Ab initio study of the structural stability of fcc-CH$_x$ phases

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**ABSTRACT**

It has recently been suggested that carbon nanocrystals obtained by chemical vapor deposition with a gaseous precursor containing CH$_4$ and H$_2$, may include hydrogen atoms in the carbon lattice, forming solid fcc- and bcc-CH$_x$ phases. In this work, we evaluate the structural stability of five fcc-CH$_x$ phases by means of first-principles calculations. The total energy is obtained as a function of the isotropic, tetragonal, and trigonal deformations for the bulk structures. First, we analyze the C$_2$(cuprite), CH$_4$(zincblende), CH$_4$(rocksalt), and CH$_2$(fluorite) structures. It is found that the four systems show a minimum in the total energy for the isotropic deformation, but are unstable against tetragonal and trigonal deformations. In the second part, we explore the structural stability of CH$_2$ in the pyrite structure. We find that CH$_2$(pyrite) with the hydrogen atoms defined by the internal parameter $u = 0.35$ and a lattice parameter of 3.767 Å is elastically stable, providing a possible explanation for the experimental observation of fcc-carbon in materials prepared in the presence of hydrogen or methane.

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1. **Introduction**

The face-centered-cubic (fcc) crystal structure does not appear in the usual pressure–temperature phase diagram of carbon [1]. Nevertheless, the observation of fcc-carbon in nanoparticles and thin films has been reported [2–9]. Palatnik et al. [2] were the first to report the observation of the fcc phase of carbon, which was obtained from low temperature annealing of an amorphous carbon film with simultaneous bombardment of argon ions. After this process, single-crystal inclusions of ~10 nm in size with a lattice constant of 3.57 Å and metallic character were observed [2]. Carbon with the fcc crystal structure has also been observed at the core of carbon particles produced by plasma-chemical synthesis [3]. More recently, it has been shown that a thin film of fcc-carbon is formed on a diamond surface as a result of treatment in a hydrogen plasma [4–6]. The crystal lattice parameter of fcc-carbon in thin films was determined by high-resolution transmission electron microscopy (HRTEM) to be 3.563 Å [5,6]. In addition, it has been reported that electron energy loss spectroscopy (EELS) can distinguish fcc-carbon from both diamond and graphite carbon phases [4,9].

The reports on the observation of carbon with the fcc crystal structure have raised many questions concerning the properties of this new phase of carbon. The electronic structure of fcc-carbon has been studied theoretically in previous work by means of first-principles methods in order to determine the bonding and electronic properties [10,11]. The ab initio calculations showed that the chemical bond in fcc-carbon is very close to an s$^2$p$^2$ bonding and exhibits metallic behavior [10], in agreement with the observations of electrical conductivity reported by Palatnik et al. [2]. However, the calculated
lattice parameter for fcc-carbon using ab initio methods is 3.08 Å [12,13], which is smaller than the experimental value of 3.563 Å by approximately 14%, suggesting that the pure carbon fcc structure is unable to explain the electron diffraction patterns and the HRTEM images [3–6]. Recently, two new pure carbon structures have been proposed in order to explain the electron diffraction patterns [14,15]. The first is a tetragonal structure called 'glitter' [14], and the second is an intermediate structure between diamond and rhombohedral graphite [15,16]. Nevertheless, to consider these structures as candidates for the new phase of carbon, until now attributed to the fcc structure, their structural stability and electronic properties need to be evaluated.

Another option for the explanation of the experimental results on the new phase of carbon is the presence of other elements. It is important to note that the synthesis of fcc-carbon, in many cases, was carried out in the presence of hydrogen or methane [3–6,8,9]. Since hydrogen is the only atom that cannot be readily detected by EELS and HRTEM the presence of this element in the carbon structure must be considered. Hydrogen incorporation in the fcc-carbon structure has been addressed by Cowley et al. [8]. They studied the fcc-CH phases for different hydrogen concentrations using first-principles calculations. It was found that the calculated lattice parameter for zincblende CH (3.583 Å) and fluorite CH2 (3.787 Å) are close to the experimental value for fcc-carbon, suggesting that the presence of hydrogen may explain the experimental results [8]. However, the structural stability of these fcc-CH phases has not yet been evaluated.

