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Toughening a superstrong carbon crystal: Sequential bond-breaking mechanisms

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A complex orthorhombic carbon allotrope in *Pbam* symmetry with 32 atoms in its unit cell, thus termed *Pbam*-32 carbon, was recently predicted [C. Y. He *et al.*, *Phys. Rev. Lett.* **121**, 175701 (2018)]. Its crystal structure comprises alternating fivefold, sixfold, and sevenfold carbon rings and exhibits reduced bonding anisotropy compared to diamond, raising the prospects of finding a superstrong material with distinct and favorable mechanical properties. Here we report findings from first-principles calculations that reveal peculiar stress-strain relations in *Pbam*-32 carbon. The obtained stress responses under various tensile and shear strains display outstanding characteristics contrasting those of traditional superhard materials like diamond and cubic boron nitride (*c*-BN). The *Pbam*-32 carbon undergoes structural deformations that produce highly isotropic stress responses under a wide variety of large tensile and shear strains, showcasing unprecedented nearly degenerate stress-strain curves along multiple deformation paths extended over ultralarge, including full-range, strains up to the bond-breaking points. These deformation modes impede or even suppress the graphitization process commonly seen in highly strained diamond and *c*-BN crystals while still sustaining large peak stresses comparable to those in diamond. Most notably, we find conspicuous bond-weakening and -breaking mechanisms stemming from bonding symmetry reduction in *Pbam*-32 carbon. At large tensile strains, a sequential bond elongation process occurs, generating a more ductile deformation past the peak stress; at large shear strains, the crystal structure goes through a similar sequential bond elongation process and, interestingly, transforms into a distinct three-dimensional network containing mixed sp^2 and sp^3 bonding states, suppressing the usual graphitization process. These more gradual bonding-state changes in the severely strained *Pbam*-32 carbon improve ductility and toughness in this superstrong carbon crystal. These insights elucidate mechanisms for toughening superstrong covalent crystals via microstructural arrangements, which shed light on rational design and development of a distinct class of superstrong materials that exhibit more isotropic mechanical responses with improved toughness under diverse loading conditions.

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I. INTRODUCTION

Materials that exhibit superior mechanical strength and toughness hold great importance in science, technology, and industrial applications [1]. Diamond and cubic boron nitride (*c*-BN) are well-known traditional superhard materials with outstanding abilities to resist structural deformations [2–4], but these materials are highly anisotropic in their mechanical properties with directionally dependent stress responses [5–7] that induce undesirable structural changes or even failure, which may complicate or impede their performances. The occurrence of graphitization under large tensile and shear loading conditions is associated with a bond-breaking process that is synonymous with these superhard covalent materials. Under increasing strains, the stress responses usually rise steeply and then drop abruptly past the peak stress that determines the limiting mechanical strength, which also defines the corresponding brittle structural failure modes without any ap-

preciable plastic deformation in this class of materials [5–7]. Materials serving under extreme loading conditions are required to be both strong and tough to withstand high stresses at large strains without developing catastrophic failures [8–11]. Superhard materials that also exhibit mechanical characters with the ability of undergoing substantial plastic deformation before fracturing are highly desired and in great demand [12].

Extensive theoretical and experimental explorations have made vigorous efforts to design and synthesize advanced superhard materials that showcase improved and more versatile mechanical characteristics [13–29]. Among these materials, carbon allotropes with densely packed and three-dimensional covalent sp^3 bonds are the preferred targets in the search for materials with superior ultrahigh hardness. In recent decades, hundreds of carbon allotropes have been theoretically proposed [13–22], and some have been experimentally synthesized [23–29]. These candidate structures can be generally characterized by their tetrahedral bonding configurations or described as corrugated layers interconnected by a combination of diverse topological stackings of carbon rings. These crystal structures exhibit extremely diverse physical properties, especially mechanical responses at equilibrium

