Carbon cage-like materials as potential low work function metallic compounds: Case of clathrates

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We present an *ab initio* calculation of the electronic affinity of the hypothetical C-46 clathrate by studying its bare and hydrogenated (100) surfaces. We show that such a system shares with the diamond phase a small electronic affinity. Furthermore, contrary to the diamond phase, the possibility of endohedrally doping these cage-like systems allows to significantly raise the position of the Fermi level, resulting in a true metal with a small work function. This is illustrated in the case of the $Li_8@C$-46 doped compound. Such a class of materials might be of much interest for the design of electron-emitting devices. © *2002 American Institute of Physics.*
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There is a strong incentive in trying to synthesize materials which could be used as efficient electron emitters for vacuum electronic devices. While alkali metals display the lowest work function ($W \sim 2-3$ eV) of all elemental metals, their poor mechanical, and chemical properties (melting temperature, resistance to ionic bombardment, etc.) forbid their use in actual devices, and therefore metals with much higher work function such as tungsten or molybdenum ($W \sim 4.5$ eV) are preferred for their superior mechanical and chemical properties.

A promising class of materials which have been extensively studied are carbon diamond based systems. Due to their large gap, carbon diamond based systems have been shown to display a small, or even negative, electronic affinity.[1,2] Furthermore, their mechanical properties are superior to the one of any existing metal. However, the difficulty of doping them ''*n* type'' in order to obtain a significant density of emitting electrons limits their efficiency as good emitters.

In the last few years, a novel structure has attracted much attention for its specific structural and electronic properties. Column IV clathrates[3] are cage-like materials composed of face-sharing X_{20}, X_{24}, and X_{28} clusters (where X = Si,Ge). All atoms are in the same sp^3 environment as in the diamond phase, but the network is composed of 87% of pentagonal rings. As a result, it has been shown in particular that Si clathrates present a band gap which is ~ 0.7 eV larger than the one of the diamond phase.[4,5] Furthermore, the possibility of filling each cage by a dopant atom allows to significantly raise the position of the Fermi level to yield a metallic system with a large density of states (eDOS) at the Fermi level (E_F).[6,7]

The possibility of efficiently doping such systems has incited us to study the case of the hypothetical carbon clathrates. Even though such phases have not been synthesized so far, the reports on the synthesis of connected C_{36} clusters,[8] of diamond-like thin films synthesized by deposition of small carbon clusters[9] or even of polymerized C_{60} suggests that the

synthesis of such phases might be at hand or that the results presented below may apply to the above-mentioned existing phases.

In this letter we present an *ab initio* study of the electronic properties of C-46 and $Li_8@C$-46 within the density functional theory (DFT).[10] We study in particular the C-46 (100) bare and hydrogenated surfaces and analyze the effect of doping on the position of the Fermi level, the affinity of the system and the density of states at E_F. We show that under doping these materials are true metals with a low work function, thus combining the advantages of diamond-like systems with a large carrier concentration.

The local-density approximation (LDA)[11] was used for all calculations and a pseudopotential approach was adopted.[12] We used the SIESTA package,[13] which is a selfconsistent DFT code, employing numerical atomic-like orbitals (NAO) as a basis set. A well-converged basis set, consisting of doubled $\{s,p_x,p_y,p_z\}$ orbitals plus polarization d- orbitals was applied. Some of the calculations were also performed using a standard plane-wave (PW) basis set. All systems studied below were fully relaxed, both with respect to cell size and atomic positions. To perform the electronic affinity analysis, we calculated the plane-averaged self-consistent potential in the direction perpendicular to the surface for each of the slabs. The positions of the valence-band maximum (VBM) and conduction-band minimum (CBM) were found by adding the energy difference between the average self-consistent potential in the bulk and the VBM (CBM) in the bulk to the average self-consistent potential inside the slab.

Before studying the C-46 clathrate phase, we have tested the method by exploring the electronic and structural properties for the well-known bare and hydrogenated diamond (100) surfaces. Following Ref. 1, we have adopted a slab geometry with ten-layers but with 2-atoms per layer. The **k**-point sampling was thus increased to a $4 \times 4 \times 1$ special grid.[14] A vacuum of 10 Å was kept between neighboring slabs.