In this paper, we report a first-principles study of the structural stability for C2H (cuprite), CH (zincblende), CH (rocksalt), CH2 (fluorite), and CH2 (pyrite). In addition to the zincblende structure for the CH-phase, we have included the rocksalt structure, which is commonly adopted by hydrides and has not been explored before. In order to evaluate the structural stability, the total energy has been calculated as a function of the isotropic, tetragonal, and trigonal deformations. Thus, the structural stability is evaluated from the behavior of the calculated total energy, based on the observation that the criteria for elastic stability for a cubic crystal dictate that the energy must show a minimum for the three deformations.

### 2. Method and computational details

The Kohn-Sham total energies were calculated self-consistently using the pseudopotentials LCAO method [17,18] as implemented in the SIESTA code [17–19]. The pseudopotentials were generated according to the procedure of Troullier and Martins [20] from the atomic configuration, [He] 2s2 2p2 for carbon and 1s1 for hydrogen. The core radii were 1.50 a.u. for the s and p orbitals, and 1.25 a.u. for the d and f orbitals in carbon. For hydrogen we use 1.25 a.u. for the core radii. For the expansion of the wave functions we employed a double-ζ plus polarization basis [19] with the radii indicated in Table 1. The radii for the orbitals obtained from the polarization are equal to the most extended orbitals of the respective chemical species. The basis for the s and p orbitals was slightly excited (270 meV) in order to limit the range of the pseudoatomic basis orbitals [21]. For the exchange-correlation potential we used the GGA as parameterized by Perdew et al. [22]. In order to obtain the potential energy we used a grid in real space which was obtained using a mesh cutoff of 311 Ry. Integrals in k-space were performed in a finite, uniform grid of the Brillouin zone. The fineness of this grid was controlled by a k-grid cutoff, a real-space radius that plays a role equivalent to the plane wave cutoff of the real-space grid [23]. For the present calculation the k-grid cutoff was 80 Å, generating 152,626 k-points in the first Brillouin zone. Self-consistency was assumed when the difference between the two density matrices belonging to successive iterations was less than 10⁻⁴.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Orbital</th>
<th>First-ζ</th>
<th>Second-ζ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2s</td>
<td>4.088</td>
<td>3.347</td>
</tr>
<tr>
<td></td>
<td>2p</td>
<td>4.870</td>
<td>3.475</td>
</tr>
<tr>
<td>H</td>
<td>1s</td>
<td>4.709</td>
<td>3.760</td>
</tr>
</tbody>
</table>

Fig. 1 – The crystal structures of C2H (cuprite), CH (zincblende), CH (rocksalt), CH2 (fluorite), and CH2 (pyrite). The black and gray spheres correspond to atoms of carbon and hydrogen, respectively.
The structural stability of the systems under study has been evaluated via the elastic stability criteria. A cubic crystal has three independent elastic moduli; these can be taken to be the bulk modulus \( B \) and two shear moduli, \( G = (C_{11} - C_{12})/2 \) and \( G = C_{44} \) [24]. In this way, the conditions for elastic stability for a cubic lattice are \( \delta = (C_{11} + 2C_{12})/3 > 0 \), \( G' = (C_{11} - C_{12})/2 > 0 \), and \( G = C_{44} > 0 \) [13,24,25]. In other words, the conditions for elastic stability of a cubic lattice dictate that the total-energy surface should have a local minimum for the isotropic, tetragonal, and trigonal deformations [13,25,26]. Therefore, in order to analyze the stability of the fcc-CH\(_x\) phases under study, the total energy was first calculated as a function of volume, and secondly as a function of the volume-conserving orthorhombic and monoclinic strains at the calculated equilibrium lattice parameter, following the method in Ref. [27]. In Fig. 1 we show the unit cells of the fcc-CH\(_x\) phases studied.

