

Pressure-induced polymorphism in SrB₆ and deformation mechanisms of covalent networksLi Zhu ^{1,*}, Gustav M. Borstad ¹, R. E. Cohen ^{1,2} and Timothy A. Strobel ^{1,†}¹*Geophysical Laboratory, Carnegie Institution for Science, 5251 Broad Branch Road NW, Washington, DC 20015, USA*²*Department of Earth and Environmental Sciences, Ludwig Maximilians Universität, Munich 80333, Germany*

(Received 5 September 2019; revised manuscript received 8 October 2019; published 4 December 2019)

We study the high-pressure structures of SrB₆ up to 200 GPa using first-principles structure prediction calculations and high-pressure x-ray diffraction experiments. The computations show that the ambient-pressure cubic phase transforms to an orthorhombic structure (*Cmmm*) at 48 GPa, and then to a tetragonal structure (*I4/mmm*) at 60 GPa. The high-pressure experiments are consistent with the theoretically predicted tetragonal structure, which was quenched successfully to ambient conditions. Pressure induces simple boron octahedra to form complex networks in which the electrons are delocalized, leading to metallic ground states with large density of states at the Fermi level. Calculated stress-strain relations for the *I4/mmm* structure of SrB₆ demonstrate its intrinsic hard nature with an estimated Vickers hardness of 15 GPa, and reveal a novel deformation mechanism with transient multicenter bonding that results in the combination of high strength and high ductility. Our findings offer valuable insights for understanding the rich and complex crystal structures of SrB₆, which have broad implications for further explorations of hexaboride materials.

DOI: [10.1103/PhysRevB.100.214102](https://doi.org/10.1103/PhysRevB.100.214102)**I. INTRODUCTION**

Metal borides often exhibit fascinating structural complexity due to the electron deficient nature of boron that enables versatile polyhedral frameworks [1,2]. There are more than 200 binary metal borides that include a broad range of structural configurations, and many of them exhibit remarkable properties. For example, magnesium diboride (MgB₂) exhibits a substantial superconducting transition temperature with $T_c = 39$ K [3–9]. Among the metal borides, hexaboride materials have been the subject of intense experimental and theoretical study because of their technological and fundamental importance [10–20]. Some of the rare-earth hexaborides are excellent thermionic electron emission materials. For examples, CeB₆ exhibits Kondo behavior and valence-fluctuations [21], and LaB₆ has extremely high thermionic emission efficiency and is used as an electron source [22]. Recently, superconductivity at 7 K was observed for YB₆ [23], while narrow-gap semiconducting behavior was found in YbB₆ [24]. Recent studies also show that SmB₆ and PuB₆ are strongly correlated topological insulators that have ideal solid-state properties for nuclear fuel materials [15,19]. Alkaline-earth metal hexaborides are also known for a range of excellent properties and applications. Boron-deficient MgB₆ exhibits the coexistence of weak ferromagnetism and antiferroelectricity [25]. Bulk CaB₆, SrB₆, and BaB₆ have very favorable Seebeck coefficients and electrical conductivities, with SrB₆ showing the highest power factor of the three [26].

At ambient conditions, most alkaline-earth metal hexaborides, MB_6 ($M = \text{Ca}, \text{Sr}, \text{Ba}$), crystallize in a cubic structure (space group $Pm\bar{3}m$), which can be represented by B₆ octahedra and metal ions arranged in a CsCl-type lattice.