The results for PW and NAO basis are reported in Table

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TABLE I. Calculated electronic affinity for the diamond and clathrate carbon surfaces (eV).

Surface	LDA-PWs	LDA-NAOs	GW
C (100)	2.17	1.99	1.3
C (100):H	−0.45	−0.59	−1.3
C-46 (100)		3.47	2.8
C-46 (100):H		1.47	0.8
Li_8@C-46 (100):H		2.18	~1.5

FIG. 1. Symbolic representation of the Li_8@C-46 (100):H slab unit cell. The structure consists of C_{20} and C_{24} clusters with carbon atoms (not shown here) located at the corners of the cages. The gray balls show Li atoms encapsulated inside the carbon clusters. The black balls represent hydrogen atoms on the surface of the slab. The same type of slab was used for C-46 (100) and C-46 (100):H surfaces.

I. As in Ref. 1, we observe that the hydrogenation, by building a surface dipole, leads to a negative affinity system. Our results are in good agreement with those previously published,[1] and the NAO-basis calculations reproduce within ~0.15 eV the results of the PW calculations.

As the DFT-LDA is well known to underestimate the band gap of insulators, we have performed a quasiparticle study within the GW approximation[15] for the bulk diamond and C-46 phases. Such an approach is known to yield quasiparticle energies to within 0.1 eV as compared to experimental photoemission data. More details about the formalism and results will be provided elsewhere.[16] The main outcome of such calculations is that the quasiparticle correction to the DFT-LDA eigenstates are very similar in both systems and that the CBM is pushed to higher energy by ~0.7 eV in both phases (while the VBM is corrected down by ~0.8 eV). This corrects the calculated affinity as reported in the right-hand side column of Table I.

The stability and electronic properties of C-34 and C-46 clathrates have already been discussed in some detail at the DFT-LDA level.[4,17–19] In particular, it has been shown that for the C-34 and C-46 clathrates, the cohesive energy, bulk modulus, and band gap are, respectively, ~0.1 eV/atom, ~10%, and ~0.2 eV smaller than those of the diamond phase. As such, the stability and mechanical properties of carbon clathrates are close to those of the diamond phase. In this work, we obtained for the lattice parameter bulk modulus and band gap the values of 6.64 Å, 376 GPa, and 3.75 eV, respectively, with both NAO and PW basis sets, which is in good agreement with previously reported results. Within the GW approximation, the gaps increase to 5.55 and 5.35 eV for the diamond and clathrate phases, respectively.

We now study the C-46 (100) surface represented in Fig. 1. There are several nonequivalent (100) surfaces and we adopt a surface consisting of "half emerging" C_{24} clusters. After structural relaxation, we find that the emerging semiclusters hardly reconstruct besides a slight contraction inward of the threefold coordinated surface atoms, leading to a minimum C–C distance of 1.40 Å on the surface. Hydrogen coverage is performed by "passivating" these surface three-coordinated atoms. At this point we note that the results presented below may certainly change quantitatively with the chosen surface but the purpose of this letter is to illustrate on this specific example the potentialities of such novel systems. Figure 2 shows the calculated plane-averaged, self-consistent potential for bare and hydrogenated C-46 (100) surfaces. The electronic affinity is reported in Table I.

The results obtained for the undoped compounds suggest that carbon clathrates are *a priori* less favorable for emission than, say, the (100) diamond surface, taking the electronic
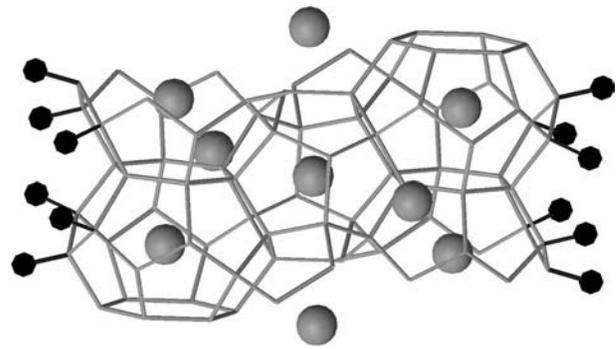
affinity as the only relevant criterion. However, we emphasize again that clathrates, contrary to the diamond phase, can be efficiently doped[19,20] by intercalating one atom in each cage in order to obtain a true metallic system with a large density of electrons available for emission. This is a crucial advantage as compared to the diamond phase.

