Ab-initio study of the ground state structure of elemental boron

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It is generally considered that an elemental material solidifies into a crystal form with a full translational symmetry. To the best of my knowledge, helium is only the well-known exception in the periodic table, which does not solidify at T=0K at ambient pressure. Boron, the fifth element in the periodic table, is known to have a peculiar solid phase; the believed-to-be most stable structure at ambient condition has partially occupied sites (POS, 23 out of 320 atoms per hexagonal cell), therefore the translational symmetry is likely to be violated. Since this solid form, β-rhombohedral boron (β-boron), is usually made from its melt by slow cooling, it might be reasonable to assume that β-boron is a thermodynamically stable only at high temperature due to the entropic contribution from the POS. Indeed, many of previous *ab-initio* studies, except for one, concluded that a simpler allotrope of boron, α-rhombohedral boron is more stable than β-boron at T=0K, though the observed POS were not fully counted in their studies.

We have performed the first-ever global optimization on the POS configuration using the method combining the discrete lattice model Monte Carlo and the *ab initio* DFT calculation and found that β-boron is more stable than α-boron at T=0K. The keys to understand the stabilization mechanisms of β-boron are the followings: The imbalance in the electron deficiency among of its building units, the local instability in the one of building units, and the three-center bond unique to boron. *Boron is likely to be an exceptional case in the periodic table, whose ground state structure is an imperfect crystal due to intrinsic frustration.* This work was performed under the auspices of the U.S. Dept. of Energy at the University of California/ LLNL under contract no. W-7405-Eng-48.