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and extreme conditions [30]. An interesting recent finding in the search for notable carbon structures is the identification of three low-energy tetrahedral carbon polymorphs crystallized in *Pbam*, *P6/mmm*, and *I $\bar{4}3d$* symmetry with 32, 36, and 94 atoms per cell, respectively, obtained using advanced crystal search techniques [31]. Among them, the orthorhombic carbon allotrope in *Pbam* symmetry (referred to as *Pbam*-32 carbon hereafter) possesses unique bonding configurations containing alternating fivefold, sixfold, and sevenfold carbon rings, forming a three-dimensional sp^3 network that exhibits a reduced directional bonding environment compared to diamond and *c*-BN. Of the three identified carbon structures, *Pbam*-32 carbon contains the fewest number of atoms in its cell, imposing the least computing constraints, and is chosen to serve as a prototype to showcase the distinct mechanical properties associated with intriguing structural features in the crystal. Given the essential and profound role of the bonding configurations in determining stress responses and bond-breaking behaviors, it is interesting to establish an understanding of the fundamental structure-property relation in *Pbam*-32 carbon under various strain conditions for a systematic examination of its deformation modes and strengths, especially in an effort to identify its distinct mechanical behaviors that showcase high strengths defined by large peak stresses characteristic of this class of strong covalent superhard crystals and, at the same time, explore possible improvement of toughness indicated by the bonding symmetry reduction of the *Pbam*-32 crystal, which may lead to reduced brittleness and enhanced ductility at large strains.

In this work, we perform systematic computational studies of *Pbam*-32 carbon crystal using first-principles calculations to examine the elastic moduli near equilibrium and to determine the stress-strain relations under a variety of tensile and shear deformations, obtaining stress responses and associated structural deformation modes at large strains past the peak stress until the occurrence of bonding structural failure or transformation. This approach provides an accurate description of material deformation modes and the associated stress responses over large ranges of strains, offering insights into key mechanical behaviors and the underlying atomistic mechanisms for bonding changes and property variations. The obtained elastic moduli reveal that *Pbam*-32 carbon exhibits an intrinsic highly incompressible and stiff nature near equilibrium characteristic of a crystal structure comprising a strong carbon bonding network. Surprisingly, the elastic moduli of *Pbam*-32 carbon are even slightly higher than the results for diamond obtained from the same computational procedure, despite its density being lower than that of diamond by about 5%. More interesting and unexpected are the intriguing deformation modes at large strains, especially distinct sequential bond-weakening and -breaking mechanisms under large tensile and shear strains that impede or even suppress the graphitization process commonly seen in traditional superstrong solids like diamond and *c*-BN, extending deformation ranges past the peak stress and enhancing ductility, thereby toughening this superstrong carbon crystal. The present findings advance the fundamental knowledge of structural and mechanical properties of the *Pbam*-32 carbon allotrope, and these results have broad implications for elucidating the stress-strain relations and the atomistic toughening

mechanisms that offer guidance for rational design and optimization of an important class of prominent superstrong covalent crystals.

II. COMPUTATIONAL METHODS

First-principles calculations to determine structural and elastic properties and to obtain strain-stress relations were performed using density functional theory as implemented in the Vienna Ab initio Simulation Package (VASP) [32]. The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [33] functional was used to describe the exchange-correlation potential. Calculations were also carried out using the local density approximation (LDA) functional [34] to make direct comparisons with selected previously reported stress-strain relations, especially peak stresses and strains under tensile and shear deformation modes, for diamond and *c*-BN. All-electron projector augmented-wave [35] pseudopotentials were adopted for a carbon atom with the electronic configuration $2s^2 2p^2$. An energy cutoff of 600 eV for the plane-wave expansion and a Monkhorst-Pack [36] k -point mesh with a grid of $0.2 \text{ \AA}^{-1}$ for Brillouin zone sampling were chosen for the subsequent computational process to obtain results with well-converged energies to be better than 1 meV per atom. The elastic constants C_{ij} were calculated using strain-stress relationships at small strain, and the isotropic elastic moduli were then derived from the Voigt-Reuss-Hill averaging scheme [37]. The quasistatic ideal strength in the various directions was determined using the established strain-stress method [38–41] in which the lattice vectors were incrementally deformed in the direction of the applied (tensile or shear) strains. At each step, the applied (tensile or shear) strain is fixed, which determines the calculated (tensile or shear) stress, while the other five independent components of the strain tensors and all the atoms inside the unit cell were simultaneously relaxed until (i) all the residual components of the Hellmann-Feynman stress tensor orthogonal to the applied strain were less than 0.1 GPa and (ii) the force on each atom became negligible. The shape of the (deformed) unit cell and atomic relaxation are determined completely at each step by the constrained structural optimization.