By analogy with the existing doped Si clathrates and intercalated carbon graphitic systems, we study the n-doped Li_8@C-46 phase. The corresponding bulk eDOS is represented in Fig. 3 where we have arbitrarily aligned the eDOS to the top of the C-46 valence bands for sake of comparison. As can be readily seen, intercalation of Li atoms leads to the filling of the conduction bands of the host carbon matrix by Li 2s electrons. The system becomes metallic with the Fermi level located near a peak in the density of states, which is in excellent agreement with previous work.[19]

As in the case of diamond surfaces, hydrogenation leads to a significant decrease in the electronic affinity of the
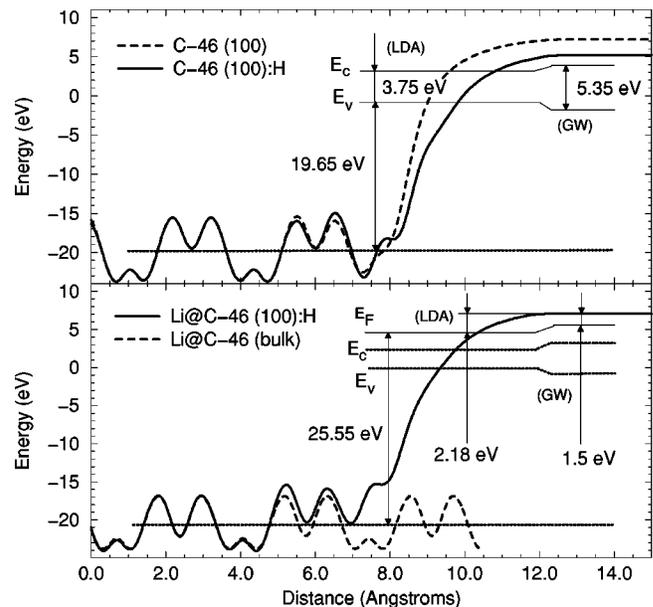

FIG. 2. Plot of the plane-averaged self-consistent potential for the C-46(100) bare and hydrogenated surfaces, and for Li_8@C-46(100):H surface. The good agreement between the bulk and slab potential on the innermost atoms of Li_8@C-46(100):H indicates that the slab is large enough.
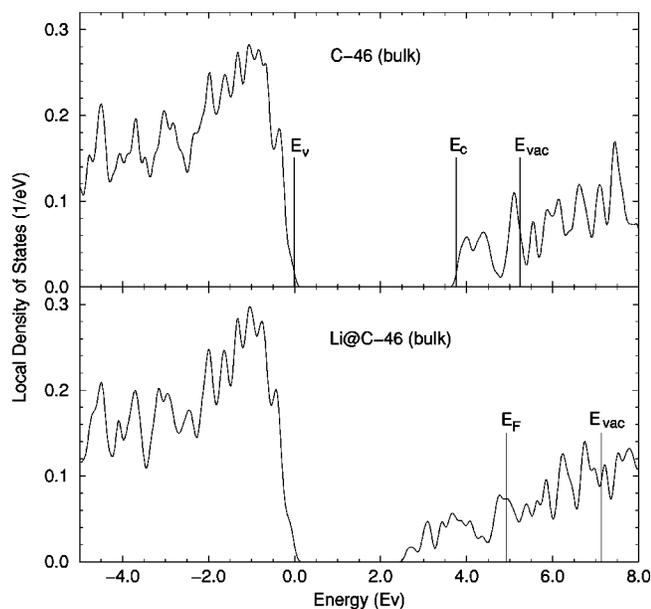
FIG. 3. Electronic density of states (eDOS) for bulk C-46 and Li$_8$@C-46. A 0.1 eV broadening has been used. The eDOS is normalized per carbon atom.