However, structure searching methods combined with first-principles calculations [27] suggest that the ambient structure of MgB₆ [25,28] may be orthorhombic. High-pressure phases of alkaline-earth metal hexaborides have also motivated extensive studies. Pressure can efficiently reduce interatomic distances and modify electronic orbitals and bonding patterns, thus leading to the formation of novel materials with atypical physical properties. A recent high-pressure study on CaB₆ showed that the ambient $Pm\bar{3}m$ structure becomes unstable above 13 GPa, and several phase transitions occur under higher pressure [29]. In contrast to the rich phase transitions in CaB₆, BaB₆ was found to be surprisingly stable, and remains in the ambient-pressure structure up to at least 49 GPa [30]. Theoretical calculations show that BaB₆ may transform into several new high-pressure phases above 78 GPa [30]. SrB₆, a member of the rare-earth hexaborides family, has also fascinated scientists for many years owing to its mechanical and electronic properties, such as incompressibility [31] and thermopower [26,32]. Despite the possibility for many novel phases with enhanced functionality, the high-pressure structures of SrB₆ remain relatively unexplored. Here, we report the high-pressure phases of SrB₆ with a joint theoretical and experimental study. We first predicted the high-pressure phase diagram of SrB₆ using swarm-intelligence-based structure prediction methods [33,34]. The predictions indicate two phase transitions in SrB₆, which follow a cubic-orthorhombic-tetragonal sequence. Powder x-ray diffraction measured at high pressure after heating SrB₆ at 2000 K can be indexed with the predicted tetragonal crystal structure. Further calculations reveal the deformation mechanism of the complex covalent network.

II. METHODS

Global structural optimization was performed using the CALYPSO code [33–35] with the particle swarm optimization

*z@zhuli.name

†tstrobel@carnegiescience.edu

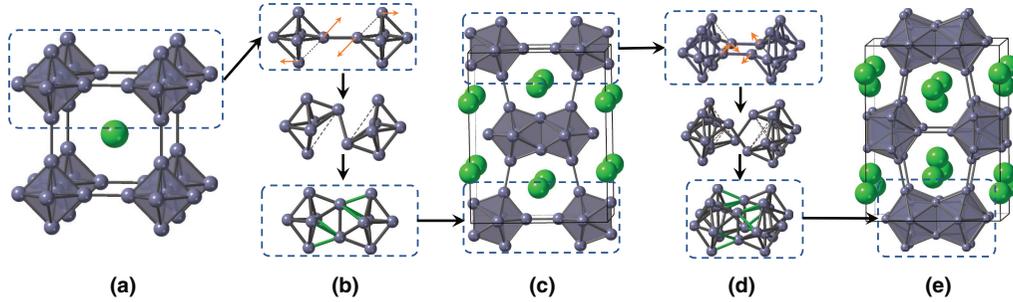


FIG. 1. Polyhedral views of (a) $Pm\bar{3}m$ structure, (c) $Cmmm$ structure, and (e) $I4/mmm$ structure of SrB_6 . The phase transition mechanisms of (b) $Pm\bar{3}m \rightarrow Cmmm$ structure and (d) $Cmmm \rightarrow I4/mmm$ structure. The black lines denote the unit cells and large and small spheres represent Sr and B atoms, respectively.

algorithm, which has successfully predicted structures of various systems ranging from elements to binary and ternary compounds [36–42]. The energetic calculations were carried out using density functional theory within the Perdew-Burke-Ernzerhof (PBE) [43] generalized gradient approximation as implemented in the VASP code [44]. We used projector augmented waves (PAW) [45] with $4s^2 4p^6 5s^2$ and $2s^2 2p^1$ electrons as valence for Sr and B atoms, respectively. The electronic wave functions were expanded in a plane-wave basis set with a cutoff energy of 520 eV. Monkhorst-Pack k -point meshes [46] with a grid of spacing $0.04 \times 2\pi \text{ \AA}^{-1}$ for Brillouin zone sampling were chosen. To determine the dynamical stability of the studied structures, we performed phonon calculations by using the finite displacement approach, as implemented in the PHONOPY code [47]. Electron-phonon coupling calculations for superconducting properties of stable phases were performed using density-functional perturbation theory (DFPT) with the QUANTUM-ESPRESSO package [48]. The stress-strain relation was obtained by calculating the stress response to structural deformation along specific loading paths using a quasistatic relaxation method [49].

