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## Exceptional Ideal Strength of Carbon Clathrates

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We study by means of *ab initio* calculations the ideal tensile and shear strengths of the C-46 clathrate phase. While its bulk modulus and elastic constants are smaller than in diamond, its strength is found to be in all directions larger than the critical stresses associated with the diamond {111} planes of easy slip. This can be related to the frustration by the clathrate cage structure of the diamond to graphite instability under hydrostatic stress conditions. The criteria for designing strong materials are discussed.

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The search for ultrahard materials has generated much work in the last few decades, both for its technological implications and the fundamental difficulty in finding relevant criteria for the design of novel structures [1,2]. In particular, as the full study of real materials with moving dislocations remains a challenge to computer simulations, there have been numerous attempts to relate hardness to the properties of the ideal crystal at equilibrium (bond length, ionicity, band gap, etc.) or close to equilibrium (bulk modulus, elastic constant, etc.) [3].

Recently, several theoretical works [4–6] focused on studying the plastic properties of diamond, the hardest known material. In particular, the stress/strain load curve beyond the elastic regime was studied in order to provide a value for the ideal shear and tensile strengths in various directions. This theoretical strength [7] is the maximum stress that a *perfect crystal* can sustain before yielding to a plastic deformation. Even though this theoretical strength is an upper limit for the real strength, such calculations were very successful in explaining that the {111} plane is the easiest slip plane in diamond. Further, it was shown [4,6] that under <111> tensile load or shear along the {111} slip systems, the diamond was unstable with respect to the graphite phase, a theoretical confirmation of the Gogotsi *et al.* [8] experimental results for the indentation of diamond.

In this Letter, we study by means of *ab initio* calculations the ideal strength under tensile and shear constraints of the C-46 clathrate phase, a carbon cage-like material. While the bulk modulus and elastic constants are found to be smaller than these of diamond (noted C-2 in what follows), its strength is shown to be in all directions larger than the ones associated with the C-2 {111} planes of easy cleavage. This is interpreted in terms of the cage structure of the clathrates, which frustrates both the existence of planes of easy slip and the instability of carbon  $sp^3$  towards graphite.

Column-IV clathrates [9] are semiconducting compounds composed of face-sharing  $X_{20}$ ,  $X_{24}$ , and/or  $X_{28}$  clusters ( $X = \text{Si, Ge}$ ). In the case of the  $X_{46}$  type-I

structure studied here (Fig. 1),  $X_{20}$  and  $X_{24}$  clusters form a simple cubic structure with 46 atoms per unit cell. As the clusters share faces, all atoms are in a fourfold diamondlike  $sp^3$  configuration. Such clathrate phases have recently attracted much attention for their large band gap [10–12] and the unique properties induced by endohedral doping: superconductivity [13], thermoelectric power [14], stabilization under pressure [15], and further increase of the band gap [16].

While silicon and germanium clathrates have been synthesized, the existence of a carbon analog has not been reported so far, even though cage-like materials with building blocks smaller than the  $C_{60}$ , such as thin films prepared by deposition of small clusters [17] or  $C_{36}$

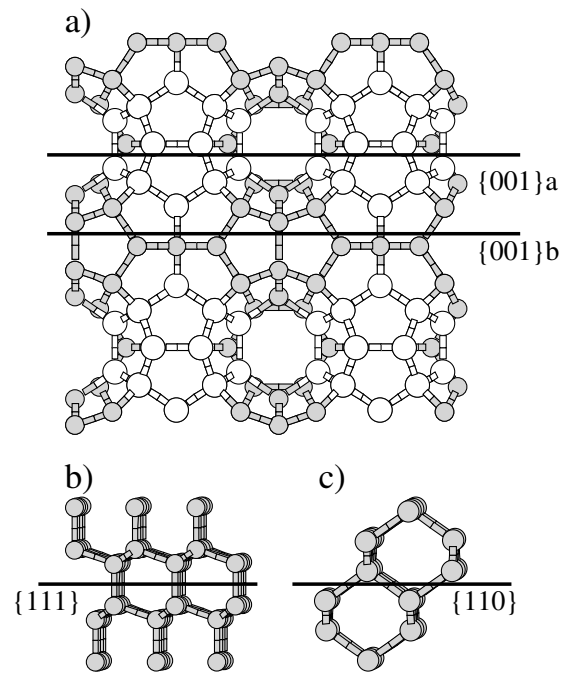


FIG. 1. Symbolic representation of (a) the C-46 clathrate, and (b),(c) the diamond phase. Different slip planes are indicated. In (a), a few  $C_{20}$  cages are indicated by white atoms.

