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Effect of pentagons in \(sp^3\) systems on electronic, elastic, and vibrational properties: Case of chiral structures

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We present first-principles calculations of carbon and silicon chiral framework structures (CFSs). In this system, proposed recently by Pickard and Needs [Phys. Rev. B 81, 014106 (2010)], atoms form only pentagonal cycles. This configuration enables unambiguous analysis of the effects of pentagons on electronic, vibrational, and thermodynamic properties. The local density approximation electronic band gaps in CFSs were found to be equal to or greater than those of clathrates using the same formalism, as confirmed by GW calculations: 1.8 and 5.5 eV for Si and C-CFS, respectively. We show that, as in clathrates, an increasing electronic band gap is correlated with the contraction of the valence bands, resulting from the frustration of the \(p\) shells. The electron localized function and Wannier analysis confirm the \(sp^3\) nature of the bonds. Finally, we discuss vibrational and related properties. We show that CFSs present singularities, in particular, that the higher frequencies are not located at the \(\Gamma\) point.

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I. INTRODUCTION

During the last decades, numerous studies have reported the discovery and understanding of the properties of new allotropic carbon/silicon structures. The theoretical and technological interests in these types of systems takes its origin in high-thermoelectrical-power materials, hard materials, and materials with a large-band-gap. Many works on nanotubes or exotic graphite, graphene, graphane, and cluster systems. Many works on nanotubes or exotic \(sp^2\) allotropic phases illustrate this.\(^1\)

Studying cage-like systems has led to the discovery of large-gap materials, exceptional plasticity, and even high electron-phonon coupling.\(^2,3\) It has been suggested that pentagons and \(sp^3\) shells are at the origin of many of the features of clathrates. These strong modifications are associated with electronic\(^2,4,5\) and vibrational\(^6\) properties. Among this research on different allotropic structures, Pickard and Needs\(^7\) recently proposed a new hypothetical allotropic three-dimensional (3D) network: a chiral framework structure (CFS) where all atoms are linked through \(sp^3\)-type hybridization. Unlike diamond or clathrates, where the networks are mostly composed of hexagonal rings, the originality of these structure is that atoms forms only pentagons.

In this paper, we study the effects of pentagons on CFSs. Local density approximation (LDA) and GW calculations are presented to evaluate electronic band gaps accurately. The electron localized function (ELF) and Wannier functions are also presented and discussed, to clarify the nature of bonds. We conclude with a discussion on vibrational (phonons and Raman spectra) and related properties.

II. COMPUTATIONAL DETAILS

Our calculations were performed within the LDA\(^8\) of the density functional theory (DFT).\(^9\) We used the QUANTUM-ESPRESSO\(^10\) (\(QE\) package. Some of the calculations (quasi-particle study, based on the so-called GW approximation) were also achieved using the ABINIT\(^11\) package. A pseudopotential approach is used,\(^12\) with a plane-wave expansion of the wave functions. To calculate cohesive energies and elastic and electronic properties, 60- and 30-Ryd cutoff energies were imposed for C and Si, respectively, and the Brillouin zones are sampled by \(15 \times 15 \times 15\) \(k\) grids. The use of such increased cutoffs allowed us to check the good convergence of our calculations. Emphasis was also placed on the calculation of accuracy band gaps using the GW approximation.\(^11,13\) The Plasmon pole approximation with Hartree convergence was employed to calculate the GW corrections. Cutoffs of 7 and 12 Ha, and 1200 bands for Si and C, respectively, were used for the magnitude of the \([q + G]\) basis vectors considered to build the screening, the susceptibility, and the dielectric matrix. We finally computed the dynamic properties from density functional perturbative theory.\(^14\) \(8 \times 8 \times 8\) \(k\) meshes and 60- or 30-Ryd cutoff energies with \(3 \times 3 \times 3\) \(q\) meshes.

III. GROUND STATE PROPERTIES

The system has hexagonal symmetry (\(P6_3/mc\); space group no. 178).\(^15\) Atoms are localized in the \(6b\) Wyckoff position (\(x,2x,1/4\)). The free parameter \(x\) is almost independent of the element (\(x \simeq 0.232\)). In this configuration, atoms form pentagonal rings.

