Unprecedented plastic flow channel in $\gamma$-B$_{28}$ through ultrasoft bonds: A challenge to superhardness

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A longstanding controversy remains whether $\gamma$-B$_{28}$ is intrinsically superhard or not, i.e., $H_c \geq 40$ GPa. Here we perform comprehensive investigations on the mechanical properties of $\gamma$-B$_{28}$ to reveal the plasticity and failure mode of $\gamma$-B$_{28}$ through the unique combination of microindentation experiment, the ideal strength approach, and the ab initio informed Peierls-Nabarro model. A low load-invariant hardness of $\sim 30$ GPa is found for both polycrystalline and monocrystalline $\gamma$-B$_{28}$. By carefully checking the strength anisotropy and strain facilitated phonon instability, a surprising ideal strength of 23.1 GPa is revealed along the (001)[010] slip system for $\gamma$-B$_{28}$, together with an inferior Peierls stress of 3.2 GPa, both of which are close to those of B$_6$O and ZrB$_{12}$, yet much lower than those of diamond and c-BN. These results suggest that $\gamma$-B$_{28}$ could not be intrinsically superhard. Atomistic simulation and electronic structure analysis uncover an unprecedented plastic flow channel through the specific ultrasharp bonding, which causes a dramatic softening of $\gamma$-B$_{28}$. These findings highlight an approach to quantifying the realistic hardness by means of two plasticity descriptors beyond the elastic limit, i.e., the ideal strength approach and the Peierls-Nabarro model.

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Superhard materials have always been an important research topic because of their fundamental importance in material science/physics and technological applications such as cutting and polishing tools in the machinery industry and drilling bits in the milling and petrochemical industry [1–3]. With the threshold of load-invariant Vickers hardness higher than 40 GPa, only diamond and c-BN can be qualified as intrinsically superhard materials unambiguously so far. Unfortunately, each of these shows some inherent shortcomings, such as the inferior thermal stability for diamond [4] and the extreme synthesis condition for c-BN [1]. In the search for new superhard materials, one of the polymorphs of elemental boron, $\gamma$-B$_{28}$, has been claimed as the second hardest elemental solid after diamond with Vickers hardness $\geq 50$ GPa (e.g., 58 [5] and 50 GPa [6]), which was also thought to be consistent with the theoretically predicted hardness of $\gamma$-B$_{28}$, i.e., 42.5 and 49 GPa according to the Lyakhov and Oganov [7] and Chen et al. [8] hardness models, respectively. It seems that a consensus between experiment and theory has been approached regarding the superhardness of $\gamma$-B$_{28}$; however, two recent fundamental contradictions have reignited scientific curiosity and general interest: (i) The load-invariant hardness of well-synthesized polycrystalline $\gamma$-B$_{28}$ was only about 30.3 GPa [9]. (ii) The determined ideal shear strength of $\gamma$-B$_{28}$ (21.6 GPa [10]) is unexpectedly much lower than that of c-BN, even much lower than that of ZrB$_{12}$ (34.5 GPa [11]) and B$_6$O (38.0 GPa [12]).

Furthermore, it is recognized that a fundamental issue exists in the adopted hardness models for predicting $\gamma$-B$_{28}$ to be superhard, that is, the model parameters are generally derived from the equilibrium structure within the elastic limit, whereas the hardness of a real material is determined by the crystal plasticity [1]. These critical issues bring researchers to reconsider the longstanding controversy of whether the $\gamma$-B$_{28}$ is intrinsically superhard or not in view of its potential application and scientific interest [13–15], and to pursue what plasticity-relevant parameters can be used to provide a more realistic quantification on the intrinsic hardness of materials.