networks [18], have been prepared. What we seek to show here, taking the clathrates as an example, is that allotropic phases of carbon, and cagelike structures, in particular, could exhibit mechanical properties superior to those of diamond. On more general grounds, we emphasize the importance of the crystallographic structure and phase stability in governing the plastic properties of materials.

Our calculations are performed within the local density approximation [19] to the density functional theory [20]. Our computational framework is identical to the one of Refs. [4,21] where the SIESTA package [22], based on a strictly localized atomiclike numerical basis, was used to study the properties of the C-2 and 3D polymerized  $C_{60}$  (poly- $C_{60}$ ) phases. Unit cells containing 46, 92, and 138 carbon atoms have been used to study the evolution of the stress in various strain directions.

The stability, elastic, and electronic properties of various carbon clathrates have been studied by a few groups already [12,23–27]. For the C-46 phase, we find here an average C-C bond length of 1.561 Å, which can be compared to the 1.548 Å we obtain for diamond. From these values, and using the recent empirical formula provided in Ref. [3], we find an estimated value for the Vickers hardness of 92.7 and 83.3 GPa for the C-2 and C-46 phases, respectively.

In previous work, the bulk modulus  $B_0$  of clathrates was found to be  $\sim 12\%$ – $15\%$  smaller than the one of diamond [23–26], as expected for a low density phase. This is what we find as well with  $B_0 = 398$  and 465 GPa for C-46 and C-2, respectively. In addition, our values for the  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  elastic coefficients are 960, 117, and 472 GPa, which we compare to 1130, 132, and 612 GPa for the C-2 phase [28]. Again, and in good agreement with the Hartree-Fock results of Ref. [26], the elastic coefficients of clathrates are significantly smaller than their diamond analogs.

Beyond the elastic response, we now study the clathrate plastic properties. We first reproduce some of the results

obtained for diamond in Refs. [4–6]. Under applied constraints, both atomic forces and components of the stress tensor orthogonal to the direction of strain were brought to zero using a conjugate-gradient algorithm, with criteria of 0.1 eV/Å and 1 GPa for forces and stresses, respectively. We provide in Fig. 2 our strain/stress load curve (full line) for pulling the C-2 phase along the  $\langle 111 \rangle$  direction [Fig. 1(b)]. Our theoretical strength is of 90 GPa, a value in good agreement with the 90 and 93 GPa of Refs. [5,6], where plane-wave bases were used. In the case of shearing the  $\{111\}$  slip plane along the  $\langle 2-1-1 \rangle$  direction [see Fig. 2(b)], we find a theoretical strength of 96 GPa, in good agreement with the 95 and 93 GPa of Refs. [4,6].

These results are now compared to the one we obtain for the clathrate structure. In the case of a tensile load [Fig. 2(a)] along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  directions, we find that the clathrate phase can sustain stresses as large as 113, 114, and 120 GPa, respectively. The structure retains tetragonal symmetry. Such results clearly lead to the surprising conclusion that, in all directions, *the ideal tensile strength in C-46 is larger by at least 25% than the ideal tensile strength of C-2 in its  $\langle 111 \rangle$  direction*. We further explore the case of shearing [Fig. 2(b)]. We find critical shear stresses of 101, 102, and 110 GPa for the  $\{100\}\langle 010 \rangle$ ,  $\{110\}\langle 001 \rangle$ , and  $\{111\}\langle 2-1-1 \rangle$  slip systems. Again, these values are larger than the 96 GPa strength found for the C-2  $\{111\}$  cleavage plane, even though the difference (5%–15%) is not as large as in the tensile case.