III. RESULTS AND DISCUSSION

The ability of carbon to form versatile bonding structures has led to the discovery of a large family of energetically favorable or competitive carbon allotropes [13–29]. Many of these carbon allotropes possess rich bonding modifications via a combination of different connecting patterns and variable-membered carbon rings. A case in point is the recently predicted orthorhombic *Pbam*-32 carbon, which contains alternating fivefold, sixfold, and sevenfold carbon rings, forming a quasi- sp^3 hybrid covalent bonding framework, as shown in Fig. 1. The optimized lattice parameters of unstrained *Pbam*-32 carbon are $a = 8.303 \text{ \AA}$, $b = 8.865 \text{ \AA}$, and $c = 2.511 \text{ \AA}$. The atomic Wyckoff positions are C1 at $4h$ (0.088, 0.499, 0.500), C2 at $4h$ (0.837, 0.341, 0.500), C3 at $4h$ (0.575, 0.555, 0.500), C4 at $4h$ (0.480, 0.276, 0.500), C5 at $4g$ (0.729, 0.351, 0.000), C6 at $4g$ (0.850, 0.580, 0.000), C7 at $4g$ (0.175, 0.979, 0.000), and C8 at $4g$ (0.586, 0.245, 0.000).

FIG. 1. A perspective view of the bonding structure of *Pbam*-32 carbon crystal [31]. Spheres in different colors indicate distinct groups of carbon atoms with inequivalent connecting features in the crystal structure.

To assess the mechanical properties of *Pbam*-32 carbon, we first calculated its elastic parameters C_{ij} (all in gigapascals): $C_{11} = 1140$, $C_{22} = 1119$, $C_{33} = 1172$, $C_{44} = 441$, $C_{55} = 557$, $C_{66} = 509$, $C_{12} = 101$, $C_{13} = 106$, and $C_{23} = 47$. For the orthorhombic crystal structure, mechanical stability requires the following conditions [42]: $C_{ij} > 0$, $C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0$, $C_{11} + C_{22} - C_{12} > 0$, $C_{11} + C_{33} - 2C_{13} > 0$, $C_{22} + C_{33} - C_{23} > 0$. The above elastic constants satisfy all these conditions, thus verifying the elastic stability of *Pbam*-32 carbon crystal structure. These elastic parameters lead to an extremely high bulk modulus (438 GPa), shear modulus (511 GPa), and Young's modulus (1104 GPa). Remarkably, the bulk modulus of *Pbam*-32 carbon is even slightly higher than the value of 435 GPa for diamond obtained from the same computational procedure, indicating equal or higher incompressibility of *Pbam*-32 carbon, despite its lower (by 5.4%) density compared to diamond. Poisson's ratio of *Pbam*-32 carbon has a very low value of 0.08, which is close to the value of 0.07 for diamond, indicating that it would exhibit very little lateral structural deformation under tensile or compressive loading conditions. To describe the orientational features of elastic properties of *Pbam*-32 carbon, we have plotted a visualization of the three-dimensional linear compressibility modulus, shear modulus, and Young's modulus by computing the directional dependence of these moduli, as shown in Fig. 2. For a perfectly isotropic system, the surface of the three-dimensional modulus would be a sphere. Our results show that *Pbam*-32 carbon exhibits quasi-isotropic elastic response to elastic deformation under small loads near the equilibrium. This behavior is associated with the spatially averaged electron density from its intriguing bonding modification and interplanar spacing from the alternating fivefold, sixfold, and sevenfold topological rings.

