Extreme anisotropy of graphite and single-walled carbon nanotube bundles

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The anisotropic elastic properties of hexagonal crystals are examined in this letter. It is found that graphite possesses extreme properties with the highest anisotropy degree and the lowest shear modulus to Young's modulus ratio compared with all other known hexagonal crystals. Further, single-walled carbon nanotube (SWNT) bundles, as a kind of hexagonal material, have higher anisotropy degree and lower modulus ratio than those of graphite. These extreme mechanical properties of graphite and SWNT bundles promise great application potentials in composites, sensors, and functional materials. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2722057]

Carbon is an extraordinary element which has been studied and used for centuries. It composes materials with diversity such as graphite, diamond, fullerenes, and carbon nanotubes. Both theoretical and experimental investigations show that these materials composed by carbon have unique properties of physics, chemistry, and mechanics especially. For instance, single crystal graphite has large Young's modulus in basal plane but very low shear modulus between layers with weak binding between the basal planes themselves. The ratio of Young's modulus to shear modulus is very high, of the order of 250:1. Because of these properties, graphite is one of the most widely used solid lubricants and, thus, is widely used in practical applications such as bearings and seals. Graphite with the particular mechanical and physical properties also has numerous industrial uses in electrodes, heat exchangers, crucibles, and moderators.

Since studies on conventional properties of known materials are developed well, extreme properties of materials have attracted scientific interests more and more. For instance, when stretch is applied most materials not only become longer in the direction of stretch but also become thinner in cross section from everyday experience. However, Baughman *et al.*[1] have studied materials with negative compressibilities in one or more dimensions occurring in certain rare crystal phases. Only about 13 of the 500 investigated compositions are stretch densified. These enable the design of materials with negative linear compressibilities and these materials concepts might find many important applications in optical telecommunications line systems and sensor systems for high pressure environments, electrode clamps for ferroelectric pressure sensors, and artificial muscles.[1,2] For extreme states of matter there could be many unexpected promising applications never thought before. Thus it is useful for studying extreme states of many kinds of materials and the extreme properties could be exploited in future technologies.

Graphite, as one widely used material, could have extreme mechanical properties as well, including the known largest Young's modulus in basal plane mentioned above. Very low friction is also observed experimentally and theoretically when graphitic layer slides on incommensurate layer.[3–5] This superlubricity behavior of graphite may provide good explanations that graphitic systems have been found remarkable nanotribological properties. Many lamellar solids like graphite such as molybdenum disulfide (MoS_2) have also the low-friction behavior between neighboring atomic layers. These layered materials have the same structural features and each of them possesses a hexagonal symmetry in the layered/basal plane, with weak bonding between layers. The symmetry of the single graphite crystal is D_h^6 and this limits the number of independent elastic coefficients to 5 in linear elastic behavior. We use $\boldsymbol{\sigma}$, $\boldsymbol{C}$, and $\boldsymbol{\varepsilon}$ to denote the stress, stiffness, and strain tensors of the material, respectively. The stress-strain relation can be expressed by the matrix notations

$$\begin{Bmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{Bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & 2c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & 2c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{11}-c_{12} \end{bmatrix} \begin{Bmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{xz} \\ \varepsilon_{xy} \end{Bmatrix}. \tag{1}$$

We have examined the elastic coefficients of all the over 200 hexagonal crystals listed in the handbook by Every and McCurdy[6] and calculated in-plane Young's modulus E_{11} and shear modulus G_{12}, out-of-plane Young's modulus E_{33} and shear modulus G_{13}, and the anisotropy degree. The anisotropy degree $\delta(\boldsymbol{C})$ is defined as

$$\delta(\boldsymbol{C}) = \frac{\|\boldsymbol{C}-\boldsymbol{C}_{\text{iso}}\|}{\|\boldsymbol{C}\|}, \tag{2}$$

where $\boldsymbol{C}_{\text{iso}}$ is the isotropic part of $\boldsymbol{C}$ (i.e., the projection of $\boldsymbol{C}$ onto the two-dimensional isotropic elastic subspace) and $\|\boldsymbol{C}\|=\sqrt{C_{ijkl}C_{ijkl}}$ is the standard norm of $\boldsymbol{C}$. We note that $\delta(\boldsymbol{C})$ is the relative magnitude of the anisotropic part $\boldsymbol{C}-\boldsymbol{C}_{\text{iso}}$ to that of $\boldsymbol{C}$. The results are shown in Table I, which lists only the elastic constants, anisotropy degree, and minimum shear modulus to Young's modulus ratio of hexagonal crystals with anisotropy degree higher than 0.3. The elastic coefficients of hexagonal crystals are from the handbook.[6] It is found that the elastic properties of graphite have the highest anisotropy degree 0.670, and the lowest modulus ratio 0.39%, compared with those of all other hexagonal crystals. Detailed formulas that correlate Young's and shear moduli and $\delta(\boldsymbol{C})$ with the elastic coefficients $c's$ are given later in this letter.