In diamond, the strength under tensile load in the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  directions was found to be 225 and 130 GPa, respectively [5], which is much larger than the 90 GPa value obtained for the  $\langle 111 \rangle$  direction. This was analyzed [5] to originate in that along the “strong directions,” the C-C bonds make an angle with the applied force, so that additional work must be performed to induce angular distortions. On the contrary, in the C-2  $\langle 111 \rangle$  direction, all bonds are parallel to the constraint [see Figs. 1(b) and 1(c)]. In clathrates, due to the radial distribution of bonds

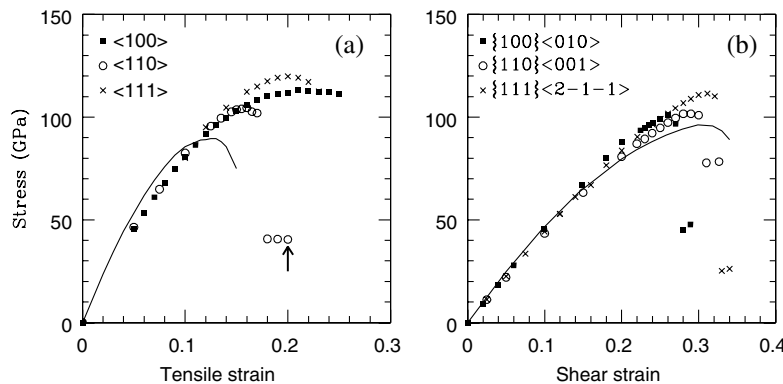


FIG. 2. Stress vs strain under (a) tensile load and (b) shear load, for several directions. The full lines correspond to the diamond phase (see text). In the case of C-46, the stress directions and slip planes are indicated next to their corresponding symbols. The arrow points to the structure shown in Fig. 3.

around the  $C_{20}$  and  $C_{24}$  clusters, any plane would cut bonds at different angles [Fig. 1(a)], thus resulting in an “averaged” strength larger than the one associated with the weakest  $\langle 111 \rangle$  direction in diamond. This distribution of angles explains as well that the clathrates are much more isotropic than diamond, with strength varying at most by a few percent from one direction to another. In particular, we do not expect to find directions or planes with a tensile/shear ideal strength significantly smaller than the ones we have explicitly calculated above.

Further, as shown in Refs. [4–6], the diamond phase is unstable with respect to graphite under load or shear along the  $\langle 111 \rangle$  direction or  $\{111\}$  slip plane. In the case of clathrates, such a transition is frustrated by the cage-like structure of the network. For example, and as shown in Fig. 3 for  $\langle 110 \rangle$  tensile strains larger than  $\sim 0.17$ , the clathrate relaxes towards a mixed  $sp^2$ - $sp^3$  structure with 70% of threefold atoms. The obtained structure (Fig. 3) is not graphitic but rather can be described as a stacking of “ $C_{20}$  layers” connected by a few fourfold atoms [29]. As the layers remain connected, the stress does not collapse to zero but adopts a lower value. Similar results are obtained under shear with the formation of various  $sp^2$ - $sp^3$  networks. The analysis of the ideal shear strength of silicon Si-46, which is found to be smaller than that of Si diamond in the  $\langle 111 \rangle$  direction [30], indicates that the  $sp^2/sp^3$  competition in carbon systems is the main reason explaining the low value of the minimum ideal strength of diamond.