We now turn to structural changes of *Pbam*-32 carbon under large strains to probe its ultimate mechanical strengths and the associated bonding variation patterns and the underlying atomistic mechanisms. Our calculations aim to determine the

FIG. 2. Calculated (a) three-dimensional linear compressibility modulus, (b) shear modulus, and (c) Young's modulus for *Pbam*-32 carbon.

ideal tensile and shear strengths along various high-symmetry crystallographic orientations that usually set the upper and lower bounds of mechanical properties [5–7,38–41]. The stress-strain relations obtained from these calculations reveal fundamental structural and mechanical properties and also provide information on local bond deformation and breaking modes under specific strain conditions. The ideal strengths set the upper bounds in material strengths in perfect crystal structures, and the results can be compared to measured data

FIG. 3. Stress-strain relations of *Pbam*-32 carbon obtained from first-principles calculations performed using the GGA functional under tensile strains along various indicated crystallographic directions. The ideal tensile strength is defined by the lowest peak stress along the $\langle 010 \rangle$ tensile direction, which is marked by a cross on the data point at a tensile strain of 0.12. The postpeak stress responses exhibit an unusually gentle descent trend in an extended strain range from 0.12 to 0.16, showing improved ductility, in contrast to the precipitous decline normally seen in superstrong crystals [5–7,44,45,52–55] that host the same type of covalent bonds arranged in more directionally anisotropic patterns. The lowest and highest stress response curves calculated using the LDA functional are also presented by the corresponding solid symbols to illustrate the effect of different exchange-correlation functionals and to make comparison with previously reported data for diamond and *c*-BN obtained from LDA calculations [6], as shown in Table I. We have performed additional calculations in a $(1 \times 1 \times 2)$ supercell to explore the stress responses along $\langle 001 \rangle$ tensile strains using both LDA and GGA functionals. The ideal strengths obtained in the unit cell and supercell coincide with each other well, which certifies the feasibility and validity of this method.

TABLE I. Calculated peak stresses (in GPa) of *Pbam*-32 carbon along the easy and hard directions under tensile and shear deformations, compared with the results for diamond and *c*-BN.

Material	Tensile strength		Shear strength	
	Direction	Peak stress	Direction	Peak stress
<i>Pbam</i> -32 Carbon	$\langle 010 \rangle$	75.7 (GGA) 84.0 (LDA)	$(010)[100]$	74.3 (GGA) 82.5 (LDA)
	$\langle 001 \rangle$	115.9 (GGA) 127.0 (LDA)	$(001)[010]$	107.5 (GGA) 114.1 (LDA)
	$\langle 111 \rangle$	93.0 (LDA) ^a	$(111)[1\bar{1}\bar{2}]$	96.3 (LDA) ^a
Diamond	$\langle 100 \rangle$	223.0 (LDA) ^a	$(111)[\bar{1}1\bar{2}]$	140.0 (LDA) ^a
	$\langle 111 \rangle$	66.0 (LDA) ^a	$(111)[11\bar{2}]$	70.5 (LDA) ^a
<i>c</i> -BN	$\langle 100 \rangle$	195.0 (LDA) ^a	$(111)[\bar{1}1\bar{2}]$	95.5 (LDA) ^a

^aReference [6].

obtained from high-quality samples [43]. This approach has been applied to study structural and mechanical properties of a wide variety of materials, including strong covalent solids [44–50]; transition-metal carbide, nitride, and boride [51–61]; and metals [62–65]. These studies demonstrate extremely rich patterns and trends of bonding deformation modes that dictate structural, mechanical, and electronic properties of strained crystals, uncovering salient material characteristics at large and often complex loading conditions. Such insights help elucidate material behaviors that dictate ultimate mechanical strengths and allow rational performance optimization.