### 3. Results and discussion

In Fig. 2 we show the calculated total energy for C\(_2\)H(cuprite), CH(zincblende), CH(rocksalt), and CH\(_2\)(fluorite) as a function of the lattice parameter. It can be seen that for all four systems, the total energy shows a minimum as a function of the isotropic deformation, which means that \( B > 0 \). Thus the four systems are stable with respect to the isotropic deformation. In order to determine the lattice parameter at the minimum energy \( (E_0) \), the calculated total energy as a function of volume was fitted to the Birch–Murnaghan equation of state [28], shown as a solid line in Fig. 2. The calculated lattice parameters at \( E_0 \) for the systems studied are presented in Table 2. The present values for CH(zincblende) of 3.574 Å and CH\(_2\)(fluorite) of 3.776 Å, are in very good agreement with previous first-principles calculations [8]. The lattice parameter for CH(rocksalt) of 3.480 Å is around 5% smaller than that corresponding to CH(zincblende), but is in the range of cell dimensions measured for the fcc-CH\(_x\) phases [8]. The lattice parameter for C\(_2\)H(cuprite) phase is even lower at 3.438 Å, but is still significantly larger than the value previously obtained for fcc-carbon without incorporated hydrogen of 3.08 Å [12,13].

The calculated total energy for C\(_2\)H(cuprite), CH(zincblende), CH(rocksalt), and CH\(_2\)(fluorite) as a function of the tetragonal distortion is presented in Fig. 3. We can see that when the cubic symmetry is broken by the volume-conserving tetragonal distortion, the total energy of C\(_2\)H(cuprite), CH(zincblende), and CH(rocksalt) decreases for both negative and positive deformations, which means that \( G' < 0 \) for these systems. In the case of CH\(_2\)(fluorite), the behavior of the total energy is more complex, as the energy increases for negative deformations and decreases for positive deformations, indicating that this system is in a saddle point for the tetragonal distortion. In Fig. 4 we present the calculated total energy for C\(_2\)H(cuprite), CH(zincblende), CH(rocksalt), and CH\(_2\)(fluorite) as a function of the trigonal distortions. In this case, we find that the total energy of C\(_2\)H(cuprite), CH(rocksalt), and CH\(_2\)(fluorite) decreases for both negative and positive deformations, indicating that \( G < 0 \) for these systems. In con-

### Table 2 – Calculated lattice parameter \( (a_0) \) for the studied fcc-CH\(_x\) phases.

<table>
<thead>
<tr>
<th>System</th>
<th>Structure</th>
<th>Symmetry</th>
<th>( a_0 ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H</td>
<td>Cuprite</td>
<td>( Pm\bar{3}m )</td>
<td>3.438</td>
</tr>
<tr>
<td>CH</td>
<td>Zincblende</td>
<td>( F-43m )</td>
<td>3.574</td>
</tr>
<tr>
<td>CH</td>
<td>Rocksalt</td>
<td>( Fm\bar{3}m )</td>
<td>3.480</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>Fluorite</td>
<td>( Fm\bar{3}m )</td>
<td>3.776</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>Pyrite (( \alpha = 0.150 ))</td>
<td>( Pn\bar{3} )</td>
<td>4.290</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>Pyrite (( \alpha = 0.347 ))</td>
<td>( Pn\bar{3} )</td>
<td>3.767</td>
</tr>
</tbody>
</table>

Fig. 2 – Calculated total energy as a function of the lattice parameter under isotropic deformation (open circles) for C\(_2\)H(cuprite), CH(zincblende), CH(rocksalt), and CH\(_2\)(fluorite). The line corresponds to a fit of the Birch–Murnaghan equation of state to the calculated energy values. The lowest energy is the reference level, and is set to zero.
In contrast, the total energy of the CH(zincblende) structure shows a saddle point behavior, where the total energy decreases for negative deformations and increases for positive deformations. Hence, these four structures are unstable against the tetragonal and trigonal strains, and therefore, the C2H(cuprite), CH(zincblende), CH(rocksalt), and CH2(fluorite) structures are elastically unstable.

It can be concluded that the presence of hydrogen at the symmetry positions defined by the C2H(cuprite), CH(zincblende), CH(rocksalt), and CH2(fluorite) structure does not result in elastically stable materials, hence, we explored the possibility of the presence of hydrogen at lower symmetry positions in the bulk of an fcc-CH4 system.