In Table I, we report the optimized lattice parameters, the formation energies, the bulk modulus (computed either from a Murnaghan fit or from the linear response), and the LDA band gaps of diamond and CFSs. Like Pickard and Needs,\(^7\) we found that in CFSs, diamond, and clathrates, lengths and angles of bonds\(^16\) are very similar. CFS phases are slightly less dense than those of diamond (\(\sim 8\%\)) and display a compressibility that is close to that of the diamond phase. Their formation energies are slightly higher than those of diamond, but of the same order of magnitude as those of clathrates.

We calculate the elastic constants as the second derivatives of the internal energy with respect to the strain tensor.
TABLE I. Lattice parameters \((a_o, c_o, \text{in } \text{Å}), \text{volume per atom (in } \text{Å}^3/\text{atom}), \text{bulk modulus } (B_o, \text{in GPa}), \text{formation energies } (E_f, \text{in meV/atom; the reference state is the diamond}), \text{and band gaps } (\Delta_g, \text{in eV}).\)

<table>
<thead>
<tr>
<th>Material</th>
<th>(a_o)</th>
<th>(c_o)</th>
<th>(V)</th>
<th>(B_o)</th>
<th>(E_f)</th>
<th>(\Delta_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-diam</td>
<td>3.58(^a) (3.57(^a))</td>
<td>5.7</td>
<td>460 (545)(^a)</td>
<td>3.9 (5.48)(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-CFS(^b)</td>
<td>3.57</td>
<td>3.37</td>
<td>6.2</td>
<td>389</td>
<td>112</td>
<td>4.12</td>
</tr>
<tr>
<td>C-CFS(^c)</td>
<td>3.55</td>
<td>3.32</td>
<td>6.0</td>
<td>428</td>
<td>141</td>
<td>4.03</td>
</tr>
<tr>
<td>C-CFS(^d)</td>
<td>3.54</td>
<td>3.34</td>
<td>6.0</td>
<td>413</td>
<td>150</td>
<td>4.02</td>
</tr>
<tr>
<td>Si-diam</td>
<td>5.41(^a) (5.43(^a))</td>
<td>19.8</td>
<td>97 (99)(^a)</td>
<td>0.62 (1.17)(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-CFS(^b)</td>
<td>5.47</td>
<td>5.11</td>
<td>22.1</td>
<td>53</td>
<td>1.46</td>
<td></td>
</tr>
<tr>
<td>Si-CFS(^c)</td>
<td>5.38</td>
<td>5.03</td>
<td>21.0</td>
<td>90</td>
<td>66</td>
<td>1.31</td>
</tr>
<tr>
<td>Si-CFS(^d)</td>
<td>5.33</td>
<td>5.15</td>
<td>21.1</td>
<td>87</td>
<td>72</td>
<td>1.19</td>
</tr>
</tbody>
</table>

\(^a\)Experimental, from Ref. 17.
\(^b\)Theoretical, from Ref. 7; PBE calculations.
\(^c\)QE simulations, Murnaghan fit.\(^{18}\)
\(^d\)ABINIT simulations, linear response calculations.\(^{19}\)

The elastic constants are listed in Table II. To illustrate the anisotropy of the elastic constants as a function of the crystallography, we have drawn 3D representations of diamond and a CFS (Fig. 1). In the basal plane, we note a cylindrical symmetry; elasticity is slightly anisotropic (in comparison to metallic systems; see Ref. 20), while perpendicular to the basal plane (along the \((c)\) axis).

### IV. ELECTRONIC PROPERTIES

#### A. LDA electronic properties

We have plotted (Fig. 2) the electron density of states (DOS) and their band structures (e-band) along high-symmetry directions. We notice, like Pickard and Needs,\(^7\) that the band gaps are indirect (between \(L\) and \(\bar{W}\)). The most striking feature is the value of these band gaps. They are found to be equal to about 1.20 and 4.03 eV for silicon and carbon CFSs, respectively (the difference between ABINIT and QE calculations is due to the difference in lattice parameters). At this level of approximation, diamond’s electron band gaps are found to be equal to 0.5 and 3.9 eV for Si and C, respectively. Gaps in CFSs are thus opened by 0.7 and 0.1 eV.