Figure 1 illustrates the distribution of hexagonal crystals with full elastic parameters listed in the handbook[6] with respect to the anisotropy degree. It is shown that the anisotropy

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TABLE I. Elastic constants, degree of anisotropy, and minimum modulus ratio of selected hexagonal crystals.

Material	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	$\delta(C)$	$\min\{G/E\}$
SWNT bundles, with diameter 1.4 nm	40.68	625.7	1.2	39.32	12.4	0.843	0.0011
Graphite (C)	1060	36.5	4	180	15	0.670	0.0039
Molybdenum sulfide (MoS_2)	238	51	18.6	−54	23	0.608	0.0888
Biotite $[K(Mg,Fe)_3AlSi_3O_{10}(OH,F)_2]$	186	54	5.8	32	12	0.557	0.0325
Phlogopite $[KMg_3AlSi_3O_{10}(OH,F)_2]$, B	178	51	6.5	30	15	0.547	0.0383
Phlogopite $[KMg_3AlSi_3O_{10}(OH,F)_2]$, A	179	51.7	5.6	32	26	0.532	0.0342
Cesium nickel fluoride $[CsNiF_3]$, B	44.5	96.6	2.4	15	7.4	0.525	0.0253
Muscovite $[KAl_2Si_3O_{10}(OH,F)_2]$	178	54.9	12.2	42.4	14.5	0.500	0.0737
Cesium nickel fluoride ($CsNiF_3$), A	44.4	94.5	4.7	20.7	10.7	0.466	0.0517
Gallium sulfide (peizoel.) (GaS)	126.5	41.6	12	35.7	14.3	0.452	0.1054
Gallium selenide (peizoel.) (GaSe)	106.4	35.8	10.2	30	12.1	0.448	0.1065
Rubidium nickel chloride ($RbNiCl_3$)	35.2	72.2	2.5	10.0	22	0.408	0.0492
Manganese arsenide (MnAs)	41	112	34.5	9	11	0.397	0.1493
Guanidinium iodide $[C(NH_2)_3I]$	22.93	7.53	2.34	11.31	5.21	0.393	0.1440
Indium selenide (InSe)	118.1	38.2	11.7	47.5	32	0.379	0.1351
Cesium nickel chloride ($CsNiCl_3$)	35.8	62.5	6.0	13.4	10	0.345	0.1027
Zinc (Zn)	165	61.8	39.6	31.1	50.0	0.310	0.3198

degrees of 90% of these crystals are less than 0.3, and only less than 20 crystals possess the anisotropy degrees which are higher than 0.3.

Carbon nanotubes, as a kind of nanostructured materials, have generated much research interests by their extreme (axial Young's modulus and tensile failure strength) and versatile (semiconducting/metallic, for example) properties. Single-walled carbon nanotubes (SWNTs) are often found in self-organized bundles[7,8] and form hexagonally packed crystal configurations in which the intertube force interactions are due exclusively to nonbonding van der Waals effects. The weak and high nonlinear intertube van der Waals interactions are of importance for determining the structural instability of the cross sections of tubes, the sliding behavior between tubes, and the stiffness and strength of bulk SWNT bundles. For device and structure applications of SWNT bundles, there have been many investigations[8,9] and theoretical predictions[10–12] on mechanical properties. Owing to their transverse isotropy, the linear elastic properties of SWNT bundles as bulk materials can be completely characterized by five independent elastic constants, i.e., the in-plane bulk modulus, in-plane shear modulus, axial Young's modulus, out-of-plane Poisson's ratio, and out-of-plane shear modulus. There have been a number of theoretical studies[10,11] on five independent moduli of SWNT bundles, but none of these studies have predicted a complete set. One of our very recent works[12] has predicted a complete set of those five moduli using a hybrid atomistic/continuum model, in which the intratube interaction energy is calculated using the molecular-dynamics-based continuum approach while the intertube interaction is modeled by a usual Lennard-Jones-type potential. We first study the instability characteristics of the lattice of SWNT bundles by analyzing the balance between the intratube atomic interactions and the intertube van der Waals interactions. Fitting the pressure-strain curves, we obtain the area modulus. We then determine the in-plane shear modulus by considering the double shear deformation mode, generated by applying tensile and compressive strain, of equal magnitude, along two mutually perpendicular directions of the lattice. Because the intertube van der Waals interaction is very weak compared with the C–C covalent bond interaction, axial Young's modulus as a bulk material can be estimated by taking account of the contribution of C–C bond only. By subjecting the SWNT bundle to axial strain, Poisson's ratio can be calculated too. For predicting the out-of-plane shear modulus, we propose a complex atomic calculation model instead of modeling a SWNT as a continuum shell. Due to several factors, such as the chiralities and orientations of SWNTs and cross-section wrapping of tubes, we can estimate the upper and lower bounds for the out-of-plane shear modulus. All the predictions and estimates agree well with the measured value available in the literature. In summary, the results are dependent on the tube diameter of SWNT bundles and for typical SWNT bundles of tube diameter 1.4 nm, the predicted elastic coefficients are $c_{11}=40.68$ GPa, $c_{12}=39.32$ GPa, $c_{66}=(c_{11}-c_{12})/2=0.68$ GPa, $c_{13}=12.40$ GPa, $c_{33}=625.72$ GPa, and (in average) $c_{44}=1.22$ GPa.