SrB_6 (EPSI Metals, 99.5%) was purchased commercially and used without further purification. The SrB_6 powder was loaded in a diamond anvil cell (DAC) with 100 μm diameter culets and a Re gasket within an inert Ar glovebox, and subsequently gas loaded using Ar [50] or Ne [51] pressure media. Powder x-ray diffraction (XRD) measurements were completed at the High-Pressure Collaborative Access Team (HPCAT) beamline 16-IDB, and GSECARS, beamline 13-IDB, at the Advanced Photon Source of Argonne National Laboratory. Calibration of the sample-to-detector distance was performed with a CeO_2 or LaB_6 standard and the DIOPTAS program [52]. After heating the sample above 2000 K using a double-sided infrared laser heating system, a monochromatic beam with $\lambda = 0.4066 \text{ \AA}$ or $\lambda = 0.3344 \text{ \AA}$ was focused on the sample, and diffraction data were recorded on an MARCCD or Pilatus 1M detector. The Le Bail fittings of the powder patterns were conducted using GSAS with EXPGUI [53].

III. RESULTS AND DISCUSSION

Structure prediction calculations were performed in the pressure range 0–200 GPa with up to four formula units (f.u.) per simulation cell. Below 40 GPa, we found that the most stable structure is the $Pm\bar{3}m$ phase, in agreement with

experiment. We uncovered a group of new structures under high-pressure conditions. Among them, two lower-symmetry structures were found as ground state structures at different pressures. At 50 GPa, we predicted an orthorhombic structure described by space group $Cmmm$ (4 f.u. per unit cell) as depicted in Fig. 1(c). Above 60 GPa, we found that the most stable structure consists of a large 48-atom boron network within a tetragonal unit cell with the space group $I4/mmm$. Figure 1 shows the structural evolution with pressure, which can be viewed as a continuous distortion of B and Sr atoms. Pressure disrupts the original cubic phase to form denser structures with more complex boron networks. The basic building blocks of the SrB_6 phases are related to different kinds of boron polyhedra. As pressure increases, all boron octahedra in the $Pm\bar{3}m$ phase open up, fuse with the neighboring ones, and result in the formation of twinned pentagonal bipyramids in the $Cmmm$ structure. On further compression, the boron atoms rebond to a more complex network composed of twinned biaugmented triangular prisms [Fig. 1(e)]. As driven by the need for denser structural packing, pressure also breaks the original line-arranged Sr atoms to form more compact configurations with Sr zigzag chains in the $I4/mmm$ structure [Fig. 1(e)].

The calculated enthalpy curves (relative to the $Pm\bar{3}m$ structure, Fig. 2) illustrate the relative thermodynamic stabilities of the predicted structures. Our results show that, up to 48 GPa, the ambient $Pm\bar{3}m$ structure is the most stable one, and a pressure-induced phase transition from $Pm\bar{3}m$ to $Cmmm$ occurs at ~ 48 GPa. The $Cmmm$ phase is the most energetically favorable structure in a limited pressure range between 48 and 60 GPa. Beyond 60 GPa, the predicted $I4/mmm$ structure becomes more stable up to at least 200 GPa. The phase transitions involve a complex evolution of the boron network in SrB_6 with the increasing pressure. To further understand the effect of pressure, we plot the enthalpy components (internal energy term and pressure-volume, pV , terms) of the $Cmmm$ and $I4/mmm$ phases relative to the $Pm\bar{3}m$ phase in Fig. 2(b). The $Pm\bar{3}m$ structure has the lowest internal energy over the entire pressure range studied in this work. However, as pressure increases, the pV terms for the $Cmmm$ and $I4/mmm$ structures decrease quickly, and are large enough to compensate for the internal energy difference. Pressure plays an important role in shifting the stability of different structures and thus is a unique tool to create a high-coordination environment for novel materials. The dynamic stabilities of the newly

