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Hardness of T-carbon: Density functional theory calculations

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We reconsider and interpret the mechanical properties of the recently proposed allotrope of carbon, T-carbon [Sheng *et al.*, Phys. Rev. Lett. **106**, 155703 (2011)], using density functional theory in combination with different empirical hardness models. In contrast with the early estimation based on Gao *et al.*'s model, which attributes to T-carbon a high Vickers hardness of 61 GPa comparable to that of superhard cubic boron nitride (c-BN), we find that T-carbon is not a superhard material, since its Vickers hardness does not exceed 10 GPa. Besides providing clear evidence for the absence of superhardness in T-carbon, we discuss the physical reasons behind the failure of Gao *et al.*'s and Šimůnek and Vackář's (SV) models in predicting the hardness of T-carbon, residing in their improper treatment of the highly anisotropic distribution of quasi-sp^3-like C-C hybrids. A possible remedy for the Gao *et al.* and SV models based on the concept of the superatom is suggested, which indeed yields a Vickers hardness of about 8 GPa.

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Recently, on the basis of first-principles calculations Sheng *et al.* proposed a carbon allotrope which they named T-carbon.[1] Strictly speaking, its actual stability needs a very large negative pressure which is far beyond currently available technologies. Structurally, this phase can be obtained by substituting each carbon atom in diamond with a carbon tetrahedron (Fig. 1), and it thus crystallizes in the same cubic structure as diamond (space group $Fd\bar{3}m$) with the carbon atoms at the Wyckoff site 32e (0.0706,0.0706,0.0706). It has been noted that T-carbon has a large lattice constant of 7.52 Å and a low bulk modulus of $B = 169$ GPa, only 36.4% of the bulk modulus of diamond.[1] In particular, its equilibrium density, 1.50 g/cm^3, is the smallest among diamond (cubic and hexagonal diamond),[1] graphite,[1] M-carbon,[2] body-centered tetragonal C$_4$,[3] W-carbon,[4] and chiral carbon,[5] as well as the newly proposed dense hp3-, tI12-, and tP12-carbon[6] phases. This results in a highly porous structural pattern, which can be viewed as a diamondlike array of superatoms (tetrahedral C$_4$ clusters), as depicted in Fig. 1. Given this peculiar clusterized arrangement of atoms exhibiting a quite low shear modulus of $G = 70$ GPa,[1] it is very surprising that T-carbon was predicted to be superhard, with an exceptionally high Vickers hardness (H_v) of 61.1 GPa,[1] comparable to that of superhard cubic boron nitride (c-BN).

The aim of our present study is to elucidate the origin of this anomalous hardness. We do this by exploring in detail the mechanical properties of T-carbon through the application of several different empirical approaches: the Gao *et al.* formula,[7] the Šimůnek-Vackář (SV) model,[8] and our recently proposed empirical treatment based on the Pugh modulus ratio.[9] Our systematic analysis provides an unambiguous and physically sound result: T-carbon is not hard. We will show that the conventional application of the Gao *et al.* and SV models leads to a much too high Vickers hardness, $H_v^{\text{Gao}} = 61.1$ GPa and $H_v^{\text{SV}} = 40.5$ GPa, substantially overestimated with respect to the value obtained using our formalism, $H_v^{\text{Chen}} = 5.6$ GPa. The prediction of a low Vickers hardness in T-carbon is consistent with the estimation of a low shear strength [7.3 GPa along the (100)⟨001⟩ slip system], which represents the upper bound of the mechanical strength.

The improper assignments derived by a conventional application of the Gao *et al.* and SV models can be attributed to the fact that these two models assume that the chemical bonds, which are significant for hardness, are distributed *uniformly* in the lattice. But in T-carbon, as already pointed out be Sheng *et al.*[1] although the carbon atoms are tetrahedrally coordinated and apparently resemble a three-dimensional quasi-sp^3-like hybrid,[1] their bonds are ordered in an extremely anisotropic and porous framework, very different from the bonding distribution in an ideal sp^3 hybrid. We propose a remedy to cure the limitations of the Gao *et al.* and SV models in dealing with anisotropic and porous systems by considering each carbon tetrahedron cluster as an artificial superatom. Indeed, this clusterlike approach leads to a low Vickers hardness in the range of 7–8 GPa, in agreement with the estimated value of 5.6 GPa using our proposed model.[9]