In this context, we evaluated the structure CH2(pyrite) similar to the FeS2 pyrite structure, which is characterized by the symmetry group $\text{P}_{\text{a}3}$. The carbon atoms form an fcc sub-lattice and the hydrogen atoms are grouped as dimers, with their position characterized by a single positional parameter, $u$ [29]. When the hydrogen dimers occupy the tetrahedral interstitial spaces of the carbon sub-lattice, the CH2(fluorite) structure is recovered, which corresponds to a pyrite structure with $u = 0.25$. The pyrite structure has recently been evaluated for PtN2 [30–32], and from the calculated total energy versus $u$ curve it was concluded that although an energy minimum is observed at $u = 0.25$ for a metastable fluorite structure, the structure was elastically unstable. A second

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**Fig. 3** – Calculated total energies under tetragonal deformation (open circles) for C2H(cuprite), CH(zincblende), CH(rocksalt), and CH2(fluorite). The lowest energy under isotropic deformation is the reference level.

**Fig. 4** – Calculated total energies under trigonal deformation (open circles) for C2H(cuprite), CH(zincblende), CH(rocksalt), and CH2(fluorite). The lowest energy under isotropic deformation is the reference level.
minimum was found at a much lower energy for \( u = 0.42 \), and this structure was found to be elastically stable [31,32].

Fig. 5 shows the total energy for the CH\(_2\)(pyrite) structure as a function of the parameter \( u \), showing two energy minima at \( u = 0.15 \) and \( u = 0.35 \), respectively; Fig. 1 shows the unit cell representations for these two pyrite structures. An energy maximum is observed at \( u = 0.25 \), indicating that the fluorite structure, besides being elastically unstable, is also unstable in terms of the position of the hydrogen atoms. The lattice parameters for the structures at the two energy minima were calculated, and found to be 4.290 Å at \( u = 0.15 \) and 3.767 Å at \( u = 0.35 \), respectively. Note that the lattice parameter for the structure with \( u = 0.15 \) is about 20% larger than that reported for fcc-carbon of 3.563 Å. The elastic stability was determined for the structures with \( u = 0.15 \) and \( u = 0.35 \), and the results are shown in Fig. 6. Both structures are stable against isotropic and trigonal deformations, however, the pyrite structure with \( u = 0.15 \) is unstable under tetragonal deformation. The CH\(_2\)(pyrite) structure with \( u = 0.35 \) is found to be elastically stable, and the calculated lattice parameter of this structure is within 6% of that observed experimentally for fcc-carbon.

It should be noted that the calculation of the elastic stability of the five fcc-CH\(_x\) phases evaluated apply to the bulk structure, while experimental observations of fcc-carbon often involve nanoparticles or thin films, indicating that surface energy considerations might be important. At sufficiently small dimensions, the surface energy contributes significantly to the total energy and strongly affects phase formation. As a result, nanomaterials often form in a metastable bulk phase, rather than the stable bulk phase. Hence, the CH\(_2\)(pyrite) structure with \( u = 0.35 \) can be considered a viable explanation for the observation of fcc-carbon in materials prepared in the presence of hydrogen or methane. Further evaluation of the CH\(_2\)(pyrite) structure with \( u = 0.35 \) would involve the theoretical determination of the vibrational and electronic properties, and experimental corroboration of the existence of this material. Thus, it would be interesting to consider the finite size effects in theoretical studies of the fcc-CH\(_x\) phases, for example via cluster simulations.

4. Conclusions

We have evaluated the structural stability of C\(_2\)H(cuprite), CH(zincblende), CH(rocksalt), CH\(_2\)(fluorite), and CH\(_2\)(pyrite) by means of ab inito calculations. The total energy has been calculated as a function of the isotropic, tetragonal, and trigonal deformations using the pseudopotential-LCAO method. We found that for the C\(_2\)H(cuprite), CH(zincblende), CH(rocksalt), and CH\(_2\)(fluorite) structures, the total energy shows a minimum for the isotropic deformation, but exhibits maxima...
for the tetragonal or trigonal deformations. Hence, these structures are elastically unstable in bulk form. The CH2\textsubscript{\textparens{pyr-

ite}} structure exhibited two energy minima with respect to the internal parameter \(u\) that describes the positions of the hydrogen atoms. For the phase with \(u = 0.35\) and lattice parameter of 3.767 Å, the structure was found to be elastically stable. Hence, this fcc-CH\(_2\) phase could explain the experimental observation of fcc-carbon in materials prepared in the presence of hydrogen or methane.

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\section*{References}