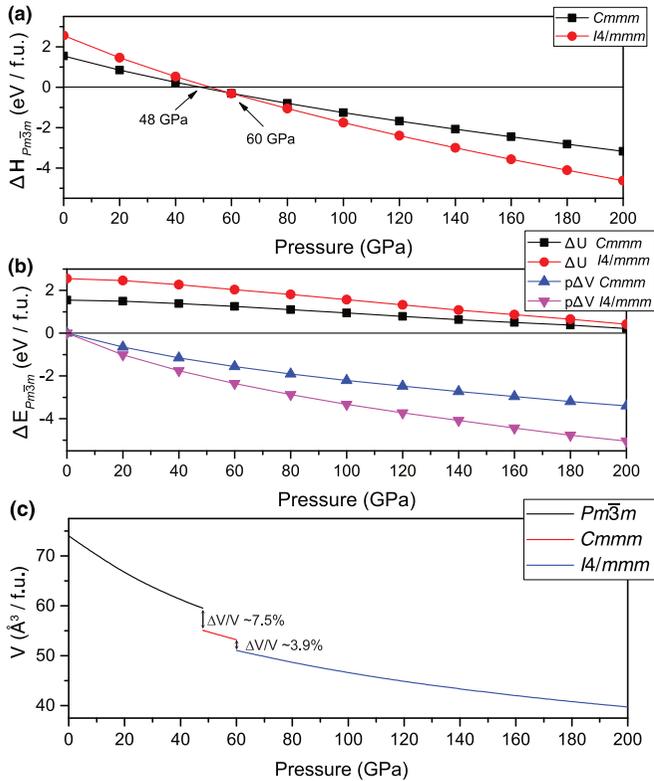


FIG. 2. (a) Calculated enthalpy curves for SrB₆ (relative to the $Pm\bar{3}m$ structure) as a function of pressure. (b) The relative internal energy ΔU and $p\Delta V$ term for the $Cmmm$ and $I4/mmm$ structures with respect to the $Pm\bar{3}m$ structure. (c) Calculated volumes as a function of pressure for different phases of SrB₆.

predicted $Cmmm$ and $I4/mmm$ structures were examined by calculating the phonon spectra using the supercell method. No imaginary phonon frequencies were found in the whole Brillouin zone over the studied pressure range, indicating the dynamic stabilities and favorable conditions for metastable recovery to ambient pressure [54].

In order to confirm the theoretically predicted phase transitions under high pressures, we performed high-pressure XRD experiments on SrB₆. Initial experiments performed near 60 GPa did not reveal the formation of new SrB₆ polymorphs, even after heating near 2000 K. This suggests either a significant kinetic barrier for the transition at 60 GPa, or means that the actual transition pressures at finite temperature are higher than those calculated. It is very common that heating is needed to promote rebonding in the strongly bound covalent network under high pressures [29,55]. For high-pressure experiments conducted with much higher thermodynamic driving force (near 150 GPa), cubic diffraction lines from $Pm\bar{3}m$ SrB₆ rapidly transformed to a series of new peaks, signifying the formation of a new high-pressure phase. The XRD patterns agree with the predicted tetrahedral $I4/mmm$ structure as shown in Fig. 3(a), although the calculated peak intensities show some variation due to incomplete powder averaging statistics. We refined the lattice parameters of the predicted $I4/mmm$ structure with the observed XRD data obtained during decompression down to 1 atm, and the pressure-volume equation of state (EoS) is consistent with that

calculated for the $I4/mmm$ structure [Fig. 3(b)], providing further evidence for the formation of the $I4/mmm$ phase of SrB₆. The experimental lattice parameters are given in the Supplemental Materials [54]. Compared with the cubic phase, the new tetragonal phase shows increased compressibility [estimated experimental $B_0 = 148(6)$ GPa compared with $B_0 = 123$ GPa for the cubic phase], and an overall decrease in volume per formula unit due to the increased connectivity of the boron biaugmented triangular prisms compared with the pristine octahedra.

The high-pressure phase behavior of SrB₆ shares similarities with that of CaB₆ [29]. Both compounds take on the cubic $Pm\bar{3}m$ structure at low pressure and transform to the tetragonal $I4/mmm$ structure at high pressure. The calculated transition pressure for $I4/mmm$ CaB₆ is 32 GPa, whereas that of SrB₆ is 60 GPa. While experimental evidence for the CaB₆ transition was observed at 31 GPa, significantly higher pressure was required for SrB₆. A possible explanation for this is related to the stability of the M -point phonon frequency for the cubic phase, which persists to higher pressure monotonically with increasing cation mass [29]. There are also noteworthy differences in the predicted phase transition sequences for CaB₆ and SrB₆. For the case of CaB₆, the cubic phase is predicted to first transform to an orthorhombic structure with 28 atoms per cell ($Cmmm$) at 13 GPa, then a second orthorhombic structure with 56 atoms per cell ($Cmcm$), before finally reaching the tetragonal structure at 32 GPa. For the case of SrB₆, we predict only the $Cmmm$ orthorhombic structure as an intermediate phase in a narrow pressure window of 48–60 GPa. None of the orthorhombic structures for CaB₆ or SrB₆ were successfully confirmed by experiment, which could be related to their limited range of stability or differences in energetics at finite temperature.

