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Ab initio equation of state of α- and β-boron: Possible amorphization of β-boron under high pressure

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The equation of state of α- and β-boron have been studied by means of density-functional theory-generalized gradient approximation-projector-augmented wave (ABINIT) calculations up to 300 GPa. No distortion is observed in the α phase. Two structures have been considered for the β phase: the classical β-105 as well as the recently proposed β-106 structure. The free-energy differences between these two structures are very small but their evolution under pressure are quite different. The β-106 structure is in better agreement with experiment by having an insulator/metal transition and a pressure-induced destabilization of the structure that could lead to an amorphization.

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I. INTRODUCTION

In the periodic table boron is just located at the boundary between metals and insulators. This special position leads to unusual chemical bonding and a great complexity of crystallographic forms. No more than 16 allotropes have been reported but most of them are probably stabilized by impurities. Three phases seem to correspond to pure boron: α-B_{12},[1] β-B_{105},[2] and T_{192}.[3] Both present the same structural unit, i.e., a boron icosahedron B_{12}. Although this unit is favorable for satisfying the bonding requirement of boron atoms B_{12} is not stable by itself. In solid state, B_{12} units are linked in such a way that the octet rule is satisfied with two kind of bonds: normal covalent two-center bonds and more unusual metallic three-center bonds. Three-center bonds are located within the icosahedron and covalent two- and three-center bonds are found between the icosahedra. Such B_{12} units may also be present in boron clusters such as B_{98-102}-stuffed fullerene systems.[4]

The simplest structure, α-boron, is constructed from one icosahedron in a rhombohedral unit cell comprising two inequivalent atomic sites B1 and B2. The atoms in the B1 site are usually called *polar* (p) atoms and form the triangles of the icosahedron. The atoms in the B2 site are called *equatorial* (e) and form an irregular hexagon. Its equation of state (EoS) has been measured up to above 100 GPa.

β-boron has a more complex arrangement of icosahedra (Fig. 1). In its ideal form, this system can be reformulated as $(B_{84})(B_{10}BB_{10})$ (Ref. 5), where B_{84} is a quasispherical entity approximately centered on a face-centered rhombohedral lattice.[6] The chain $(B_{10}BB_{10})$ is aligned with the threefold axis and is located at the center of the octahedron formed by the B_{84} units. Three kinds of more or less irregular icosahedra could then be viewed in this picture. It should be emphasized that such a structure has many holes which are large enough to host extra atoms. Thereof, the distribution of extra boron atoms as well as some partial occupancy of crystallographic sites contribute to a somehow more complex structure for the true β-boron. It was experimentally shown that the hexagonal unit cell may contain 320 atoms with interstitial and partial occupations.[7,8] As a matter of fact this crystal structure is not fully elucidated up to now.

Contrary to experimental results density-functional theory (DFT) in local density or generalized gradient approximation (LDA, GGA) found the α-boron form more stable than the β-B_{105} form.[9] Taking into account some partial occupations of crystallographic sites in β-boron was not able to change this conclusion until the recent paper of van Setten *et al.*[10] Including the zero-point energy in their calculations they found β-boron as the most stable system with a cell containing 106 atoms. In this structure one atom is moved from a B13 (6h) Wyckoff position (site numbering from Ref. 5) to a new B16 (6h) site and one more atom is added in this same B16 site. Although the insulating character is not reproduced for β-B_{105} (Ref. 11) with or without atomic disorders, β-B_{106} presents a dielectric gap in the density of states (DOS) which seems an essential result. At high temperature it was also

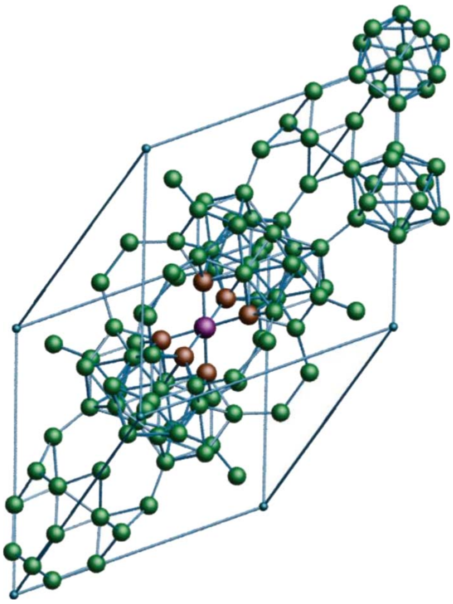

FIG. 1. (Color online) Side view of the unit cell of β-boron (courtesy of Ref. 10). Most atoms are part of icosahedra. The central atom (purple) is in B15 position and connects two groups of three interpenetrating icosahedra via atoms at B13 sites (red).

