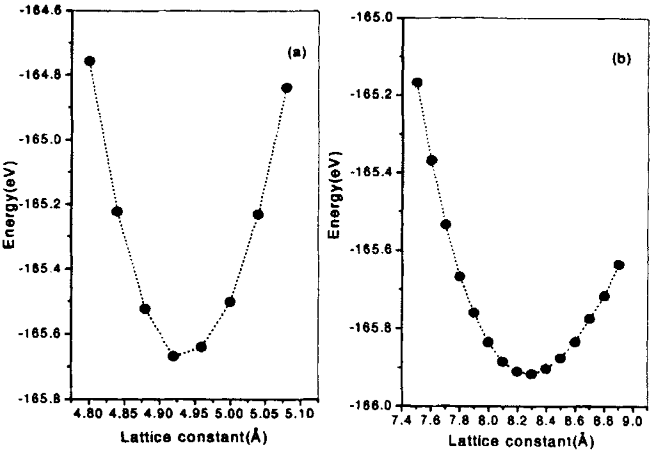
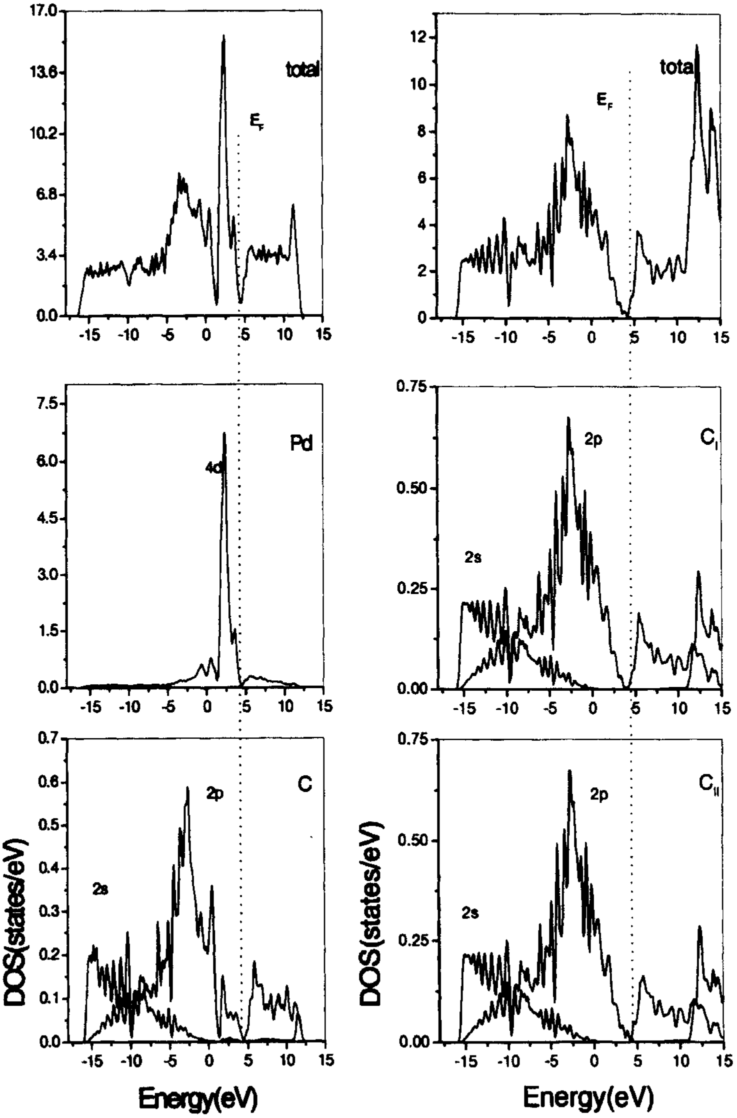


FIGURE 1 Binding energy vs lattice constant a (a) and c (b).