The high-pressure polymorphs of SrB₆ reveal the rich chemistry of B, enabling the formation of various kinds of unique polyhedra. Under pressure, the enthalpies and volumes decrease as a result of additional B-B bonds, which increases the overall widths of the valence and conduction bands. A sufficiently large bandwidth expansion will force valence and conduction bands to overlap at the Fermi level, leading to metallic behavior. To investigate the electronic properties, we calculated the projected density of states (DOS) for the three structures of SrB₆, as shown in Fig. 4. The modified Becke-Johnson type of meta GGA was used here to obtain band gaps with an accuracy similar to hybrid functional or GW methods [57,58]. The DOS around the Fermi level is dominated by the B p and Sr d orbitals for all structures, with no Sr s component, indicating that the $5s$ electrons of Sr are entirely transferred to the boron networks. At ambient pressure, SrB₆ is predicted to be a semiconductor with a band gap of around 1.1 eV [Fig. 5(a)], which is consistent with the experimentally measured optical band gap of 1.15 ± 0.01 eV [13]. As the localized B₆ octahedra in the $Pm\bar{3}m$ structure transform to more extended edge-sharing polyhedra in the $Cmmm$ and $I4/mmm$ structures, electrons tend to become more delocalized. This electron delocalization is significant enough to induce metallic states for the $Cmmm$ and $I4/mmm$ structures (Fig. 5). This observation is in line with other boron compounds where metallicity increases when boron edge-sharing polyhedra are formed at the expense of intercluster