We first present and analyze the stress responses of *Pbam*-32 carbon under various tensile strains on selected deformation paths along many of its high-symmetry crystallographic directions, which usually set the range and bounds for the crystal strengths that provide the basis for understanding wide-ranging mechanical properties [5–7,62–64]. From the results presented in Fig. 3, it is seen that the stress values along all the studied different deformation paths are nearly identical for strains reaching around 0.05 with the corresponding stresses rising to about 50 GPa. This phenomenon indicates a highly isotropic stress response of *Pbam*-32 carbon up to fairly large tensile loadings. Upon further deformation, the tensile stress curves split into two groups, and the stress values for different curves in each group stay very close for an additional extended strain range. Of particular interest are the stress responses of the lower group that set the minimal threshold strain and stress for crystal deformation, transformation, and failure, thereby fundamentally dictating crystal stability and load-bearing ability. The three cases studied here involve tensile deformations along the $\langle 010 \rangle$, $\langle 110 \rangle$, and $\langle 011 \rangle$ directions, and the stresses on all three curves remain almost identical throughout the entire tensile deformation range up to the bond-breaking points. These cases highlight an interesting phenomenon in which the reduced bonding symmetry can have a profound influence on mechanical properties at very large loadings. This phenomenon is unprecedented in superstrong covalent crystals, and it reflects the remarkably isotropic bonding environment in *Pbam*-32 carbon crystal,

FIG. 4. (a)–(c) The structural snapshots and (e)–(g) the corresponding charge distribution (showing the charge isosurface at $1.0 e/\text{\AA}^3$) of *Pbam*-32 carbon deformed in the easy (i.e., with the lowest peak stress) $\langle 010 \rangle$ tensile direction at key strains between the peak stress (strain = 0.12) and bond-breaking (strain = 0.16) point. Also shown are the tensile strain evolution of selected (d) bond lengths and (h) bond angles in the crystal structure, showcasing the highly nonuniform, sequential bond-weakening and -breaking patterns in the severely strained *Pbam*-32 carbon structure. Bonds between two carbon atoms are considered broken when there is no obvious charge between the two atoms involved. While there is some degree of ambiguity involved in this criterion, which depends on the choice of the cutoff charge amount, the distinct sequential bond elongation and breaking pattern is clearly defined and robust. All the examined bond angles reach 120° at a tensile strain of 0.16 after the release of the initially built up strain energy when the crystal structure graphitizes.

FIG. 5. Stress-strain relations of *Pbam*-32 carbon obtained from first-principles calculations performed using the GGA functional under shear strains along various indicated crystallographic directions. The ideal shear strength is defined by the lowest peak stress along the (010)[100] shear slip direction, which is marked by a cross on the data point at a shear strain of 0.20. The postpeak stress responses exhibit an unusually gentle descent trend in an extended strain range from 0.20 to 0.23, showing improved ductility, in contrast to the precipitous decline normally seen in superstrong crystals [5–7,44,45,52–55] that host the same type of covalent bonds arranged in more directionally anisotropic patterns. The lowest and highest stress response curves calculated using the LDA functional are also presented by the indicated solid lines to illustrate the effect of different exchange-correlation functionals and to make a comparison with previously reported data for diamond and *c*-BN obtained from LDA calculations [6], as shown in Table I.

which represents highly desirable mechanical performance characters.

