Comment on “New Ground-State Crystal Structure of Elemental Boron”

In a recent Letter, density functional theory (DFT) calculations were carried out on a structure observed by high resolution transmission electron microscopy experiments and used to predict that \( \tau \)-B is the ground state structure of elemental boron at atmospheric pressure [1]. We have performed DFT total energy calculations on the structures provided in the Supplemental Material (SM) of Ref. [1] using the same code (VASP v.5.3.5) and calculation conditions used in that work, and with two projector-augmented wave pseudopotentials distributed with the VASP code that have different core radius for the projection operator: RMAX = 2.583 (PS 1) and RMAX = 1.732 (PS 2) [2–5]. In Ref. [1], it was reported that the pseudopotential from Ref. [5] was used for all calculations. An additional set of calculations were performed using PWSCF v.5.2.0 [6] with a cutoff energy of 40 Ry using an ultrasoft pseudopotential [7] and with a well converged numbers of \( k \) points. The relative energies of our three independent calculations are all in agreement (within about 0.2 meV/atom) and indicate that \( \tau \)-B106 is higher in energy than both \( \alpha \)-B12 and \( \beta \)-B106 (\( \delta E_{\tau-B} = +12.9 \) meV/atom and \( \delta E_{\tau-B} = +11.8 \) meV/atom); i.e., the ground state of elemental boron is not \( \tau \) boron. To understand the source of discrepancy between our results and the results presented in Ref. [1], we compared the total energies of these systems calculated with VASP, the code that was used to obtain the results of Ref. [1], using the two different pseudopotentials PS 1 and PS 2 (see Fig. 1). It has turned out that our total energies of \( \tau \)-B105 and \( \beta \)-B106 calculated with PS 2 are identical to the corresponding values in the SM for Ref. [1] (Fig. 1). This observation strongly suggests that the total energies provided in the SM of Ref. [1] were obtained with two different pseudopotentials. Finally, we comment on the revised conclusions provided in the Erratum [8] regarding relative stabilities of \( \beta \) boron and \( \tau \) boron at high temperature. The claim that \( \tau \) boron may be more stable than \( \beta \) boron for \( T > 950 \) K, is in contradiction with the experimental observation that liquid boron solidifies into \( \beta \) boron, not \( \tau \) boron [9,10].

In summary, we have performed DFT total energy calculations of the boron allotrope structures published in Ref. [1] using two different \textit{ab initio} codes, VASP and PWSCF, and two different pseudopotentials for VASP. None of our simulation results support the conclusion of Ref. [1], and instead indicate that \( \tau \) boron is not the ground state. We have shown clear evidence that the total energies calculated with VASP and published in Ref. [1] were most likely obtained by the inconsistent use of pseudopotentials, which has led to an incorrect conclusion.

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FIG. 1. Total energies of boron allotropes calculated with two different pseudopotentials compared to the data published in Ref. [1]. It appears that the published data in Ref. [1] were generated with two different pseudopotentials: PS 1 for \( \alpha \)-B12, \( \beta \)-B105, \( \beta \)-B106 and \( \gamma \)-B28, and PS 2 for \( \tau \)-B105 and \( \tau \)-B106.