A difficult issue is the relation between the ideal strength and the plastic properties of a real crystal. In particular, how will clathrate systems, and cage-like materials in general, behave in a scratching experiment or under an indenter tip? Even though empirical correlation laws between strength and hardness are used routinely to test materials, the complexity of the distribution of local

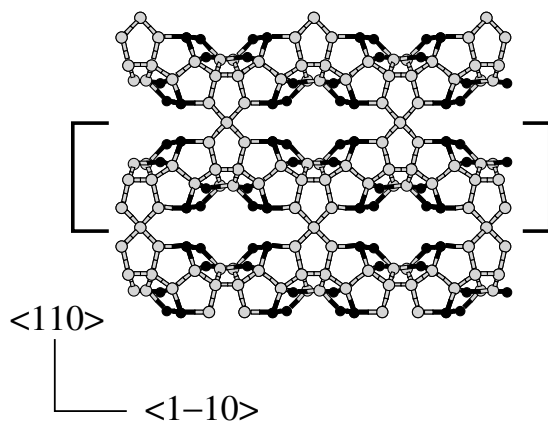


FIG. 3. Representation in the  $\{001\}$  plane of the C-46 clathrate under an  $\epsilon = 0.2$   $\langle 110 \rangle$  tensile strain, with the opening of the “lines” of hexagons. The formation of  $C_{20}$  layers is indicated by the two brackets. Black atoms are threefold coordinated. A  $1.7 \text{ \AA}$  criterion is chosen for bond breaking.

constraints in such mechanical tests and the role of dislocations and fractures are several factors that hinder the relations between the ideal strength and, e.g., the measured hardness [31]. We can, however, adopt a pragmatical point of view and rely on the experimental observations.

In the indentation experiment of Gogotsi *et al.* [8], a transformation of diamond into graphite was observed under the tip of a sharp diamond indenter. Further, the nominal stress at the maximum load was found to be slightly below 100 GPa, that is, in the same pressure range than the diamond to graphite transition predicted theoretically. Such results are consistent with earlier analysis [32] that under polishing, diamond transforms into “less dense forms of carbon,” suggesting again a diamond to graphite transformation.

These results show that under a sharp indenter, stresses close to the theoretical strengths can be reached locally. Further, the observed mechanisms of plastic yield are consistent with the diamond to graphite transition. This invites one to interpret the experimental results [33] that various carbon-based cage-like phases are observed to be able to scratch diamond. Such phases were identified to be 3D poly- $C_{60}$  structures [21,33–36]. However, the bulk modulus or elastic constants of various poly- $C_{60}$  phases were calculated [21,34,36] to be significantly smaller than their diamond analogs so that the interpretation of the experimental results and their relation to hardness [37] remained elusive.

Our study clearly indicates that despite smaller bulk modulus or shear coefficients, the carbon clathrate phase is superior to diamond in that it does not offer planes of cleavage as easily as the C-2  $\{111\}$  plane and does not exhibit any instability towards graphite under constraint, allowing them to withstand larger critical stresses than the one at which this instability occurs in diamond. In a scratching experiment, local constraints induced by surface asperities can induce a transformation into graphite that will take place exclusively in the diamond phase. The removal of the graphite layer produced in the scratching process will therefore lead to a permanent deformation of the diamond surface.

We emphasize that the exceptional strength of the clathrate phase could not be expected from the analysis of its equilibrium or elastic properties. In particular, the phase stability (or instability) under constraints is a crucial property that cannot be inferred from the linear regime behavior. This shows that in order to design strong or hard materials, *predictions based on the definition of a “bond chemical hardness” (length, ionicity, etc.) should be complemented by what we may call “crystallographic hardness.”* The carbon clathrates offer an excellent compromise between these two criteria. Further studies of the various poly- $C_{60}$  phases beyond the linear elastic regime are needed to see if the properties of the clathrates can be extended to other carbon cage-like materials with different  $sp^3/sp^2$  ratios and density.

In conclusion, we have shown that the minimum strength of the carbon clathrates should be larger than that of diamond. In particular, the cagelike structure of clathrates frustrates the presence of easy slip planes and any instability towards the graphite phase. Such results provide a first explanation for the reports on the existence of pure carbon phases able to scratch diamond. In addition, new criteria for the design of materials with improved strength and hardness—based on topological considerations and phase stability—have been considered.

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- [30] We find values of 22 and 18 GPa for the tensile ideal strength of Si-2 and Si-46 along the  $\langle 111 \rangle$  and  $\langle 100 \rangle$  directions, respectively.
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