shown that the introduction of extra B atoms in the cell could stabilize the system.[12] Quantum molecular-dynamics simulations confirmed that symmetry-broken forms of β-boron containing more than 105 atoms are required to stabilize this system.[13] Such structures allowed to take into account partially occupied sites—intrinsic disorders—according to thermodynamics. Monte Carlo techniques combined with *ab initio* calculations led to more complex and realistic pictures of defected β-rhombohedral boron and some explanations of the origin of such defects are proposed.[14]

As the packing efficiency of icosahedral structures is very low, a destruction of icosahedron is expected under pressure. Indeed the formation of denser systems are proposed like an α-Ga-type structure[15,16] or a tetragonal T_{192} phase at high temperature above 10 GPa.[17] The EoS of β-boron has been measured up to 100 GPa and an amorphization has also been observed beyond 100 GPa at ambient temperature.[18] Very recently Oganov *et al.*[19] proposed a new structure (γ-B_{28}) which would be stable in the range 30–90 Gpa at high temperature.

Giving up the tricky question of allotropic stability at room conditions we have undertaken the determination of EoS of α and β-boron—keeping the usual 105 structure as well as the new 106 structure—by first-principles calculations. Opposite to systems proposed in (Ref. 13) Pearson *hR*141 models and supercells and[14] such a simpler 106 structure allows to perform more convenient calculations under pressure. This is an important starting point for further studies. The aim of this work is to see if the pressure behavior of the β-106 structure is in better agreement with experiments than the 105 structure.

II. COMPUTATIONAL DETAILS

The electronic structure, EoS, and total energies are calculated using the projector-augmented wave (PAW) method,[20] one of the most accurate techniques in the framework of the density-functional theory using GGA approximation. This method is based on the coupling of two basis to develop the electronic wave functions: a plane-wave basis on which "pseudo" quantities are expressed and a local basis (partial-wave basis), centered on each atoms, used to retrieve "true" quantities from pseudo ones. The local basis set is defined by nonoverlapping spheres delimited by a radius r_{PAW}. A PAW calculation requires the definition of several quantities defining the atomic entity and a partial-wave basis. For boron, we choose to treat three valence states—1*s* states as frozen—with four projectors (two *s* and two *p*). The PAW radius is 1.7 a.u. and convergence tests gave a kinetic-energy cutoff as 324 eV.

The code used for the generation of the PAW dataset[21] is ATOMPAW (Ref. 22) and the PAW-DFT calculations are performed with the ABINIT code.[23,24] The widely used exchange-correlation functional PBE (Ref. 25) is used. A smearing scheme (with σ=0.14 eV) is applied in order to reduce the number of *k* points needed to reach the convergence.[26] A set of Monkhorst-Pack **k** meshes[27] of $8\times8\times8$ and $2\times2\times2$ for α-B_{12} and β-B_{105} (106) are used to sample the Brillouin zone. These grids were, respectively, extended to $12\times12\times12$ and $4\times4\times4$ for the calculations of densities of states. In the framework of the β-105 form the whole symmetries of the rhombohedral Space Group (n°166:R$\bar{3}$m) are preserved and the simulations are easier than for the monoclinic β-106 structure.

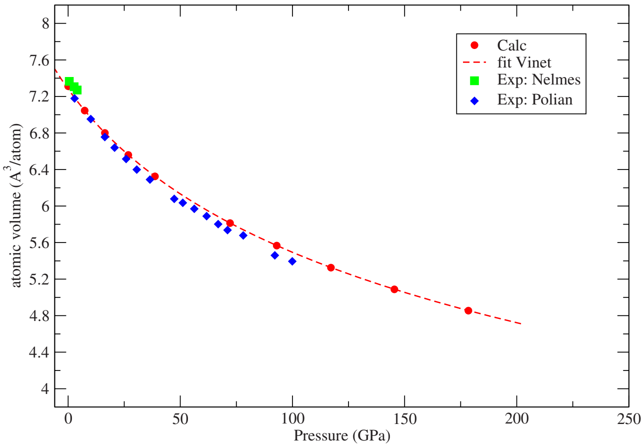

FIG. 2. (Color online) $P(V)$: the equation of states of α-B_{12} compared to the results of Nelmes *et al.* (green points) and those of Polian *et al.* (red points).

For the three boron phases we have first performed a global relaxation of all the internal degrees of freedom at ambient pressure. Then the EoS are built by calculating the total energy for several values of the volume. For each volume a full relaxation is again performed and the pressure is calculated.