All calculations were performed using the Vienna *ab initio* simulation package[10] (VASP) in the framework of density functional theory (DFT), and we adopted the Perdew, Burke, and Ernzerhof approximation[11] to treat the exchange-correlation kernel. Well-converged results were obtained using an energy cutoff of 500 eV and a k-point grid 11 × 11 × 11.[12] The DFT results were then employed as input for the three different hardness empirical models, with which we have computed the Vickers hardness H_v:

(a) The Gao *et al.* model:[7]

$$H_v^{\text{Gao}} = 350\big[\big(N_e^{2/3}\big)e^{-1.191 f_i}/(d^{2.5})\big], \tag{1}$$

where N_e is the electron density of valence electrons per Å^3, d is the bond length, and f_i is the ionicity of the chemical bond in the crystal on the Phillips scale. As already mentioned, this model gives $H_v^{\text{Gao}} = 61.1$ GPa.[1]

(b) The SV model:[8]

$$H_v^{\text{SV}} = \frac{C}{\Omega}\sqrt{e_i e_i}/(d_{ii} n_{ii}), \tag{2}$$

TABLE I. Comparison between measured (H_v^{expt}) and theoretically computed values of the Vickers hardness values (in GPa), along with available bulk modulus (B, GPa), shear modulus (G, GPa), and Pugh modulus ratio $k = G/B$. The last column lists the references of previously reported and calculated elastic moduli of bulk and shear and experimentally measured Vickers hardness.

	G	B	k	H_v^{Chen}	H_v^{expt}	H_v^{Gao}	H_v^{SV}	References
Diamond	536	442	1.211	95.7	60–120	93.6	95.4	15,17
	548	466	1.178	93.9	115			15,18
	520	432	1.205	93.5	95 ± 5			16,19
	535	443	1.208	95.4				14
c-BC$_2$N	446	403	1.107	76.9	62,75	78	71.9	17,18,20
	445	408	1.091	75.4	76 ± 4			14,18,21
c-BC$_5$	394	376	1.048	66.7	71,73			18,22
c-BN	405	400	1.014	65.2	47	64.5	63.2	17,23
	403	404	0.999	63.8	55			15,21
	382	376	1.017	63.1	62			15,21
	404	384	1.053	68.2	66			24,25
	409	400	1.023	66.2	63 ± 5			14
γ-B$_{28}$	236	224	1.054	49.0	50,58 ± 5			26–28
ReB$_2$	273	382	0.715	32.9	48 ± 5			29,32
	273	383	0.712	32.8	39.5 ± 2.5			31
	183	230	0.795	29.3	27 ± 4.7			31
	289	365	0.794	39.0	37.2–40.5			33,37
	283	264	0.808	39.4	28			33,38,39
	350	343	0.769	35.4	39.3–26.2			34,38,39
					30.8–35.8			35
					18			36
					30.1 ± 1.3			40
					37 ± 1.2			41
T-carbon	70	169	0.414	5.6		61.1	40.5	1

where C is a constant (1550) and Ω is the equilibrium volume of T-carbon. $e_i = Z_i/R_i$ represents the reference energy, with Z_i indicating the valence number of element i. For carbon $e_i = 4.121$ (taken from Ref. 8). n_{ii} and d_{ii} are the number of bonds and bonding lengths between atom i and neighboring atoms. In T-carbon, each carbon has four nearest neighbors with two different bonding lengths: three intratetrahedron carbon-carbon bonds of length 1.502 Å and one intertetrahedron bond of length 1.417 Å.[1] By using the average bonding length of 1.480 75 Å we obtained $H_v = (1550/26.5785) \times 4.121/(1.480\,75 \times 4) = 40.5$ GPa, which is 33.5% smaller than the corresponding value from the Gao model.[1]

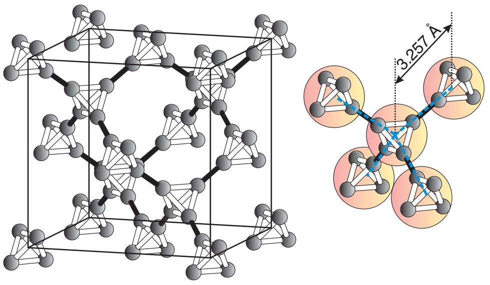

FIG. 1. (Color online) Lattice structure of T-carbon (space group $Fd\bar{3}m$). By considering each carbon tetrahedron (C$_4$ unit) as an artificial superatom, the corresponding structure is isotypic to that of diamond. The local environment of each superatom is illustrated in the right panel.