The ideal tensile strength of *Pbam*-32 carbon is 75.7 GPa (calculated at the GGA level), reached at a strain of 0.12 along the (010) direction, as shown in Fig. 3 and also summarized in Table I. We also calculated selected tensile stress responses at the LDA level, and the obtained ideal tensile strength of 84.0 GPa is lower than the ideal tensile strength of diamond (93.0 GPa at the LDA level) but much higher than that of *c*-BN (66.0 GPa at the LDA level). From the data listed in Table I, it is seen that the ratios of the highest and lowest peak tensile stresses for diamond and *c*-BN are 2.40 and 2.96, respectively [6], reflecting high degrees of anisotropy in the directional bonding patterns and the stress responses. Strikingly, this ratio for *Pbam*-32 carbon is only 1.51, using the data calculated at the LDA level, which is close to the ratio of 1.53 using the data calculated at the GGA level. This ratio for *Pbam*-32 carbon is much lower not only compared to the above two traditional superhard materials but also relative to those found in a large variety of light-element strong covalent solids [44–50] and transition-metal carbide, nitride, and boride compounds [51–61]. This behavior in sharp contrast to most other cases in the large class of strong and superstrong crystals indicates salient deformation modes in *Pbam*-32 carbon structure. To probe pertinent

atomistic mechanisms, we have examined the deformation processes, paying special attention to structural responses at large strains where bond-weakening and -breaking processes occur. We present in Fig. 4 structural snapshots of the strained *Pbam*-32 carbon crystal structures, showcasing the detailed bond-weakening and -breaking process of *Pbam*-32 carbon strained along the weakest (010) direction. Interestingly, there does not exist a critical strain point, but rather a critical strain range of 0.12–0.15, where the tensile stress decreases gently from the peak value without the precipitous drop that is normally seen in strong covalent crystals [5–7,44,45,52–55]. This is in sharp contrast to the situations in diamond and *c*-BN that possess a higher degree of bonding symmetry and therefore more uniform bond elongation that lead to simultaneous breaking of all major load-bearing bonds, causing a sudden and steep stress drop past the peak stress [6]. A close analysis of the bond deformation process indicates (see Fig. 4) that at increasing tensile strains past the peak stress, various inequivalent carbon bonds elongate and break in sequence, thereby extending the deformation range from around 0.12 to 0.16. This large expansion of the strain range at the near-peak stress considerably enhances the crystal's ability to accommodate ductile deformation and absorb strain energy under large tensile strains, which plays a crucial role in increasing the toughness of *Pbam*-32 carbon.

We next turn to the evaluation of structural and stress responses under shear strains along various slip directions in several of the most prominent low-index crystal planes. The results calculated at the GGA level are presented Fig. 5, along with some results obtained from LDA calculations for selected cases with the lowest and highest peak shear stresses for comparison with the previously reported results for diamond and *c*-BN [6]. It is seen that the lowest peak shear stress (i.e., the ideal shear strength) of *Pbam*-32 carbon calculated at the GGA (LDA) level is 74.3 (82.5) GPa along the (010)[100] shear direction, which is almost identical to the ideal tensile strength of 75.7 (84.0) GPa in the (010) direction. This phenomenon is similar to the situation for diamond and *c*-BN, which also possess ideal tensile and shear strengths that are close to each other (see data shown in Table I). There is a subtle distinction here in that the ideal tensile strength of *Pbam*-32 carbon is slightly less than the ideal shear strength in *Pbam*-32 carbon, while it is the other way around in diamond and *c*-BN. This result indicates a higher degree of ductility of *Pbam*-32 carbon, judging from the ratio of ideal tensile and shear strengths. A more prominent role, however, is played by the reduced symmetry of the bonding arrangements in *Pbam*-32 carbon containing multiple inequivalent atomic sites and bond types. The sequential bond-weakening and -breaking pattern at large tensile strains presented above is also seen here at large shear strains, as shown in Fig. 6. This result indicates an increased ductility of severely sheared *Pbam*-32 carbon crystal, but the relative extent of this increased ductility under shear strains is much less than that seen under tensile strains (Fig. 3). These contrasting results on the ductility enhancement under tensile and shear strains signify an overall enhancement of fracture toughness of *Pbam*-32 carbon crystal since the larger enhancement under the tensile strains compared to the case under the shear strains means that the *Pbam*-32 carbon crystal possesses a stronger ability