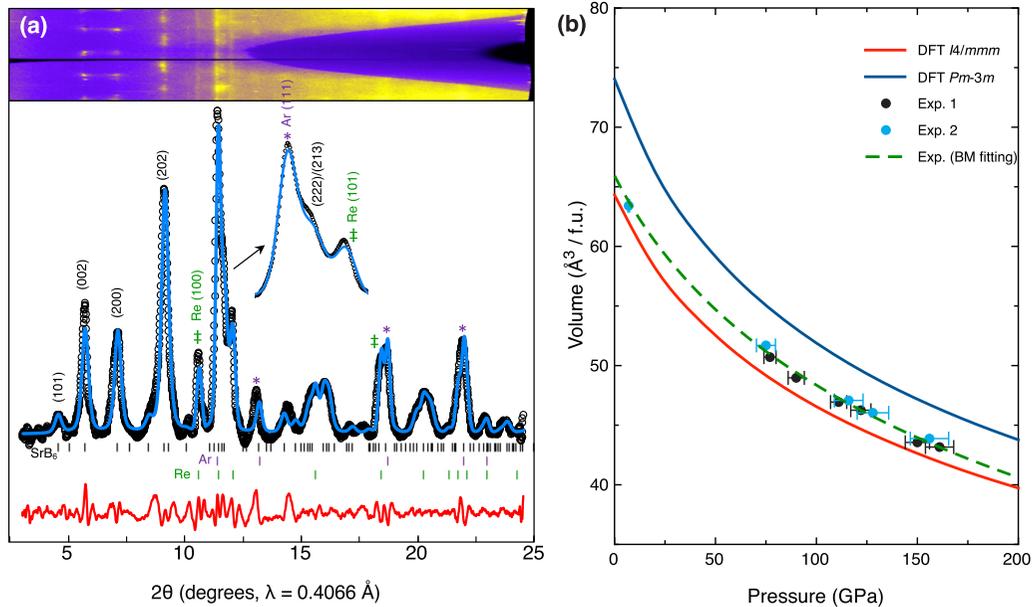


FIG. 3. X-ray diffraction and equation of state of the $I4/mmm$ structure of SrB_6 . (a) Experimental XRD data (black points) collected at 159(9) GPa with Le Bail fitting (blue line). Green and purple ticks (and selected Bragg reflections) indicate contributions from Re and Ar, respectively. The upper panel shows the cake-type image of the two-dimensional XRD pattern with incomplete powder averaging. (b) Experimental pV data for $I4/mmm$ SrB_6 are shown as points, and the solid line is the theoretical result (GGA PBE). The estimated error in volume is smaller than the symbol size. The pV data were fitted using the second order Birch-Murnaghan EoS [56], and the estimated experimental bulk modulus $B_0 = 148(6)$ GPa is consistent with the calculated $B_0 = 152$ GPa for $I4/mmm$ SrB_6 . The calculated EoS with $B_0 = 123$ GPa for cubic SrB_6 is shown for comparison.

bonds [27]. It is clear that the calculated densities of states at the Fermi level increase with elevated pressures, implying enhanced metallicity, which potentially sets a favorable condition for superconductivity. Metal borides, such as MgB_2 [3] and YB_6 [23], were reported to exhibit superconductivity. In this study, we find that the DOS at the Fermi level in the $Cmmm$ and $I4/mmm$ structures of SrB_6 are substantial, which suggests that the electron-phonon coupling could be large. We therefore estimated the superconducting transition

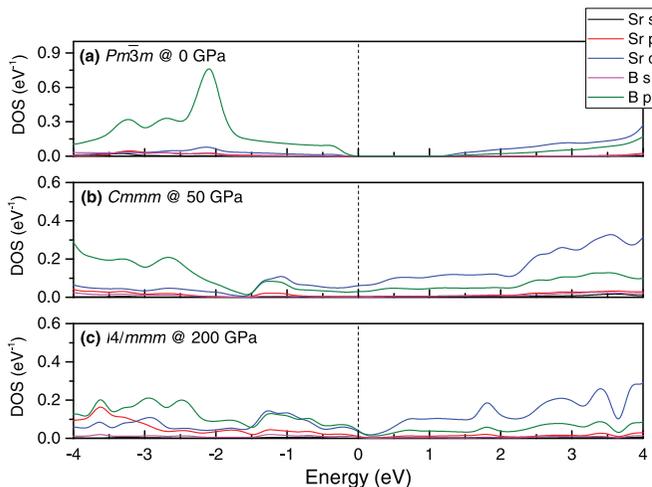


FIG. 4. The projected density of states (DOS) for (a) the $Pm\bar{3}m$ structure at 0 GPa, (b) the $Cmmm$ structure at 50 GPa, and (c) the $I4/mmm$ structure at 200 GPa. The densities of states at the Fermi level increase with pressure, indicating enhanced metallicity.

temperature, T_c , from the Allen-Dynes modified McMillan equation [59]. With a Coulomb potential (μ^*) of 0.1, we obtained an estimated T_c value of 9 K for the $I4/mmm$ structure at 1 atm.

Borides are expected to be very hard. The increase in valence electron density from metallic elements can contribute to the strong covalent network, thereby enhancing the incompressibility of metal borides. The Vickers hardness for $I4/mmm$ SrB_6 was estimated to be 19 GPa by using the microscopic hardness model [60]. We also determined the stress-strain relations for the recoverable $I4/mmm$ structure of SrB_6 along different crystallographic directions, which provides insights into the local bond deformation mechanisms that establish key benchmarks for the intrinsic mechanical properties of a material. The calculated peak stresses provide a comprehensive and quantitative understanding of the value, range, and trend of the stress response under each type of strain. Tensile stresses along high-symmetry directions are first examined to find the weakest tensile directions that determine the easy cleavage planes. As shown in Fig. 5(a), we can find that the $I4/mmm$ structure has strong stress responses in the $\langle 001 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$, and $\langle 101 \rangle$ directions with a peak tensile stress between 21 and 27 GPa. The weakest tensile direction is along the $\langle 100 \rangle$ direction with an ideal strength of 15 GPa, and thus the $\{100\}$ planes represent the easy cleavage planes. Structural snapshots [Fig. 5(c)] show that the boron bonds between the two biaugmented triangular prisms are the main load-bearing component where significant B-B stretching and breaking occur under large tensile strain. To investigate the nature of bonding states, we plot the two-dimensional electron localization function (ELF) for the key