(c) The Chen *et al.* model.[9] This is the empirical formula we recently proposed, based on the Pugh modulus ratio $k = G/B$:[13]

$$H_v^{\text{Chen}} = 2(k^2 G)^{0.585} - 3. \tag{3}$$

This model not only reproduces well the experimental values of Vickers hardness of a series of hard materials including all experimentally verified superhard materials (see Fig. 2 and Table I), but also provides a theoretical foundation for Teter's empirical correlation[14] in its simplified form.[9]

Before discussing the results for T-carbon we start by presenting some general considerations regarding the calculation of the Vickers hardness and the trustability of our proposed model.[9] Hardness is a highly complex property, which depends on the loading force and on the quality of samples (i.e., the presence of defects such as vacancies and dislocations). Because Vickers hardness is experimentally measured as a function of the applied loading forces, the saturated hardness value (or experimental load-invariant indentation hardness) is usually considered to be the hardness value of a given material. Therefore, the theoretically estimated Vickers hardness within Gao *et al.*'s, SV's, and Chen *et al.*'s models should be directly compared to the experimentally saturated hardness value of polycrystalline materials. The experimental and theoretical values of H_v for the experimentally verified superhard materials (diamond, c-BC$_2$N, c-BN, c-BC$_5$, and γ-B$_{28}$) are summarized in Fig. 2 and Table I. The experimental results are highly scattered, reflecting the inherent

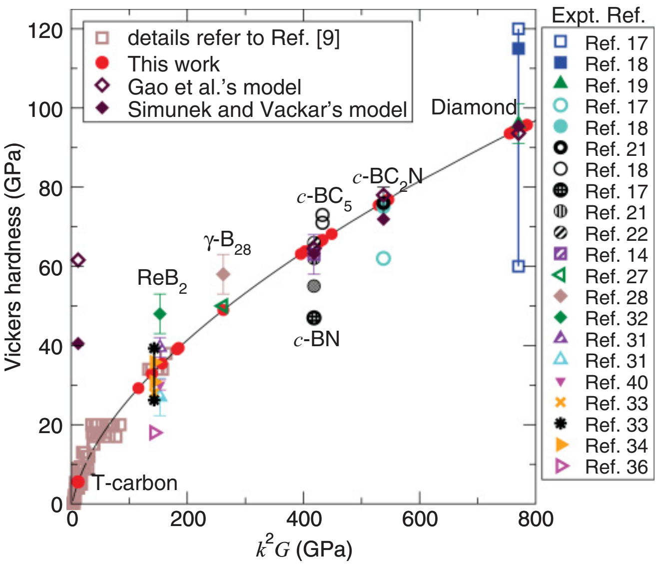

FIG. 2. (Color online) Vickers hardness H_v as a function of the product (k^2G) of the squared Pugh modulus ratio ($k = G/B$), and shear modulus (G). The curve corresponds to the empirical relation of Eq. (3). (For other data and more details, see Ref. 9.) The elastic moduli and experimental Vickers hardnesses are collected in Table I. Note the huge discrepancies among the three theoretical estimations for T-carbon.

difficulties in achieving a trustable and precise estimation of hardness. For instance, the reported values for the hardness of diamond, the archetype superhard material, range from 60 to 120 GPa.[16–19] Similar trends have been observed for the other two well-known superhard materials c-BC$_2$N and c-BN. The most typical case is probably ReB$_2$, whose actual hardness has been extensively debated[29–42] since the first value of its Vickers hardness (48 ± 5 GPa at the loading force of 0.49 N) was reported.[31] Depending on different samples, synthetic methods, and measurement techniques, the values obtained range from 18 to 48 GPa (Table I). In contrast to experimental results, theoretical estimations of the Vickers hardness given by different models[7–9] agree within a few gigapascals, including the data obtained by our proposed model [Eq. (3)]. Overall, the comparative trend displayed in Fig. 2 provides robust evidence for the reliability of our proposed formalism.[9]

