Mechanical and Electronic Properties of XC$_6$ and XC$_{12}$

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Abstract: A series of carbon-based superconductors XC$_6$ with high $T_c$ were reported recently. In this paper, based on the first-principles calculations, we studied the mechanical properties of these structures, and further explored the XC$_{12}$ phases, where the X atoms are from elemental hydrogen to calcium, except noble gas atoms. The mechanically- and dynamically-stable structures include HC$_6$, NC$_6$, and SC$_6$ in XC$_6$ phases, and BC$_{12}$, CC$_{12}$, PC$_{12}$, SC$_{12}$, ClC$_{12}$, and KC$_{12}$ in XC$_{12}$ phases. The doping leads to a weakening in mechanical properties and an increase in the elastic anisotropy. C$_6$ has the lowest elastic anisotropy, and the anisotropy increases with the atomic number of doping atoms for both XC$_6$ and XC$_{12}$. Furthermore, the acoustic velocities, Debye temperatures, and the electronic properties are also studied.

Keywords: first-principles calculations; carbides; mechanical properties; elastic anisotropy

1. Introduction

Elemental carbon exhibits a rich diversity of structures and properties, due to its flexible bond hybridization. A large number of stable or metastable phases of the pure carbon, including the most commonly known, graphite and diamond, and other various carbon allotropes [1–4] (such as lonsdaleite, fullerene, and graphene, etc.), and diversified carbides [5–11], have been studied in experiments and theoretical calculations. Graphite, which is the most stable phase at low pressure, has a $sp^2$-hybridized framework and is ultrasoft semimetallic, whereas diamond, stable at high pressure, is superhard, insulating with a $sp^3$ network. Recently, a novel one-dimensional metastable allotrope of carbon with a finite length was first synthesized by Pan et al. [1], called Carbyne. It has a $sp$-hybridized network and shows a strong purple-blue fluorescence. The successful synthesis of Carbyne is a great promotion for the further analysis on properties and applications. The 2D material MXenes as a promising electrode material, which is early transition metal carbides and carbon nitrides, is reported [11], owing to its metallic conductivity and hydrophilic nature. These properties of different carbides are appealing. To find superhard superconductors, researchers designed some carbide superconductors, such as boron carbides and XC$_6$ structure with cubic symmetry. The diamond-like B$_x$C$_y$ system, which is superhard and superconductive, has also attracted much interest [5–10]. The best simulated structure of the synthesized d-BC$_3$ (Pmma-b phase) has a Vickers hardness of 64.8 GPa, showing a superhard nature, and its $T_c$ reaches 4.9–8.8 K [5]. The P-4m2 polymorph of d-BC$_7$ with a low energy also has a high Vickers hardness of 75.2 GPa [8]. Furthermore, Wang et al. [9] explored more potential superhard structures of boron carbide, uncovering the stability is mainly contributed by the elemental boron at low pressure, and by the carbon at high pressure. The novel metastable carbon structure C$_6$ bcc is predicted with a cubic symmetry [12]. It is an indirect band gap semiconductor with 2.5 eV, calculated by the local density approximation. Recently, doped with simple metals, Lu et al. [13]
studied a series of sodalite-based carbon structures, similar to the boron-doped diamond. Although they found these structures are all metastable, some of these structures show a superconductivity, e.g., the critical temperature of NaC$_6$ is 116 K. In this paper, we mainly study the mechanical properties of these eleven XC$_6$ phases (HC$_6$, LiC$_6$, NC$_6$, OC$_6$, FC$_6$, NaC$_6$, AlC$_6$, SiC$_6$, PC$_6$, SC$_6$, and ClC$_6$) which is of dynamical stability and, for comparison, C$_6$ is also calculated. In addition, the XC$_{12}$ structures are systematically explored, in which the X atom is from H to Ca, except He, Ne, and Ar. The doping-induced changes in elastic constant, modulus, the anisotropy of elasticity and acoustic velocity, Debye temperature, and the electronic structures are also studied.

### 2. Results and Discussion

As shown in Figure 1a, the structure of XC$_6$ is obtained by doping the X atom into the C$_6$ bcc structure at (0, 0, 0). It is of Im-3m symmetry (No. 229), consisting of two formula units (f.u.) per unit cell. Each C atom has four nearest neighbors with the bond angle of 90° or 120°. The XC$_6$ structure has four C$_4$ rings and eight C$_6$ rings. In Table 1, the calculated lattice parameter $a$ of C$_6$ has a good agreement with the available result [12], and is smaller than that of the XC$_6$ structures. By removing the corner atoms and only leaving the center X atom, the XC$_{12}$ structure is obtained (Figure 1b). All of the XC$_{12}$ phases are smaller than the corresponding XC$_6$ phases, but larger than the C$_6$ phase in the lattice parameter.