III. ALPHA-BORON STRUCTURE

The zero-pressure volume of the hexagonal cell was found to be equal to 262 Å^3 (7.28 Å^3/atom) which is in very good agreement with the experimental value [264 Å^3 (Ref. 28)]. Similar good results are also obtained for the two internal parameters of the boron atoms in the cell.

The equation of state $P(V)$ is drawn in Fig. 2 and the data were fitted to the Vinet equation.[29] We also reported the three experimental low-pressure points ($P<4$ GPa) (Ref. 28) used for the determination of bulk modulus and the recently measured EoS.[30] The bulk modulus B_0=212 GPa and its derivative B'=3.79 are close to the values determined previously[31] as well as in this last study (B_0=207.1 GPa and B'=4.2).

The **a** parameter smoothly decreased as expected. The variation in the apex angle of the rhombohedral unit cell related to **c**/**a** in the hexagonal cell is weak. In order to check a possible deformation of the icosahedron under compression, we measured the *polar-polar* and one of the *equatorial-equatorial* bond lengths found in the B_{12} entity. These two normalized values $R_p(P)/R_p(0)$ and $R_e(P)/R_e(0)$ decreased monotonically and the spreading out the curves barely increased with increasing pressure. Such results point out a quasiregular compression and stability of boron icosahedron in the α structure. We extended our calculations to 490 GPa, higher limit of diamond anvil cells apparatus and the integ-

TABLE I. Lattice parameters (rhombohedral), bulk modulus, and its pressure derivative of β-boron.

Phase	β-105	β-106	Literature[a]	Experiments
a (Å)	10.107	10.073	9.996	10.145[b]
α	65.01	65.15	65.22	65.17[b]
B_0 (GPa)	220	216	203.5	210[c]
B'	2.60	2.45	4.5	2.23[c]

[a]Reference 9.
[b]Reference 5.
[c]Reference 18.

rity of the B_{12} icosahedron is kept. At this pressure it is worth noticing a small overlap (5%) between PAW spheres. Upon compression the α-boron structure maintains its rhombohedral lattice up to high pressure.

Concerning the electronic density of states, as the boron-boron interactions get strength the bands broaden and the gap is reduced. Some small states grow around the Fermi level (E_F) and a pseudogap is observed. Nevertheless the full band-gap closure is never achieved and the weak peak at Fermi level does not increase a lot with compression: 0.015 eV^{-1} at 178 GPa and 0.031 eV^{-1} at 378 GPa.

IV. BETA-BORON STRUCTURE

A. Beta-105 form

To start the calculation we performed a full relaxation of the ideal structure as well as the defect structure proposed by Hoard.[5] In this case the B13 (6h) is partially occupied by four atoms and the remaining two atoms are located in a new B16 (6h) site. As this last configuration led to a slightly less stable system, we chose to keep the ideal β structure for all further calculations. The calculated equilibrium hexagonal volume (2430 Å^3 and 7.71 Å^3/atom) is 30 Å^3 lower than the experimental one leading to a small relative difference of 1.2%. The bulk modulus and its first derivative (Table I) are also in good agreement with experiments.

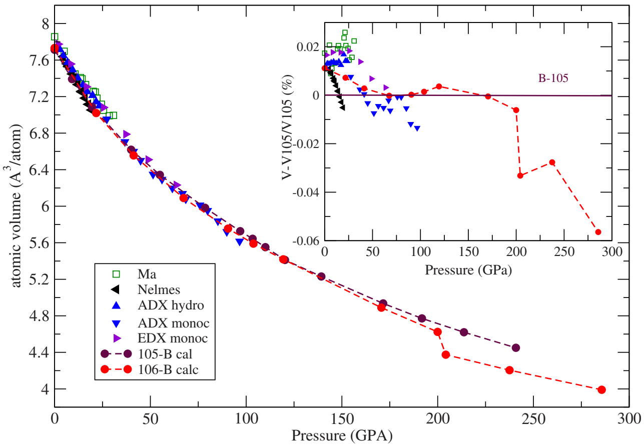

FIG. 3. (Color online) $P(V)$: the equation of state of β-boron compared to experimental results. The insert shows $P(V)$ with volume relative to β-105 equilibrium volume.