Now, let us turn our attention to T-carbon. By using the values of the shear and bulk moduli from Ref. 1 as input ($B = 169$ GPa and $G = 70$ GPa) for Eq. (3) we obtain a Vickers hardness of 5.6 GPa, dramatically smaller than the corresponding Gao *et al.* (61.1 GPa) and SV (40.5 GPa) estimations. Furthermore, we noted that Sneddon defined the concept of ideal elastic hardness by $H_{id} = \frac{E\cot\phi}{2(1-v^2)}$ where E is Young's modulus, v is Poisson's ratio, and $\cot\phi \approx 0.5$ for the standard pyramid indentation,[43] and suggested that the real hardness would be $(0.01–0.2)H_{id}$ at high loads.[43] Utilizing this definition and the derived $E = 185$ GPa, the real hardness for T-carbon should be in the range from 0.5 to 10 GPa, in agreement with our obtained value. In particular, it is still necessary to note that the occurrence of this serious discrepancy among the three different methods (Gao *et al.*'s, SV's and Chen *et al.*'s models), which is not observed for the other test cases of Fig. 2 and Table I, urges for a clarification aiming to discern which method provides the most reliable description of the hardness of T-carbon and, consequently, to help us to answer a naturally arising question: is T-carbon a real superhard material?

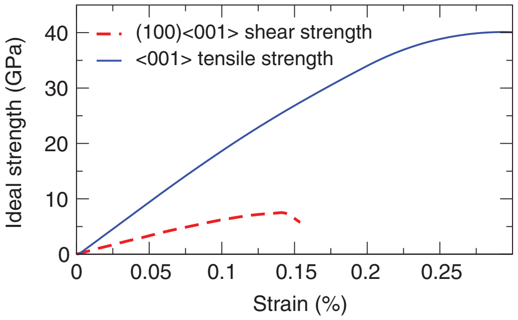

FIG. 3. (Color online) DFT-calculated ideal tensile and shear strengths of T-carbon.

A useful concept for understanding high mechanical strength—but still relying on elastic properties—is based on the ideal shear and tensile strengths[45] at which a material is becoming unstable under direction-dependent deformation strains.[44] To shed some light on the nature of T-carbon we have thus investigated the ideal tensile strength along the $\langle 001\rangle$ direction and the shear strength along the $(100)\langle 001\rangle$ slip system. We found a tensile strength of 40.1 GPa along the $\langle 001\rangle$ direction and a shear strength of 7.3 GPa in the $(100)\langle 001\rangle$ slip system (see Fig. 3). Therefore, we can conclude that the failure mode in T-carbon is dominated by the shear deformation type in the $(100)\langle 001\rangle$ slip system. The calculated shear stress of 7.3 GPa basically sets the upper bound on its mechanical strength at zero pressure,[44,45] because the ideal strength is the stress where a defect-free crystal becomes unstable and undergoes spontaneous plastic deformation. It is well known that the measurement of hardness has to first encounter the elastic deformation and then experience permanent plastic deformation. Therefore, it can be conjectured that the hardness of T-carbon should not exceed 7.3 GPa. These arguments provide a strong support for our estimated Vickers hardness of 5.6 GPa on the basis of Eq. (3).

In order to gain further insights into this intricate subject and to reach a consistent and satisfactory conclusion on the hardness of T-carbon, we consider now the relation between hardness and brittleness on the basis of the Pugh modulus ratio[13]. There is no doubt that all experimentally verified superhard materials, such as diamond, c-BN, c-BC$_2$N, γ-B$_{28}$, and c-BC$_5$ are intrinsically brittle. As shown in Table I the Pugh modulus ratios[13] of these superhard materials [$k = 1.211–1.178$ (diamond), 0.999–1.053 (c-BN), 1.107–1.091 (c-BC$_2$N), 1.054 (γ-B$_{28}$), and 1.048 (c-BC$_5$)] are larger than 1.0. They clearly obey the empirical relation that considers the Pugh modulus ratio as an indicator of the brittleness or ductility of materials. The higher k, the more brittle (and less ductile) the material is. Pugh proposed that when k is larger than 0.571 materials are brittle and with k less than 0.571 materials are ductile.[13] This relation has been extensively applied not only to metals and alloys but also to high-strength materials. In the case of T-carbon, the calculated Pugh modulus ratio $k = 0.414$ is smaller than 0.571, clearly in the range of ductility. The ductile behavior of T-carbon is a further indication of its nonsuperhardness.