![Figure 1. Unit cell of XC$_6$ (a) and XC$_{12}$ (b). The black and blue spheres represent C and X atoms, respectively.](image)

**Table 1.** Calculated lattice parameter $a$, elastic constants $C_{ij}$ (GPa), mechanical stability, bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young’s modulus $E$ (GPa), Poisson’s ratio $\nu$, and $B/G$ ratio.

| Materials  | $a$   | $C_{11}$ | $C_{12}$ | $C_{44}$ | Mechanical Stability | $B$   | $G$   | $E$   | $\nu$ | $B/G$ |
|------------|-------|----------|----------|----------|----------------------|-------|-------|-------|-------|-------|
| Diamond    | 3.566 | 1053     | 120      | 563      | stable               | 431   | 522   | 1116  | 0.07  | 1.018 |
| C$_6$      | 4.375 | 803      | 95       | 307      | stable               | 331   | 325   | 735   | 0.13  | 1.018 |
|            | 4.34  |          |          |          |                      | 352   |       |       |       |       |
| HC$_6$     | 4.390 | 607      | 215      | 344      | stable               | 346   | 275   | 652   | 0.186 | 1.258 |
| LiC$_6$    | 4.491 | 634      | 118      | −78      | unstable             | 335   | 108   | 293   | 0.354 | 3.102 |
| NC$_6$     | 4.446 | 414      | 295      | 162      | stable               | 335   | 108   | 293   | 0.354 | 3.102 |
| OC$_6$     | 4.434 | 196      | 407      | 216      | unstable             |       |       |       |       |       |
| FC$_6$     | 4.427 | 269      | 370      | 335      | unstable             |       |       |       |       |       |
| NaC$_6$    | 4.566 | 659      | 91       | −548     | unstable             |       |       |       |       |       |
| AlC$_6$    | 4.618 | 497      | 162      | −59      | unstable             |       |       |       |       |       |
| SiC$_6$    | 4.614 | 527      | 165      | −66      | unstable             |       |       |       |       |       |
| PC$_6$     | 4.605 | 542      | 179      | −132     | unstable             |       |       |       |       |       |
| SC$_6$     | 4.608 | 683      | 115      | 90       | stable               | 305   | 146   | 378   | 0.294 | 2.089 |
| ClC$_6$    | 4.613 | 92       | 374      | 104      | unstable             |       |       |       |       |       |
are also dynamically stable [13]. The XC mechanical stability criteria of cubic phase are given by [15]:

\[ \Delta H_{\text{XC}} = (H_{\text{XC}} - H_X - 6H_C)/7, \] and \( \Delta H_{\text{XC}12} = (H_{\text{XC}12} - H_X - 12H_C)/13, \] and the calculated results are shown in Figure 2. The positive values indicate these phases are metastable. The two curves of the formation enthalpy follow a similar trend, where the F-doped carbides have the lowest \( \Delta H \), and the PC_6 and CC_12 have the largest \( \Delta H \) in XC_6 and XC_12, respectively. Compared to other doped elements of the second and the third periods in the XC_6 and XC_12, fluorine (F) possesses the largest electronegativity difference relative to C, leading to a stronger interaction between F and C atoms; thus, FC_6 and FC_12 phases are more stable.

![Figure 2. Formation enthalpy of XC_6 and XC_12.](image)

The calculated elastic constants and moduli are listed in Table 1. The generalized Born’s mechanical stability criteria of cubic phase are given by [15]: \( C_{11} > 0, C_{44} > 0, C_{11} > |C_{12}|, \) and \( (C_{11} + 2C_{12}) > 0. \) In Table 1, the C_6 and HC_6, NC_6, and SC_6 have the mechanical stability, and they are also dynamically stable [13]. The XC_12 has ten mechanically stable phases, but only six of these phases have the dynamical stability (BC_12, CC_12, PC_12, SC_12, ClC_12, and KC_12) due to the absence of
the imaginary frequency in the whole Brillouin zone (see Figures 3 and 4). The S is the only element that is capable to make not only XC6, but also XC12, stable.

Figure 3. Phonon spectra of dynamically stable phases (a) BC12; (b) CC12; (c) PC12; (d) SC12; (e) ClC12; and (f) KC12.

Figure 4. Phonon spectra of dynamically unstable phases (a) LiC12; (b) BeC12; (c) MgC12; and (d) AlC12.