The analysis of the top of the valence bands shows that these states are essentially composed of \(p\) shells (see projected DOS on orbitals; Fig. 2). As in clathrates,\(^5\) \(p\) states in CFSs are also frustrated by pentagonal cycles. This frustration induces two main effects. First, a comparative analysis of the valence band width in CFS and in diamond reveals that the range...
FIG. 3. Quasiparticle corrections $E^{QP} - E^{LDA}$ as a function of the quasiparticle energies $E^{QP}$ for Si-CFS (left) and C-CFS (right).

of the C or Si bandwidth is strongly reduced (a reduction of about 3 and 1.5 eV for carbon and silicon, respectively) and that the main contraction is associated with the $p$ shells. The second consequence is the high DOS at the top of the valence bands. As in the case of the Si-46 phase, we note that, in Si-CFS, a pseudogap opens within the valence bands.

B. GW CORRECTIONS

We then performed a quasiparticle energy calculation for both tetrahedral CFSs and compared them to those for diamond and clathrates. The corrections to the $GW$-Plasmon pole approximation are of the same order of magnitude as those found for tetrahedral analog systems: about 0.6 and 1.4 eV for Si and C, respectively (see Fig. 3). The correction for Si/C systems seems to be little dependent on the crystallography in $sp^3$ systems. The valence bands are “pushed” down, and conduction bands up. The electronic band gaps are also equal to 1.8 and 5.5 eV for Si and C CFS systems, respectively. Unlike carbon clathrates, the C-CFS gap is greater than that of diamond.

C. NATURE OF BONDS

To get a better understanding of the bonds, we have calculated the ELF$^{21}$ for the carbon-CFS. According to its definition, the value of ELF is limited to the range of 0 to 1. A high value can be interpreted as a covalent interaction and a low ELF corresponds to an ionic interaction between unpaired electrons. From the calculated ELF displayed in Fig. 4 (see level curves), high values of contribution occur along C-C
bonds, which is ascribed to the strong hybridization of the carbon states; this is consistent with the eDOS analysis. We can also see that the low ELF contribution draws helicoidal channels (see isosurfaces). These channels should be ideal spaces for inserting elements.

Complementary to the ELF, we calculated Wannier functions associated with valence states. The results—presented in Fig. 4—are characteristic of \( sp^3 \) systems (see Ref. 3).

**V. VIBRATIONAL PROPERTIES**

Finally, we report vibrational properties. Phonon spectra of CFSs also show differences in comparison to those of diamond. Uppermost branches are ("red-") shifted (see vibrational DOS same order of magnitude as we find in clathrates. The decrease in frequencies in optical modes is to be related to the frustration of modes. In the case of carbon, acoustic modes completely vanish, and the maximum of the optical branches is not located in \( \Gamma \) but in \( K \) and \( M \). In Si, we also find that the uppermost frequencies are not in \( \Gamma \). Although it is a known feature in carbon systems (diamond, clathrates, nanotubes), in silicon it is unusual and is characteristic of the crystallography. The decrease is the result of an "overbending" of the highest optical frequencies and is associated with sufficiently large interatomic force constants between second-nearest neighbors.

Raman spectra have also been computed from first principles (see Fig. 6). CFSs (space group 178; \( P6_322 \)) have 18 modes in \( \Gamma \), distributed as: \( A_1 + 2A_2 + 2B_1 + B_2 + 3E_1 + 3E_2 \). \( E_1 \) and \( E_2 \) could be Raman active. \( A_2 \) and \( E_1 \) are infrared active. In Table III, we report the frequencies and their irreducible representations.

From the vibrational DOS, thermodynamic properties (\( C_v \), \( S_v \), and \( F_v \)) were calculated within the harmonic approximation. The evolutions of these quantities with regard to the temperature (not represented here) are quantitatively the same as those obtained for diamond structures. Thus, the zero-point energies do not modify the relative stability of the phases: 61 and 60 meV/atom for Si-diamond and Si-CFS, respectively.

**VI. CONCLUSION**

In conclusion, we report a complete study of C- and Si-CFS properties. We show that these structures should display large electron band gaps, greater than those of diamond and clathrate analog structures. The quasiparticle band gaps are found to be equal to 1.8 and 5.6 eV for Si- and C-CFSs, respectively. Analysis of the electron states shows that opening of the electron band gaps is the consequence of the contraction of the valence bands by the frustration of the shells, as in clathrate structures. Moriguchi et al., who have studied silisils—"zeolite without oxygen"—have proposed many energetically favorable structures (in comparison to diamond). Such structures, which present numerous odd cycles, should present original electronic and vibrational properties. A consequence of the high DOS at the top of the valence bands would be, for C-CFSs, strong electron-phonon coupling. Vibrational properties are presented. We show that silicon should present an unusually low frequency of higher modes at \( \Gamma \).

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