FIG. 6. (a)–(c) The structural snapshots and (e)–(g) the corresponding charge distribution (showing charge isosurface at $1.0 e/\text{\AA}^3$) of *Pbam*-32 carbon deformed in the easy (i.e., with the lowest peak stress) (010)[100] shear slip direction at key strains between the peak stress (strain = 0.20) and bond-breaking (strain = 0.23) point. Also shown are the shear strain evolution of selected (d) bond lengths and (h) bond angles in the crystal structure, showcasing the highly nonuniform, sequential bond-weakening and -breaking patterns in the severely strained *Pbam*-32 carbon structure. The same as in the case of tensile deformation, bonds between two carbon atoms are considered broken when there is no obvious charge between the two atoms involved. While there is some degree of ambiguity involved in this criterion, which depends on the choice of the cutoff charge amount, the distinct sequential bond elongation and breaking pattern is clearly defined and robust. It is noted that, however, unlike in the case of tensile deformation shown in Fig. 4, not all the examined bond angles reach 120° at a shear strain of 0.23 after the release of the initially built up strain energy since the crystal structure does not graphitize, but instead transforms into a mixed $sp^2 + sp^3$ bonding network configuration.

to sustain tensile deformations relative to shear deformations, thus reducing the chance of cleavage-type brittle structural failure [66]. Another remarkable feature of the calculated shear stress-strain relations of *Pbam*-32 carbon (see Fig. 5) is the near-degenerate stress responses up to very large strains (around 0.2), signifying an extensive quasi-isotropic shear stress range up to exceptionally large loadings around 80 GPa. Analysis of the fracture mode and bonding charge density near the breaking points at large shear strains shows that *Pbam*-32 carbon undergoes a striking bond-weakening and -breaking process, generating a three-dimensional structure with both sp^2 and sp^3 bonding states past the peak shear stress (Fig. 6). This behavior is uncommon among strong covalent crystals with higher bonding symmetries, as exemplified in diamond and *c*-BN, where a sudden and precipitous graphitization process occurs right past the peak stress, transforming the crystal into a layered structure in pure a sp^2 bonding configuration. The intriguing stress response and bond evolution of *Pbam*-32 carbon offer insight for microstructural design and development aimed at toughening superstrong covalent materials.

IV. SUMMARY

In summary, we have carried out first-principles calculations to evaluate the mechanical properties for a recently identified orthorhombic carbon allotrope in *Pbam* symmetry containing 32 atoms per unit cell arranged in alternating five-, six-, and sevenfold carbon rings. Our results show that this *Pbam*-32 carbon structure possesses extremely high elastic moduli

that are slightly higher than those of diamond, although the density of *Pbam*-32 carbon is lower than that of diamond by about 5%. This unusual phenomenon stems from the reduced degree of bonding anisotropy in the *Pbam*-32 carbon and the associated more evenly distributed bonding charge distribution in the crystal. The calculated stress-strain relations reveal intriguing structural deformation mechanisms showcasing sequential bond-weakening and -breaking modes at large tensile and shear strains. These distinct atomistic mechanisms originate from the presence of multiple nonequivalent bonds that deform and break at different paces, resulting in much different mechanical behaviors. In particular, these bonding symmetry reduction induced deformation modes lead to a more gradual and gentle decrease of stresses past the peak values without the precipitous drop that normally occurs in strong covalent crystals like diamond and *c*-BN that contain more directional bonding configurations. Such nonuniform deformation modes impede or even suppress the graphitization process and the accompanying sudden catastrophic structural failure past the peak stress seen in traditional superstrong crystals, resulting in considerable enhancements of the ductility and toughness of *Pbam*-32 carbon. The present results highlight extraordinary structural and stress responses in a superstrong carbon structure and unveil the underlying mechanisms for the distinct bonding evolution modes. These insights are helpful to further exploration of superstrong covalent crystals that possess favorable bonding structures that balance strength and ductility, making such materials more durable and versatile for wide-ranging applications.

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