By Voigt-Reuss-Hill approximations [16–18], the bulk modulus $B$ and shear modulus $G$ can be obtained, and the Young’s modulus $E$ and Poisson’s ratio $\nu$ are defined as $[19,20] E = 9BG/(3B + G)$ and $\nu = (3B - 2G)/(2(3B + G))$. HC$_6$ has the largest bulk modulus of 346 GPa, showing the best ability to resist the compression. The shear modulus is often used to qualitatively predict the hardness, and Young’s modulus $E$ is defined as the ratio between stress and strain to measure the stiffness of a solid material. In Table 1, C$_6$ is the largest in shear modulus and Young’s modulus, which means
that doping leads to a weakening in mechanical properties. The Poisson’s ratio exhibits the plasticity; usually, the larger the value, the better the plasticity. According to Pugh [21], C_6, HC_6, BC_{12}, CC_{12}, and PC_{12} are brittle materials (B/G < 1.75), while NC_6, SC_6, SC_{12}, CIC_{12}, and KC_{12} are ductile materials (B/G > 1.75). This conforms the calculated results of Poisson’s ratio.

The elastic anisotropy is important for the analysis on the mechanical property and, thus, the universal elastic anisotropy index \((A^{U})\), Zener anisotropy index \((A)\), and the percentage anisotropy in compressibility and shear are calculated. For the cubic phase, the universal elastic anisotropy index [22] is defined as: 

\[ A^{U} = 5G_{V}/G_{R} + B_{V}/B_{R} - 6 \]

The non-zero value suggests an anisotropy characteristic. Furthermore, it is known that \(C_{44}\) represents the resistance to deformation with respect to a shear stress applied across the (100) plane in the [010] direction, and \((C_{11} - C_{12})/2\) represents the resistance to shear deformation by a shear stress applied across the (110) plane in the [110] direction. For an isotropic crystal, the two shear resistances turn to identical. Therefore, Zener [23] introduced \(A = 2C_{44}/(C_{11} - C_{12})\) to quantify the extension of anisotropy. The value of 1.0 represents the isotropy, and any deviation from 1.0 indicates the degree of the shear anisotropy. The percentage anisotropy in compressibility and shear are given by: 

\[ A_{B} = (B_{V} - B_{R})/(B_{V} + B_{R}) \]

\[ A_{C} = (G_{V} - G_{R})/(G_{V} + G_{R}) \]

The \(A_{B}\) is always 0.0 for a cubic phase. As shown in Table 2, \(C_{6}\) has the lowest anisotropy. The universal elastic anisotropy index and the percentage anisotropy in shear is increasing with the atomic number of doped element for both \(XC_{6}\) and \(XC_{12}\), and the anisotropy which obtains from the shear anisotropic factor is also increasing, except \(SC_{6}\) and \(KC_{12}\). Furthermore, owing to the percentage anisotropy in shear of \(C_{6}, BC_{12}\), and \(CC_{12}\) being slight, they are almost isotropic.

Table 2. Universal elastic anisotropy index \((A^{U})\), Zener anisotropy index \((A)\), and percentage anisotropy in shear (\(A_{C}\)).

| Parameter | \(C_{6}\) | HC_{6} | NC_{6} | SC_{6} | BC_{12} | CC_{12} | PC_{12} | SC_{12} | CIC_{12} | KC_{12} |
|-----------|-----------|--------|--------|--------|---------|---------|---------|---------|---------|--------|
| \(A^{U}\) | 0.024     | 0.398  | 1.30   | 1.77   | 0.032   | 0.068   | 0.3814  | 2.752   | 11.084  | 21.252 |
| \(A\)    | 0.8672    | 1.755  | 2.723  | 0.317  | 0.851   | 0.788   | 0.572   | 4.048   | 11.346  | 0.0496 |
| \(A_{C}\) (%) | 0.243    | 3.752  | 11.567 | 15.016 | 0.315   | 0.678   | 3.714   | 21.596  | 53.098  | 68.612 |

The elastic anisotropies are calculated with the elastics anisotropy measures (ELAM) code [25,26] which makes the representations of non-isotropic materials easy and visual. For the cubic phase, the representation in \(xy\), \(xz\), and \(yz\) planes are identical, as a result, only the \(xy\) plane is presented. The 2D figures of the differences in each direction of Poisson’s ratio are shown in Figure 5. The maximum value curves and minimum positive value curves of \(C_{6}\) and \(XC_{6}\) stable phases are illustrated in Figure 5a,b, and those of \(XC_{12}\) stable phases are shown in Figure 5c,d. Particularly, the \(SC_{12}\) and \(CIC_{12}\) have the negative minimum Poisson’s ratio. It is seen that all of the structures are anisotropic and \(C_{6}\) has the lowest anisotropy, suggesting the doping increase the elastic anisotropy. The largest value of maximum curve is in the same direction of the lowest value of minimum positive value curve for each structure. Furthermore, for \(XC_{12}\) phases, the anisotropy of Poisson’s ratio is increasing with the atomic number. The negative minimum Poisson’s ratio of \(SC_{12}\) and \(CIC_{12}\) indicate these two phases have auxeticity [27], and \(CIC_{12}\) is more prominent than \(SC_{12}\).