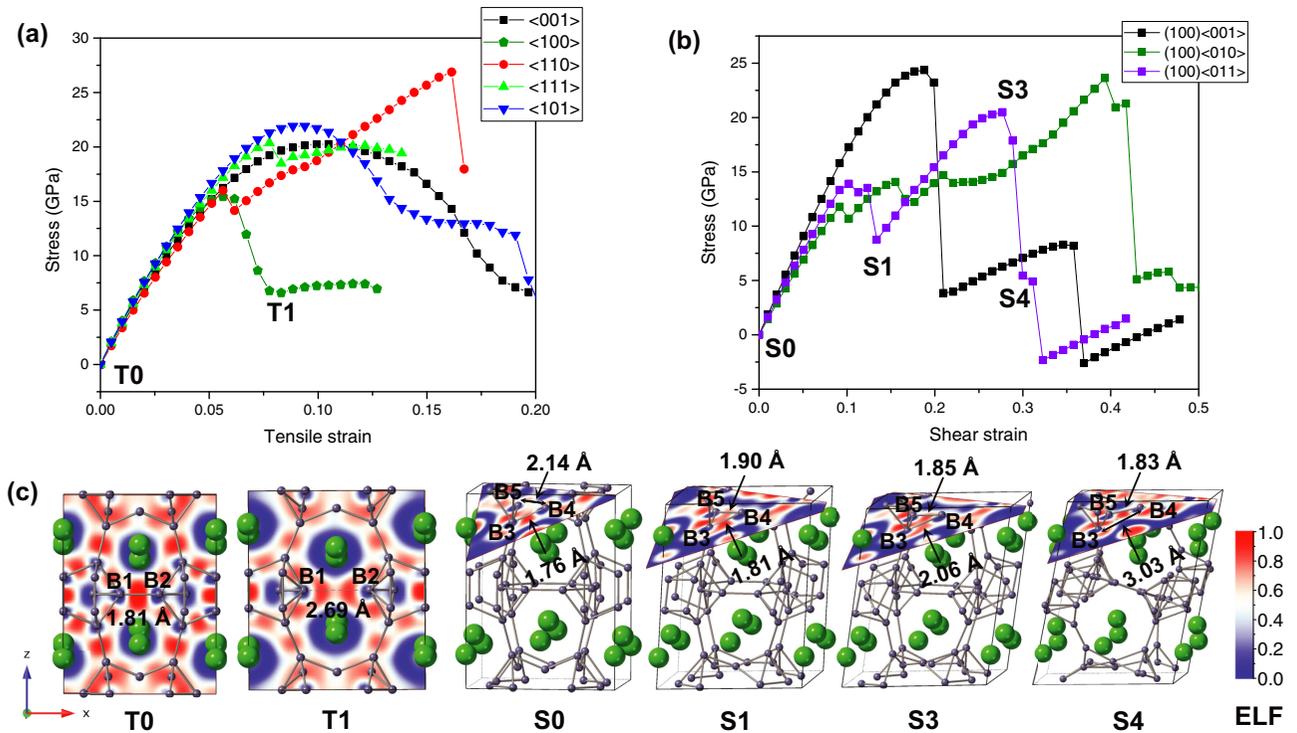


FIG. 5. (a) Calculated tensile stress-strain relations for the $I4/mmm$ structure. (b) Calculated shear stress-strain relations for the $I4/mmm$ structure in the (100) easiest cleavage plane. (c) Two-dimensional electron localization function (ELF) for the key structural snapshots of the $I4/mmm$ structure in the tensile and shear directions. The small and large spheres represent B and Sr atoms, respectively.

snapshots of $I4/mmm$ SrB₆ under several critical tensile (T) and shear (S) strains [Fig. 5(c)]. The covalent bonding nature of B₁-B₂ (1.81 Å) bonds is clearly visible at equilibrium (T0). As the tensile deformation along the <100> direction increases, the B₁-B₂ bond is continuously stretched and eventually broken when the tensile strain reaches $\epsilon = 0.08$ (T1). The calculated ELF shows localized electrons separated by a clear gap, indicating bond breakage.