For this purpose, in the present paper, both polycrystalline and monocrystalline $\gamma$-B$_{28}$ samples were prepared by means of high-pressure and high-temperature experiments, and then their hardnesses were carefully determined and compared with other typical hard or superhard materials at the same
FIG. 1. The average measured $H_v$ for polycrystalline $\gamma$-B$_{28}$ and c-BN under different loads. The measured $H_v$ of B$_6$O [21–25] and ZrB$_{12}$ [11] under different loads are also shown for a global realistic comparison, including both the hardness values at low load and those until load invariance.

sufficiently high loading conditions. The results suggest that $\gamma$-B$_{28}$ could not be intrinsically superhard but has a low load-invariant hardness of $\sim$30 GPa. On the other hand, two plasticity-relevant qualities, i.e., the ideal strength and the Peierls stress, were incorporated to explore the two plastic deformation mechanisms in hard and superhard materials at the atomic scale: (1) atomically sharp step induced bond rupture due to the lack of independent slip systems [16] and (2) dislocation networks surrounding the crack tip under indentation, which have been concluded to be a crucial role for extensive plasticity of brittle materials [16]. The former quality is determined by electronic instability of a perfect crystal under affine deformation with a large strain [17,18], while the latter one provides a quantitative lattice resistance to dislocation slip, which can be modeled by means of the Peierls-Nabarro (P-N) model [19,20]. Our calculated ideal shear strength and Peierls stress provide consistent support of the experimental observations, and the atomistic mechanism underlines that both the lattice instability under affine deformation and the sliding under alias deformation are dominated by the ultrasoft bonds appearing between icosahedral boron nanocages.

Figure 1 shows the determined polycrystalline Vickers hardness ($H_v$) as a function of applied loads from 0.25 to 9.8 N. It is seen that $\gamma$-B$_{28}$ has a load-invariant hardness of 29 GPa at 9.8 N, which is similar to that of B$_6$O [21–25] and ZrB$_{12}$ [11] but much lower than that of c-BN (see Fig. 1). The measured $H_v$ of $\gamma$-B$_{28}$ in our experiments is much lower than the previous results of 58 [5] and 50 GPa [6], but in good agreement with the experimental data of 30.3 GPa for polycrystalline $\gamma$-B$_{28}$ in Ref. [9]. The single crystalline $\gamma$-B$_{28}$ with grain sizes ranging from tens of micrometers to 100 micrometers was also prepared and its experimentally determined hardness is shown in Fig. S2 in the Supplemental Material [26]. Interestingly, with tens of indentation measurements on different planes of single-crystal grains from three batches of samples, the statistic hardness data of the anisotropic hardness range from 32 to 26 GPa under a 9.8-N loading, which is almost the same as that of the polycrystal sample and suggests a weakly anisotropic hardness behavior of $\gamma$-B$_{28}$. In the following, we will suggest theoretically, via the ideal strength model and P-N model, that $\gamma$-B$_{28}$ is intrinsically hard but not superhard, as determined experimentally in our paper.

Figure 2(a) shows the calculated stress-strain curves of $\gamma$-B$_{28}$ along the weakest tensile and shear paths via affine deformation considering both pure and simple shears; Fig. 2(b) presents the anisotropy of ideal shear strength of $\gamma$-B$_{28}$ on the (001) and $\perp$[011] planes [27] to identify the lowest shear strength via affine simple shear deformation. It reveals that the lowest shear strength (23.8 GPa) is indeed along the (001)[010] path, while on the $\perp$[011] plane the lowest shear strength of 25.9 GPa is observed along the direction of 30° or 150° deviating from the [100] direction. Furthermore, the phonon dispersion curve of the structure under shear strain of 0.1487 (at peak) along the weakest (001)[010] path was also investigated and compared with that of the unstrained
structure [see Fig. 2(c)]. It is interestingly found that the phonon instability, that appears in Al [28] and Si [29] under strain, does not occur for $\gamma$-B$_{28}$ as the shear deformation is applied along the (001)[010] slip system. All in all, $\gamma$-B$_{28}$ has the lowest tensile strength of 25.6 GPa along the [011] direction, and the lowest shear strength of 23.8 GPa along the (001)[010] shear deformations, which are consistent with the previous results, i.e., 25.3 GPa for tension and 21.6 GPa for shear [10]. These values are only about 31 and 45% of those of diamond and c-BN for ideal tensile strength, and 27 and 40% of those of diamond and c-BN for ideal shear strength, respectively (see Table I [10–12,30,31]). Notably, the ideal shear strength of $\gamma$-B$_{28}$ is about 37 and 32% lower than that of B$_6$O (51.2 GPa) and ZrB$_{12}$ (55.2 GPa), respectively, indicating that $\gamma$-B$_{28}$ is more brittle and has a lower interplanar cleavage resistance as compared to B$_6$O and ZrB$_{12}$.