On the basis of the above considerations we can now understand why T-carbon is not a superhard material. One common feature of superhard materials is that they not only need a three-dimensional network composed of short, strong, and covalent bonds[46] but also have a uniform distribution of strong covalent bonds. The prototypical example is diamond, which is characterized by an isotropic array of tetrahedrally bonded sp^3 carbon atoms. Conversely, in soft graphite the sp^2-type covalent bonds, though strong, are localized in two-dimensional sheets. At first glance, T-carbon seems to be a good candidate for superhardness since each carbon atom has four nearest-neighboring carbon atoms tetrahedrally bonded by short and strong carbon-carbon covalent bonds. However, due to the extremely anisotropic arrangement of these carbon-carbon bonds and the associated formation of a large proportion of porosity in the lattice space as well as the low density of the bonds, the framework of T-carbon will be more easily bendable in comparison with that of diamond, as manifested by its low shear strength.

Having this in mind, we can look back at the Gao *et al.* and SV models. Although these two models perform very well for many hard materials, they deliver questionable numbers for T-carbon, in sharp contrast with our findings, as we have documented above. The reason for this apparent failure is that in these two models all bonds are treated as uniformly distributed in the lattice space. Clearly, this constraint will not affect the predictions for an isotropic material but it will be inadequate to describe the hardness of extremely anisotropic compounds such as T-carbon. However, if we give a closer look at each individual C_4 tetrahedral unit (see Fig. 1), the distribution of six strong carbon-carbon covalent bonds within each C_4 unit is highly dense. It is therefore to be expected that the Vickers hardness of each individual C_4 unit will be comparable to (or even harder than) that of diamond because the bond density and strength within each C_4 unit are higher than those of diamond. The strength and rigidity of each individual C_4 unit appear to be so strong that the unit cannot be broken easily. Based on this fact, in order to render Gao *et al.*'s and SV's methods applicable to T-carbon, each carbon tetrahedron (C_4 unit) is considered to be an artificial superatom (see right panel of Fig. 1). The cubic unit cell of T-carbon consists of eight superatoms and each superatom has four nearest neighbors with the bonding length of $d = 3.257$ Å . In terms of Gao *et al.*'s and SV's methods, this distance d should be the bonding length between exact atomic positions with positively charged cores, representing the real force center of each atom. Based on our assumption, the distance d is defined as the spatial separation between two nearest-neighbor superatom positions, $d = 3.257$ Å. Although it remains disputable whether the center of mass of the C_4 superatom could be assigned its real force center (thus allowing the applicability of Gao *et al.*'s and SV's models), the high strength and rigidity of each individual C_4 unit manifested by the dense and strong carbon-carbon bonds seem to validate this assumption on d. Obviously, each superatom contains 16 valence electrons, and $N_e = 8/26.61 = 0.3$. By inserting these values of d and N_e in Gao *et al.*'s formula [Eq. (1)], we derive a Vickers hardness of 8.2 GPa, in agreement with our value of 5.6 GPa. To apply the same adjustment to the SV model one needs to define the crucial parameter R_i for the superatom. From our first-principles calculations, it can be inferred that $R_i = 2.32$ Å represents the optimum radius containing all 16 valence electrons for each superatom. By inserting $e_i = 16/2.32 = 6.896$ in Eq. (2), a Vickers hardness of 7.7 GPa is obtained, again in agreement with our analysis. Within this superatom approach, all three methods discussed in the present paper convey the same answer: T-carbon is not superhard. The anomalous behavior of the Gao *et al.* and SV models observed in Fig. 2 for T-carbon is cured and the general agreement among the three Gao *et al.*, SV, and Chen *et al.* models is reestablished. This provides clear evidence that the hardness of T-carbon should not exceed 10 GPa.

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