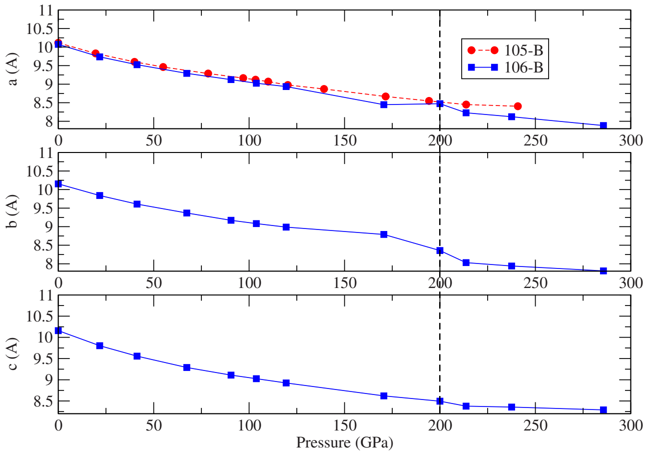

FIG. 4. (Color online) Cell parameters of β-105 (a) and β-106 boron (a,b,c) as a function of pressure.

The different available experimental equations of state[16,18,28] are compared with our calculation (Fig. 3). For the sake of clarity we have also drawn in the inset the EoS as relative differences ($V-V_{105}/V_{105}$) between experiments and calculation.

The evolution of cell parameters (a and α) are presented in Figs. 4 and 5. The variation in the rhombohedral angle α—related to $\mathbf{c}/\mathbf{a}$ in an hexagonal representation—under compression is different from those of the α-B_{12} system.

Over the pressure range investigated here, α hardly changes ($\sim$1.5°), only by a small monotonic increase. Such a curve is linked to the pressure variation in the different bond lengths found in the β-boron structure. It was already pointed out (Ref. 6 histogram Fig. 1) the system presents a great range of interatomic bonding lengths due to very distorted boron icosahedra. In this paper, no more than 19 different bond lengths ranging from 1.623 to 1.912 Å were counted. The average distances within the central, rhombohedral, and equatorial entities were, respectively, measured to 1.762, 1.840, and 1.808 Å. Under compression, all these distances are modified in a complex and coupled way leading to a strong deformation of the system. For example, the B11-

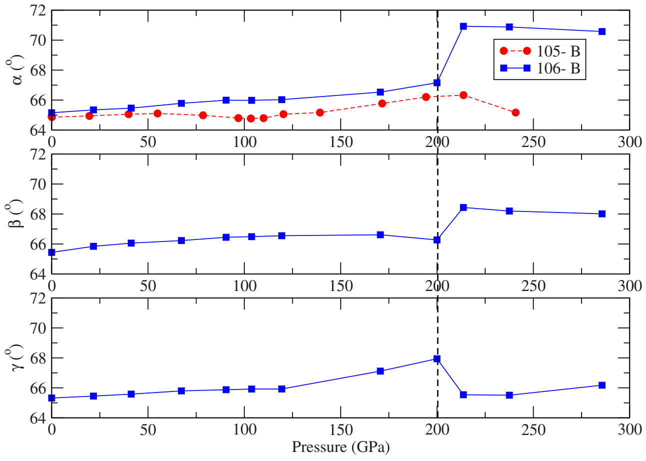

FIG. 5. (Color online) Cell parameters of β-105 (α) and β-106 boron (α,β,γ) as a function of pressure.

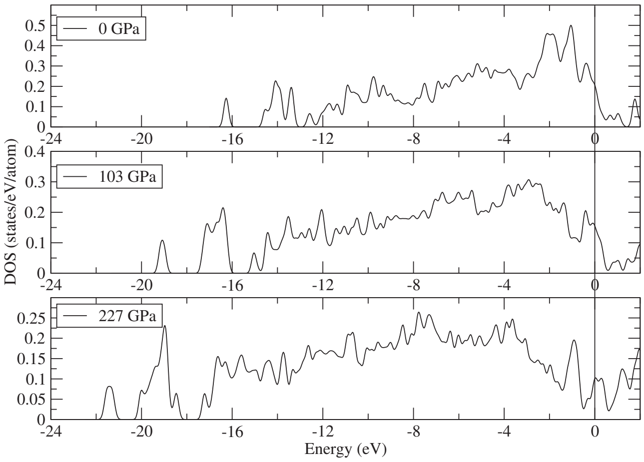

FIG. 6. Densities of states (states/eV/atom) for β-105 boron—energy relative to E_F.