We next evaluate the shear stress response in the (100) “easy cleavage planes” of SrB₆, and an ideal shear strength of 21 GPa is obtained in the (100)<011> shear direction [Fig. 5(b)]. Intriguingly, our calculations reveal that the ideal shear strength first experiences a small drop and then increases quickly when the shear strain achieves $\epsilon = 0.13$ (S1) in the (100)<011> shear direction. These results point to unusual bonding characteristics in the $I4/mmm$ structure of SrB₆. To examine the nature of these bonding states, we further plot the ELF for the structural snapshots at several critical shear-stress strains [Fig. 5(c)]. With the increase of the shear deformation in the (100)<011> direction, the B₃-B₄ bond continuously stretches and becomes weaker, resulting in a small decrease of the shear strength at S1. We also found that the bond length of B₄-B₅ decreases while that of B₃-B₄ increases, accompanying charge transfer from the B₃-B₄ bond to the center of an interesting three-center bond ($\Delta B_3B_4B_5$). The strong three-center covalent bonding makes the structure stronger with high ductility and it undergoes a second elastic response regime until the shear strain reaches $\epsilon = 0.29$ (S3), resulting in a high peak stress of 22 GPa. This ductility and extended elastic behavior is in stark contrast to the results for other borides, e.g., the bonds break simultaneously at the peak strain

with a precipitous drop in FeB₄ [61]. Once the shear strain reaches $\epsilon = 0.3$ (S4), the three-center bond of $\Delta B_3B_4B_5$ collapses, eventually causing structural deformation. The B₃-B₄ bond length drastically changes to 3.03 Å, and there are no localized electrons between the B₃ and B₄ atoms. These ideal strength results suggest a theoretical hardness of 15 GPa for the quenched $I4/mmm$ structure of SrB₆. The multicenter bonding transition produces a simultaneously high-strength and high-ductility state in $I4/mmm$ SrB₆, making it suitable candidate for various applications, such as cutting, drawing, and rolling.

IV. CONCLUSION

We combined automatic structure searching methods with first-principles calculations to investigate the high-pressure phase behavior and electronic/mechanical properties of crystalline SrB₆. We predicted two new high-pressure phases of SrB₆ that exhibit complex B covalent networks. Under high pressure, the ambient-pressure $Pm\bar{3}m$ structure of SrB₆ is first predicted to transform into the $Cmmm$ structure with the formation of a boron framework comprised of twinned pentagonal bipyramids. At higher pressure, SrB₆ develops a more complex network composed of twinned biaugmented triangular prisms in the $I4/mmm$ phase. The experimental XRD results are consistent with the predicted $I4/mmm$ structure, and the high-pressure phase was successfully recovered to ambient conditions. Our calculations suggest that the $I4/mmm$ structure of SrB₆ exhibits excellent mechanical behavior through a subtle quantum effect, which introduces the formation of three-center boron bonds from two-center bonds

via continuous charge transfer under shear strain. This unique behavior makes the $I4/mmm$ structure of SrB_6 promising as a material for applications that require conventionally “decoupled properties” due to the combination of high strength and enhanced ductility under shear strain. This work represents a significant step forward in understanding the high-pressure phase diagram of SrB_6 , and the results obtained will provide insight and guidance to future studies on other borides.

ACKNOWLEDGEMENTS

This work was supported by DARPA under Grant No. W31P4Q1310005. Computations were carried out at the supercomputer Copper of DoD HPCMP Open Research Systems under Project No. ACOMM35963RC1 and the Memex cluster of Carnegie Institution for Science. R.E.C. was also supported by the European Research Council Advanced Grant ToMCaT.

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