empty phase. We now explore the effect of doping on the electronic affinity (Table I) of the hydrogenated surface. The important finding is that Li doping leads to the formation of a true metallic system with a quite low work function (~ 1.5 eV GW value). This work function is significantly lower than the one of alkali metals and much lower than the one of, e.g., tungsten. The eDOS for states located around E_F can be further shown to have a strong weight on both bulk and surface atoms, a factor which is crucial for emission. One can conclude that doped carbon clathrates are potentially true metals with a work function lower than the lowest affinity of all elemental metallic systems but with much superior mechanical properties.

It is interesting to note that the work function of the Li-doped clathrate is actually larger than the electronic affinity of the empty phase, despite the raise of the Fermi level under doping. This means that the entire band structure is shifted to lower energy with respect to the vacuum level under doping. This shift can originate in two effects: a decrease of the average potential inside the slab (bulk effect) and an increase of the surface dipole barrier (surface effect). An analysis of both effects show that in the present case it is mainly a bulk effect.

In conclusion, we have shown that doped carbon clathrates are potentially true metallic systems with a work func-

tion significantly lower than the one of alkali metals but with a stability typical of the carbon diamond phase. This opens new perspectives for the making of efficient electron emitters. An alternative choice of dopant atom and/or surface treatment (e.g., cesium coverage) may lead to even smaller work function.

[1] J. van der Weide, Z. Zhang, P. K. Baumann, M. G. Wensell, J. Bernholc, and R. J. Nemanich, Phys. Rev. Lett. **50**, 5803 (1994).
[2] W. E. Pickett, Phys. Rev. Lett. **73**, 1664 (1994).
[3] J. Kasper, P. Hagenmuller, M. Pouchard, and C. Cros, Science **150**, 1713 (1965).
[4] G. B. Adams, M. O'Keeffe, A. A. Demkov, O. F. Sankey, and Y.-M. Huang, Phys. Rev. B **49**, 8048 (1994).
[5] J. Gryko, P. F. McMillan, R. F. Marzke, G. K. Ramachandran, D. Patton, S. K. Deb, and O. F. Sankey, Phys. Rev. B **62**, R7707 (2000).
[6] S. Saito and A. Oshiyama, Phys. Rev. B **51**, 2628 (1995).
[7] V. I. Smelyanski and J. S. Tse, Chem. Phys. Lett. **264**, 459 (1997).
[8] C. Piskoti, J. Yarger, and A. Zettl, Nature (London) **393**, 771 (1998).
[9] V. Paillard, P. Mélinon, V. Dupuis, J. P. Perez, A. Perez, and B. Champagnon, Phys. Rev. Lett. **71**, 4170 (1993).
[10] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964); W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).
[11] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[12] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991); K. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[13] P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996); D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
[14] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[15] M. Hybertsen and S. G. Louie, Phys. Rev. B **30**, 5777 (1984); and references therein.
[16] In the case of the Li$_8$@C-46, the quasiparticle correction to E_F is taken to be the same as the one for the CBM of C-46. While in the conduction bands the GW correction can be shown to slightly increase with the energy of the states (see Ref. 15), the enhanced screening under doping is expected to reduce it. Despite such a compensation, the quasiparticle correction to E_F should be taken as an approximate value. X. Blase (unpublished).
[17] R. Nesper, K. Vogel, and P. Blöchl, Angew. Chem. **32**, 701 (1993).
[18] A. San-Miguel, P. Kéghélian, X. Blase, P. Mélinon, A. Perez, J. P. Itié, A. Polian, E. Reny, C. Cros, and M. Pouchard, Phys. Rev. Lett. **83**, 5290 (1999).
[19] S. Saito, Proceedings of the First Symposium on Atomic-Scale Surface and Interface Dynamics, March 13–14, 1997, Tokyo.
[20] M. Bernasconi, S. Gaito, G. Benedek, Phys. Rev. B **61**, 12689 (2000).