To account for the dislocation mediated plastic resistance, the stacking fault energy (SFE) profile of $\gamma$-B$_{28}$ is 46.8 GPa, which is lower than that of B$_6$O (56.4 GPa) and ZrB$_{12}$ (56.7 GPa), suggesting that $\gamma$-B$_{28}$ is more brittle and has a lower interplanar cleavage resistance as compared to B$_6$O and ZrB$_{12}$.

By comparing the calculated ideal strengths via affine deformation, one can determine the weakest link in a perfect crystal, which corresponds to the cleavage or sliding plane where fracture occurs or dislocation resides. To account for the fracture of dislocation mediated crystal plasticity, alien deformation, i.e., only one layer of the crystal displaced along the tensile or shear direction, is more relevant since the localized deformation governs the inhomogeneous fracture or plastic deformation in a crystal. Therefore, the ideal cleavage and slide stresses by alien deformation are further explored to see if they may explain the considerable hardmesses between $\gamma$-B$_{28}$, B$_6$O and ZrB$_{12}$. Figure 3(a) shows the calculated cleavage energy $E_b(d)$ [32] and associated stress $\sigma(d) \equiv dE_b/d$ versus cleavage opening $d$ normal to the (001) plane of $\gamma$-B$_{28}$. It is found in Table I that the ideal cleavage stress $\sigma_{IC} = \max (\sigma(d))$ of $\gamma$-B$_{28}$ is 46.8 GPa, which is lower than that of B$_6$O (56.4 GPa) and ZrB$_{12}$ (56.7 GPa), suggesting that $\gamma$-B$_{28}$ is more brittle and has a lower interplanar cleavage resistance as compared to B$_6$O and ZrB$_{12}$.
FIG. 3. (a) Cleavage energy $E_b(d)$ vs cleavage opening $d$ for the $\gamma$-B$_{28}$-(001) plane together with those of diamond-(111), c-BN-(111), B$_6$O-(0001), and ZrB$_{12}$-(110) planes for comparison. Only the associated stress $\sigma(d) \equiv \partial E_b/\partial d$ of $\gamma$-B$_{28}$ is shown with a solid line. (b) The SFE profile vs displacement ($u/b$) and (c) the disregistry $u(x)$ and misfit density $\rho(x)$ of edge dislocation for the (001)[010] slip system. The SFE profiles and dislocation core structures of B$_6$O-(0001)[10\bar{1}0] and ZrB$_{12}$-(111)[1\bar{1}0] slip systems are also shown for comparison. (d) The pressure field (in gigapascal) around the dislocation core of the $\gamma$-B$_{28}$-(001)[010] slip system as defined in Ref. [20].