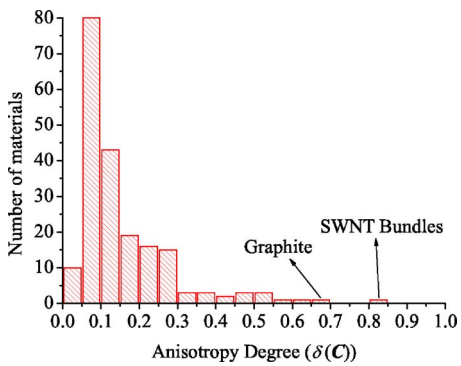

FIG. 1. (Color online) Number of hexagonal crystals vs the anisotropy degree $\delta(C)$.

We list the elastic moduli of SWNT bundles in Table I comparing with other hexagonal crystals. We further find that the predicted elastic properties of SWNT bundles have higher anisotropy degree and lower modulus ratio than those of graphite. For instance, for SWNT bundles of tube diameter 1.4 nm, the anisotropy degree is 0.843, and the smallest modulus ratio is 0.11%. Such inherent extreme mechanical anisotropy properties of SWNT bundle material promise many interesting applications, such as connecting elements

of a hingeless and bearingless rotor system for a helicopter, reinforcement agents in nanocomposites, artificial muscles, and sensor systems.[13–16] Together with unique electronic properties of SWNTs including high temperature superconductivity, rectifying behavior, and field effect transistors, all these excellent properties provide these high anisotropic materials more opportunities to become potential functional materials.

To be self-contained, we provide below the detailed formulas for calculating the moduli and anisotropy degrees from all the known elastic coefficients $c's$ in the handbook by Every and McCurdy.[6] In-plane and out-of-plane Young's moduli E_{11} and E_{33}, shear moduli G_{12} and G_{13}, and Poisson's ratios ν_{12} and ν_{13}, respectively, are associated with the elastic coefficients $c's$ in the following forms:

$$\begin{bmatrix} 1/E_{11} & -\nu_{12}/E_{11} & -\nu_{13}/E_{33} & 0 & 0 & 0 \\ -\nu_{12}/E_{11} & 1/E_{11} & -\nu_{13}/E_{33} & 0 & 0 & 0 \\ -\nu_{13}/E_{33} & -\nu_{13}/E_{33} & 1/E_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2G_{13} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/2G_{13} & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2G_{12} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & 2c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & 2c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{11}-c_{12} \end{bmatrix}^{-1}. \tag{3}$$

The Cartesian components of $\boldsymbol{C}_{\mathrm{iso}}$ are

$$C^{\mathrm{iso}}_{ijkl} = \lambda \delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \tag{4}$$

with

$$\lambda = (2C_{iijj} - C_{ijij})/15,$$

$$\mu = (-C_{iijj} + 3C_{ijij})/30, \tag{5}$$

where δ_{ij} is the Kronecker delta. Therefore, we have

$$\delta(\boldsymbol{C}) = \sqrt{1 - \frac{2I_{\boldsymbol{C}}^2 - 2I_{\boldsymbol{C}}II_{\boldsymbol{C}} + 3II_{\boldsymbol{C}}^2}{15\|\boldsymbol{C}\|^2}}, \tag{6}$$

where $I_{\boldsymbol{C}}=C_{iijj}$ and $II_{\boldsymbol{C}}=C_{ijij}$. For hexagonal crystals (or in more general, for any transversely isotropic materials), we further have

$$I_{\boldsymbol{C}} = C_{iijj} = 2c_{11} + 2c_{12} + 4c_{13} + c_{33},$$

$$II_{\boldsymbol{C}} = C_{ijij} = 3c_{11} - c_{12} + 4c_{44} + c_{33},$$

$$\|\boldsymbol{C}\|^2 = C_{ijkl}C_{ijkl} = 3c_{11}^2 + 3c_{12}^2 + 4c_{13}^2 + c_{33}^2 + 8c_{44}^2 - 2c_{11}c_{12}. \tag{7}$$