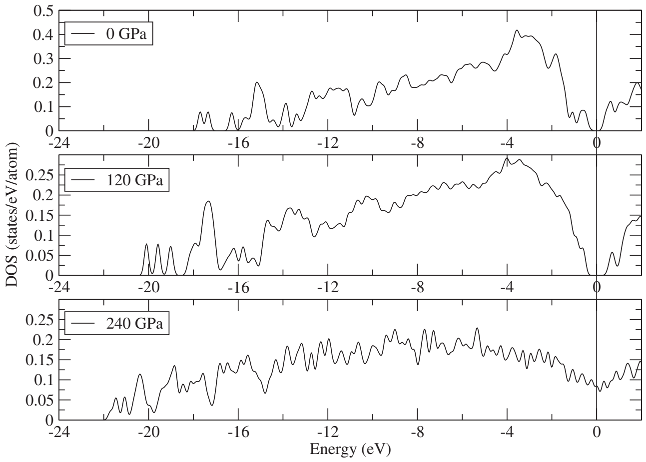

FIG. 7. Densities of states (states/eV/atom) for β-106 boron—energy relative to E_F.

B12 distance—inside the B_{10} cluster—hardly changes between 0 and 100 GPa (1.77 Å in our calculation) although the B5–B7 distance evolves from 1.748 to 1.520 Å. Then, although the relationship to α is not straightforward an important modification of this angle could be expected.

At ambient pressure, although a gap is present on the DOS (Fig. 6), the Fermi level falls just below the gap and a density of states is observed at E_F. This feature, already pointed out in the literature, is in complete disagreement with experiments as boron is a semiconductor. At high pressure the DOS evolve and E_F is classically shifted above the gap.

B. Beta-106 form

The EoS of the β-106 structure is also reported in Fig. 3. As the equilibrium properties such as equilibrium volume, bulk modulus, and its first derivative are close to those of the β-105 form (Table I), the two EoS are very close. These results show the little impact of intrinsic disorder on these mechanical properties, at least for low pressures. Nevertheless the equilibrium volume of β-106 (2460 Å^3 and 7.73 Å^3/atom) is closer to experiment than the one of β-105. The energy difference between the two phases is 4 meV confirming the β-106 form as the stablest. We must mention that in this calculation the zero-point energy is not included and the α structure remains the lowest in energy.

The DOS (Fig. 7) is very different from that of the β-105 because it presents a true dielectric gap. The adjunction of a single atom in the rhombohedral lattice completely modifies the electronic structure as expected in a rigid-band model. Under pressure, the gap reduces and a complete closure is obtained around 205 GPa. The metallization accompanies a phase transformation and the system evolves toward an apparent triclinic structure (Figs. 4 and 5). Above the transition no more icosahedra are noticeable in the cell and some hexagonal arrangements of boron atoms begin to appear. The EoS also presents a drastic modification beyond 205 GPa with a strong decrease in the volume (3.9%).

V. CONCLUSION

We have performed first-principles (DFT, GGA) calculations on α, β-105, and β-106 boron under pressure. This β-106 structure was proposed in order to reproduce the energetic hierarchy of α and β phases and also the dielectric gap.[10] The EoS are obtained and compared to available experiments. Good agreement with experiments is obtained for both α and β phases. That gives confidence in the ability and accuracy of theoretical predictions within the DFT-GGA with PAW formulation.

The behavior of the three structures is very different. The α-boron allotrope remains undistorted up to very high pressure. The β-boron structure exhibits strong deformations of icosahedra under high compression. The bond lengths vary in a complex manner leading to a phase transition around 205 GPa for the β-106 case. This structural transition is accompanied by a metallization.

The amorphous configurations could only be obtained by a quantum molecular-dynamics simulation starting in the liquid phase above 200 GPa and by quenching in a metastable state at low temperature. Nevertheless we believe that the pressure evolution of the β-106 structure matches the experimental pressure evolution of β-boron at low temperature: (i) the general shape of the calculated EoS—related to the experimental one, (ii) the structural transition and the metallization, and (iii) the disappearance of icosahedra. The observed 100 GPa pressure shift between the measurements of Sanz *et al.*[18] and the calculated transition pressure at 205 GPa is not unusual in the calculations of solid-solid phase transition and it could stem either from the DFT-GGA approximation or from the lack of a true representation of the amorphous phase. This shift also may be due to the chosen model (106 atoms in the cell). As already stated in Refs. 13 and 14, and according to partial crystallographic occupancies a single unit cell may be not enough to accurately describe the true β-boron behavior. Taking into account more complex structures may improve the pressure transition.

To summarize, the pressure behavior of the β-106 structure is in closer agreement with experiment than β-105. The semiconducting behavior is reproduced and a structural instability is evidenced at high pressure. The simple β-106 structure model seems to be a better candidate for further simulations (electrical conductivity).

The present study also confirms the importance of intrinsic disorder on the properties of boron, not only at low pressure where zero-point effects are large but also at very high pressure.

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