FIG. 4. Isosurfaces of the VCDD of $\gamma$-B$_{28}$ under (a) affine simple shear deformation with different strains $\gamma = 0.0000$, 0.0824, 0.1486 (at peak), and 0.3458 (after lattice instability) and (b) alias shear deformation with different displacements $u/b = 0.0000$, 0.1500, 0.3000 (at unstable SFE), and 0.5000 (at stable SFE) along the (001)[010] slip system. A same isosurface level of $\pm 0.022 \epsilon$/bohr$^3$ is used in these plots. The plastic flow channel through ultrasoft bonds is illustrated as the cyan area.
Based on the aforementioned discussions, it is undoubtedly concluded that the hardness of γ-B28 must be much lower than that of diamond and c-BN due to its much lower ideal strengths of both affine and alias deformations as well as the Peierls stress, which agrees with that the experimental Vickers hardness of diamond ($H_v = 96$ GPa [35]) and c-BN ($H_v = 47\sim 63$ GPa [22, 35, 36]) versus that of γ-B28 ($H_v = 29$ GPa in this paper). In addition, due to its larger Peierls stress, γ-B28 has a slightly larger hardness than that of ZrB12 (see Fig. 1), though the ideal strengths of ZrB12 are much greater than those of γ-B28. Meanwhile, due to the nearly equal Peierls stress but a lower ideal strength, the hardness of γ-B28 is close to that of B2O under large load (e.g., 35 versus 33 GPa [21–25] at a load of 1.98 N and 29 versus 28 GPa at a load of 9.8 N as shown in Fig. 1). This illustrates why γ-B28 with a lower ideal strength could be harder than γ-B28. It is also confirmed that γ-B28 is not intrinsically superhard by the previous experimental results of 58 [5] and 50 GPa [6], but has a low hardness of 30 GPa obtained in our experimental work, providing a consistency between theoretical analysis and experimental observation.

To gain an in-depth insight into the electronic origin of the low hardness and strength of γ-B28, the variations of valence charge density difference (VCDD) of γ-B28 under affine and alias deformations along the (001)[010] slip system are presented in Fig. 4. It is found surprisingly that the ultrasoft bonds, which connect the icosahedral B12 clusters (highlighted by orange arrows), provide a plastic flow slip system are presented in Fig. 4. It is found surprisingly that the ultrasoft bonds, which connect the icosahedral B12 clusters (highlighted by orange arrows), provide a plastic flow channel in γ-B28 (see the cyan area in Fig. 4), along which a much lower Peierls stress is found for dislocation mobility than that of diamond and c-BN. Moreover, a new stable state is reached as the charge depletion regions disappear, and consequently a new configuration of B2 dumbbell pairs forms, as highlighted by black arrows in Fig. 4(a), which causes an anomalously large creeplike plasticity of γ-B28 along the (001)[010] slip system [10]. In a similar manner to affine deformation, a plastic flow channel is also observed under alias shear deformation [see Fig. 4(b)], and also when the charge depletion regions disappear the initial configuration of B2 dumbbell pairs will recover, resulting in the formation of stable SFE at $u/b = 0.5000$.

In summary, we have performed comprehensive investigations on the mechanical properties of γ-B28 to identify different failure (plasticity) modes of γ-B28 through the synergic techniques of microindentation experiment, the ideal strength approach, and the ab initio informed Peierls-Nabarro model. It is found that γ-B28 has an ideal strength of 23.8 GPa along the (001)[010] slip system, together with an inferior Peierls stress of 3.2 GPa, both of which are close to those of B2O and ZrB12 yet much lower than those of diamond and c-BN. All of these results confirm that γ-B28 is not intrinsically superhard, but has a low asymptotic hardness of ∼30 GPa, as determined experimentally in our paper. Electronic structure calculations suggest that a plastic flow channel in γ-B28 is accomplished through ultrasoft bonds, limiting it to be superhard. These findings highlight that a combined analysis of the ideal strength and Peierls stress provides a unique quantification on the hardness of materials compared with the widely used hardness model and elastic moduli, because of their direct plasticity relevancy.

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[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevMaterials.2.123602 for details of the methods of experiment, first-principles calculation, ideal strength model, ideal cleavage stress and ab initio informed P-N model, as well as the average measured $H_v$ for monocrystalline $\gamma$-B$_{28}$ under different loads.

[27] These two specific planes are chosen because they correspond to the weakest slip system, i.e., (001)[010], and the weakest tensile direction, i.e., [011], respectively.