We conclude this letter with two remarks. Several other measures $\Delta(\boldsymbol{C})$ of anisotropic degree defined as the relative magnitude of the anisotropic part $\boldsymbol{C}-\boldsymbol{C}_{\mathrm{iso}}$ to that of $\boldsymbol{C}$ based on other norms (e.g., the maximum norm), say, $p(\boldsymbol{C})$, were proposed in the literature. We note that $\Delta(\boldsymbol{C})$ and $\delta(\boldsymbol{C})$ are equivalent in the sense that there exist positive constants k_1, k_2 and κ_1, κ_2 such that $k_1\delta(\boldsymbol{C}) \leqslant \Delta(\boldsymbol{C}) \leqslant k_2\delta(\boldsymbol{C})$ and $\kappa_1\Delta(\boldsymbol{C}) \leqslant \delta(\boldsymbol{C}) \leqslant \kappa_2\Delta(\boldsymbol{C})$ for any $\boldsymbol{C}$. For example, we can take $k_1=m/M$ and $k_2=M/m$, where M and m are the maximum and minimum of $p(\boldsymbol{C})$ for all $\boldsymbol{C}$ such that $\|\boldsymbol{C}\|=1$. Therefore, different $\Delta(\boldsymbol{C})$ are not substantial to measure the anisotropy degree. However, we should emphasize that to be a proper measure of anisotropy degree, the $\Delta(\boldsymbol{C})$ as a scalar-valued function of $\boldsymbol{C}$ should be isotropic. We choose $\delta(\boldsymbol{C})$ as the measure because of its simplicity to calculate and its isotropy as a function of $\boldsymbol{C}$. Finally, we note that any given positive definite fourth order tensor satisfying the usual symmetries of elasticity tensors has been theoretically proven to be realized as the effective elasticity tensor of a two-phase composite.[17] Therefore, it is possible to achieve even higher anisotropy degree than that of the SWNT bundles in artificially engineered materials with microstructure.

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[1] R. H. Baughman, S. Stafström, C. X. Cui, and S. O. Dantas, Science **279**, 1522 (1998).
[2] R. H. Baughman, S. O. Dantas, S. Stafström, A. A. Zakhidov, T. B. Mitchell, and D. H. E. Dubin, Science **288**, 2018 (2000).
[3] M. Dienwiebel, G. S. Verhoeven, N. Pradeep, J. W. M. Frenken, J. A. Heimberg, and H. W. Zandbergen, Phys. Rev. Lett. **92**, 126101 (2004).
[4] A. Socoliuc, R. Bennewitz, E. Gnecco, and E. Meyer, Phys. Rev. Lett. **92**, 134301 (2004).
[5] G. S. Verhoeven, M. Dienwiebel, and J. W. M. Frenken, Phys. Rev. B **70**, 165418 (2004).
[6] A. G. Every and A. K. McCurdy, in *Numerical Data and Functional Relationships in Science and Technology*, Landolt-Börustein, New Series, edited by D. F. Nelson (Springer, Berlin, 1992), Vol. 29A, pp. 105–138.
[7] A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, Science **273**, 483 (1996).
[8] M. J. López, A. Rubio, J. A. Alonso, L. C. Qin, and S. Iijima, Phys. Rev. Lett. **86**, 3056 (2001).
[9] J. P. Salvetat, G. A. D. Briggs, J. M. Bonard, R. R. Bacsa, A. J. Kulik, T. Stöckli, N. A. Burnham, and L. Forró, Phys. Rev. Lett. **82**, 944 (1999).
[10] V. N. Popov, V. E. Van Doren, and M. Balkanski, Solid State Commun. **114**, 395 (2000).
[11] E. Seather, S. J. V. Frankland, and R. B. Pipes, Compos. Sci. Technol. **63**, 1543 (2003).
[12] J. Z. Liu, Q. S. Zheng, L. F. Wang, and Q. Jiang, J. Mech. Phys. Solids **53**, 123 (2005).
[13] M. Zhang, K. R. Atkinson, and R. H. Baughman, Science **306**, 1358 (2004).
[14] K. L. Jiang, Q. Q. Li, and S. S. Fan, Nature (London) **419**, 801 (2002).
[15] A. Y. Cao, P. L. Dickrell, W. G. Sawyer, M. N. Ghasemi-Nejhad, and P. M. Ajayan, Science **310**, 1307 (2005).
[16] R. H. Baughman, Science **308**, 63 (2005).
[17] G. W. Milton and A. V. Cherkaev, ASME J. Eng. Mater. Technol. **117**, 483 (1995).