The directional dependence of the Young’s modulus [28] are demonstrated in Figures 6 and 7. The distance from the origin of system of coordinate to the surface equals the Young’s modulus in this direction, and thus any departure from the sphere indicates the anisotropy. As shown, all of the phases are anisotropic, and the anisotropy of Young’s modulus is increasing with the doping atomic number. For the S-doped phases, which have stable \(XC_{6}\) and \(XC_{12}\) structures, the maximum (minimum) values of \(SC_{6}\) and \(SC_{12}\) are 650 (291) and 371 (175) GPa, respectively. The \(E_{\max}/E_{\min}\) ratio of \(SC_{6}\) (2.23) is slightly larger than that of \(SC_{12}\) (2.12), indicating the \(SC_{6}\) is more anisotropic.
Figure 5. 2D representations of Poisson’s ratio. (a) Maximum of \( C_6 \) and \( X C_6 \) stable phases; (b) minimum positive of \( C_6 \) and \( X C_6 \) stable phases; (c) maximum of \( X C_{12} \) stable phases; and (d) minimum positive and minimum negative of \( X C_{12} \) stable phases; particularly, only \( S C_{12} \) and \( C I C_{12} \) have the negative minimum Poisson’s ratio, the solid and dash lines represent the minimum positive and minimal negative, respectively.

Figure 6. Directional dependence of the Young’s modulus of \( C_6 \) (a); \( H C_6 \) (b); \( N C_6 \) (c); and \( S C_6 \) (d).
The acoustic velocity is a fundamental parameter to measure the chemical bonding characteristics, and it is determined by the symmetry of the crystal and propagation direction. Brugger [29] provided an efficient procedure to calculate the phase velocities of pure transverse and longitudinal modes from the single crystal elastic constants. The cubic structure only has three directions [001], [110], and [111] for the pure transverse and longitudinal modes and other directions are for the quasi-transverse and quasi-longitudinal waves. The acoustic velocities of a cubic phase in the principal directions are [30]:

\[ \Theta = \frac{h}{k_B} \left[ \frac{n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} \]

where \( \rho \) is the density of the structure, \( v_l \) is the longitudinal acoustic velocity, and \( v_{t1} \) and \( v_{t2} \) refer the first transverse mode and the second transverse mode, respectively. It should be noted that there is a misprint for equation of [110]\( v_{t1} \) in [30]. Here, the correct expression is given. Based on the elastic constants, the anisotropic properties of acoustic velocities indicate the elastic anisotropy in these crystals. As a fundamental physical parameter which correlates with many physical properties of solids, the Debye temperature can be obtained from the average acoustic velocity:

\[ \Theta_D = \frac{h}{k_B} \left[ \frac{n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} \]

The average acoustic velocity is:

\[ v_m = \left( \frac{2/v_{t1}^3 + 1/v_{t2}^3}{3} \right)^{-1/3} \]

where \( v_{t1} \) is the average longitudinal acoustic velocity, and \( v_{t2} \) is the average transverse acoustic velocity. The densities are increasing and the average acoustic velocities are decreasing with the atomic number, except NC\(_6\), which has a much smaller shear modulus. Compared to C\(_6\), the doping results in a decrease in the average acoustic velocity and Debye temperature. For the element S, which makes both XC\(_6\) and XC\(_{12}\) phases stable, the average acoustic velocity of SC\(_6\) decreases by
38.65% than C_6, and that of SC_{12} by 35.96%. Furthermore, it can be found that the Debye temperature is decreasing with the atomic number, except SC_6. The Θ_D characterizes the strength of the covalent bond in solids, so the strength of the covalent bond is lower for the phase which has the larger atomic number of doping atom.