RESULTS AND DISCUSSIONS

According to the experimental information, we find that the space group of Pd intercalated graphite is P2/a differing from that of P63/mmc for pure graphite. To optimize the lattice constants, the total energy as a function of the volume is calculated. We first set c to the experimental value, the lattice constant a is obtained by energy minimization, then fix a and optimize c. Figure 1 shows the results: a=4.924Å and c=8.3Å, in agreement with the experimental values (a=4.92 Å and c=7.8Å). The total binding energy for the unit cell with the optimized lattice constants is -165.917eV. In order to get the heat of formation, we calculated the binding energies per atom for pure graphite and pure bulk Pd with the experimental lattice constants (for Pd, a=3.89Å; for graphite, a=2.46Å, c=6.70Å): E_C=-10.051eV, E_{Pd}=-5.00eV. Therefore the heat of formation can be obtained: $\delta E = E(Pd_2C_{16}) - 16E_C - 2E_{Pd}$, which gives 4.90eV, suggesting that at least 2.45eV energies are needed to intercalate one Pd atom into the graphite. Figure 2(a) shows the density of states (DOS), and for comparison the DOS for pure graphite are also given in figure 2(b). In the latter case, the DOS at the Fermi energy is nearly zero, displaying the features of semimetal; However, in the former one, the DOS at the Fermi energy is 0.75 states/eV, exhibiting the features of metal. This can be further confirmed by the band structure, as shown in figure 3, where the dotted line stands for Fermi energy E_F, there are somebands across the Fermi level, which do not appear in the pure graphite. The



(a) (b)

FIGURE 2 Density of states for Pd intercalated graphite (a) and pure graphites (b).

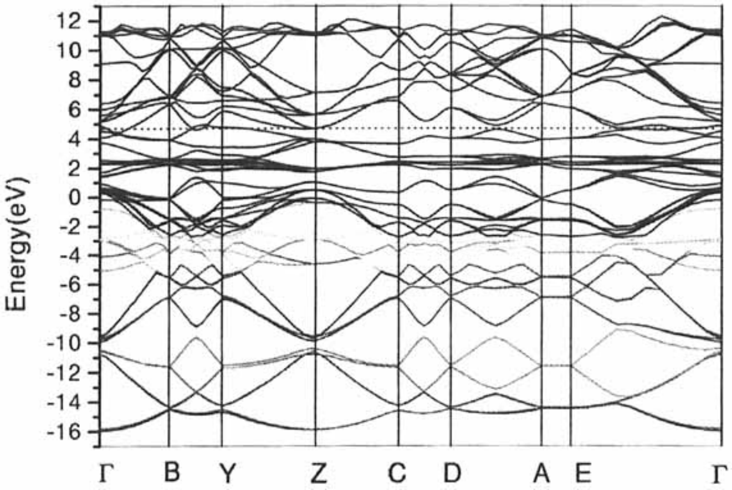


FIGURE 3 Band structure for Pd intercalated graphite.

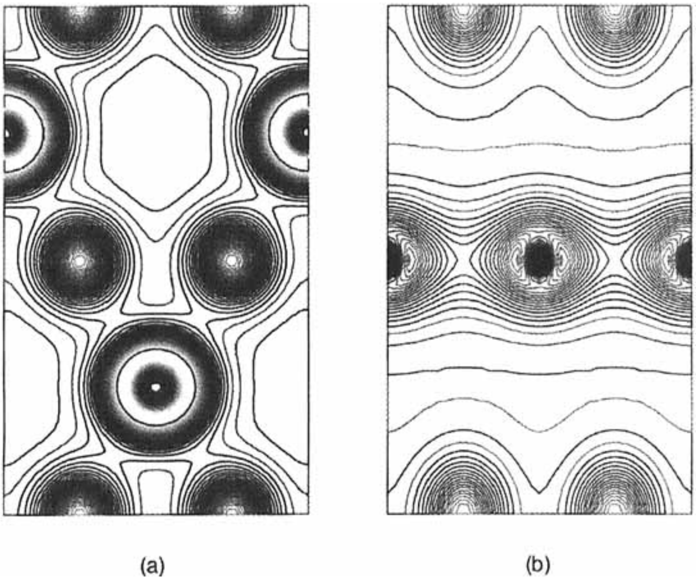


FIGURE 4 Charge density distributions for intercalated graphite (a) and pure graphite (b).

main interaction between Pd and C is the hybridizations of Pd-4d orbitals with C-2p orbitals.

According to Pauling electronegetivity (EN) [14], the EN for Pd and C are 2.20 and 2.55, so the charge transfers from Pd to C should be existed. By using geometrical partitioning of charge (i.e. Wigner-Seits cell partitioning), we found that there are 0.165 electrons per Pd atom are transferred to C. We know that in the graphite intercalation compounds with Li there are complete charge transfers of 2s electrons of Li to graphite, while as in our case only partial charge transfers occur. This is due to the fact that the 4d electrons are much localized than the 2s electrons in Li. Figure 4(a) and 4(b) show the charge density distributions in Pd intercalated graphite and in pure graphite, respectively. The difference in charge density distributions can be clearly seen.

In a summary, the lattice constants, heat of formation and electronic structures are studied by using first-principles for Pd intercalated graphite, which has quite different electronic structures compared to pure graphite. Applications of this new intercalated compound would be expected in the future.

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