Table 3. Density (g/cm^3), anisotropic acoustic velocities (m/s) and average acoustic velocity (m/s).

| Parameters | Diamond C_6 | HC_6 | NC_6 | SC_6 | BC_{12} | CC_{12} | PC_{12} | SC_{12} | ClC_{12} | KC_{12} |
|------------|--------------|------|------|------|---------|---------|---------|---------|----------|---------|
| ρ          | 3.517        | 2.857| 2.869| 3.252| 3.535   | 2.941   | 2.992   | 3.182   | 3.206    | 3.265   |
| [100]      | v_t          | 17,303| 16,765| 14,546| 11,283 | 13,900  | 15,251  | 15,175  | 14,237   | 11,128  | 10,339 |
|            | v_{11}       | 12,652| 10,366| 10,950| 7058   | 5046    | 8901    | 8457    | 6727     | 8848    | 9505   |
|            | v_{12}       | 12,652| 10,366| 10,950| 7058   | 5046    | 8901    | 8457    | 6727     | 8848    | 9505   |
| [110]      | v_t          | 18,079| 16,267| 16,222| 12,603 | 11,762  | 14,786  | 14,528  | 12,991   | 13,520  | 13,758 |
|            | v_{11}       | 11,517| 11,131| 8265  | 4277   | 8963    | 9652    | 9526    | 8999     | 4398    | 2822   |
|            | v_{12}       | 12,652| 10,366| 10,950| 7058   | 5046    | 8901    | 8457    | 6727     | 8848    | 9505   |
| [111]      | v_t          | 18,330| 16,989| 16,744| 13,013 | 10,956  | 14,628  | 14,306  | 12,548   | 14,228  | 14,722 |
|            | v_{11}       | 11,907| 10,882| 9247  | 5367   | 7877    | 9409    | 9184    | 8239     | 6244    | 5952   |
|            | v_{12}       | 12,652| 10,366| 10,950| 7058   | 5046    | 8901    | 8457    | 6727     | 8848    | 9505   |
|            | v_{13}       | 11,907| 10,882| 9247  | 5367   | 7877    | 9409    | 9184    | 8239     | 6244    | 5952   |
| Θ_D        | 2219         | 1823 | 1766 | 1047  | 1118   | 1598    | 1551    | 1303    | 1165     | 1069    | 926    |

Figure 8 shows the electronic band structure and density of state (DOS) of XC_{12} stable phases. The dash line represents the Fermi level (E_F). The electronic properties of XC_6 have been studied in [13]. For XC_{12}, all of the band structures cross the Fermi level in the Brillouin zone, showing the metallic nature. The conduction band and valence band are mainly characterized by the contributions of C-p states, whereas the DOS near the Fermi level originated from the p orbital electrons of the doped element, except the ClC_{12} and KC_{12}. 

![Figure 8](image)
Figure 8. Cont.
Figure 8. Electronic band structure and density of state of BC$_{12}$ (a); CC$_{12}$ (b); PC$_{12}$ (c); SC$_{12}$ (d); ClC$_{12}$ (e); and KC$_{12}$ (f).

3. Computational Methods

The calculations are performed with the first-principles calculations. The structural optimizations are using the density functional theory (DFT) [31,32] with the generalized gradient approximation (GGA), which is parameterized by Perdew, Burke, and Ernzerhof (PBE) [33]. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [34] was used in the geometry optimization, and the total energy convergence tests are within 1 meV/atom. When the total energy is $5.0 \times 10^{-6}$ eV/atom, the maximum ionic Hellmann-Feynman force is 0.01 eV/Å, the maximum stress is 0.02 GPa and the maximum ionic displacement is $5.0 \times 10^{-4}$ Å, the structural relaxation will stop. The energy cutoff is 400 eV, and the K-points separation is 0.02 Å$^{-1}$ in the Brillouin zone.

4. Conclusions

By using the first-principles calculations, the analyses on the mechanical properties of XC$_6$ and the further exploration of XC$_{12}$ structures are given. The formation enthalpies of dynamically stable XC$_6$
phases and all of the XC\textsubscript{12} structures, and the elastic constants, are calculated. There are ten structures which have the mechanical and dynamical stability (C\textsubscript{6}, HC\textsubscript{6}, NC\textsubscript{6}, SC\textsubscript{6}, BC\textsubscript{12}, CC\textsubscript{12}, PC\textsubscript{12}, SC\textsubscript{12}, ClC\textsubscript{12}, and KC\textsubscript{12}). The elastic modulus and anisotropy of the ten structures are studied and, in these structures, C\textsubscript{6} has the lowest elastic anisotropy and the anisotropy increases with the atomic number. The doping leads to the weakening in mechanical properties and the increase in the elastic anisotropy. In addition, Debye temperatures and the anisotropy of acoustic velocities are also studied. The electronic properties studies show the metallic characteristic for XC\textsubscript{6} and XC\textsubscript{12} phases.

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