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Published on Web 01/21/2009

Imperfect Crystal and Unusual Semiconductor: Boron, a Frustrated Element

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Abstract: All elements, except for helium, appear to solidify into crystalline forms at zero temperature, and it is generally assumed that the introduction of lattice defects results in an increase in internal energy. β-Rhombohedral boron, a thermodynamically stable form of elemental boron at high temperature, is known to have a large amount of partial occupied sites, seemingly in conflict with our common knowledge. By using lattice Monte Carlo techniques combined with ab initio calculations, we find that the β-phase is stabilized by a macroscopic amount of intrinsic defects that are responsible not only for entropic effects but also for a reduction in internal energy. These defects enable the conversion of two-center to three-center bonds and are accompanied by the presence of localized, nonconductive electronic states in the optical gap. In addition we find that the ab initio Ising model describing the partial occupancy of β-boron has macroscopic residual entropy, suggesting that boron is a frustrated system analogous to ice and spin ice.

Introduction

In the periodic table, boron occupies a peculiar, crossover position: on the first row, it is surrounded by metal-forming elements on the left and by nonmetals on the right. In addition, it is the only nonmetal of the third column. Therefore, it is perhaps not surprising that the crystallographic structure and topology of its thermodynamically stable allotrope (β-boron, space group $R\bar{3}m$),[1-3] composed of interconnecting icosahedra, is not shared by any other element, and is extremely complex.

It is experimentally known that β-boron contains many partially occupied sites (POS), with occupation rates that are not integer numbers, varying roughly from 2% to 75% from site to site.[3] The most accurate experimental estimate of the number of atoms in the hexagonal cell is 320.1,[4] which corresponds to approximately $106^2/_3$ atoms per rhombohedral cell, implying a violation of rhombohedral symmetry. No experimental evidence of lower symmetry and/or longer-range ordering, presumably detectable by X-ray diffraction, has been reported. Although at finite T the presence of POS appears to be disordered, at zero T the true ground state of boron is expected to be fully ordered, so as to satisfy the third law of thermodynamics. Therefore, if the β-rhombohedral phase is the ground state, the disordered POS occupation observed at finite T should eventually exhibit a phase transition to an ordered phase at very low T.

A simpler allotrope of boron is the α-phase, which has a crystalline structure with 12 atoms per rhombohedral cell (space group $R\bar{3}m$ and no POS). To date, there is no direct experimental evidence that discriminates between the relative stability of the boron allotropes.[5] Large kinetic barriers and/or high melting temperatures ($T_{\text{melt}} = 2349$ K for β-boron) have possibly prevented accurate measurements by unambiguous techniques, such as calorimetry. However, α-rhombohedral boron has been extensively examined by ab initio density functional theory (DFT) calculations,[6-12] and there are a number of ab initio investigations where α- and β-boron total energies have been directly compared.[8-12] In the vast majority of these studies, a small subset of the possible POS configurations was considered

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(1) Hughes, R. E.; Kennard, C. H. L.; Sullenger, D. B.; Weakliem, H. A.; Sands, D. E.; Hoard, J. L. *J. Am. Chem. Soc.* **1963**, *85*, 361–362.

(2) Hoard, J. L.; Sullenger, D. B.; Kennard, C. H. L.; Hughes, R. E. *J. Solid State Chem.* **1970**, *1*, 268–277.

(3) Slack, G. A.; Hejna, C. I.; Garbauskas, M. F.; Kasper, J. S. *J. Solid State Chem.* **1988**, *76*, 52–63.

(4) This is an average value over different samples estimated by fitting to X-ray data. See page 60 of ref 3 for more detail.

(5) (a) There are experimental reports of the transition temperature from α-rhombohedral to β-rhombohedral boron. The transition is believed to be irreversible (no transition from β- to α-boron has ever been observed), and "*a large increase in the time required for the transformation with decreasing temperature was observed, indicating a large activation energy*",[5b] clearly indicating that the α to β "transition temperature" discussed in the literature is not the thermodynamic limit, in conflict with the interpretation of ref 9. (b) Carlsson, J.-O. *J. Less-Common Met.* **1980**, *70*, 77–96.

(6) Haussermann, U.; Simak, S. I.; Ahuja, R.; Johansson, B. *Phys. Rev. Lett.* **2003**, *90*, 065701.

(7) Mailhiot, C.; Grant, J. B.; McMahan, A. K. *Phys. Rev. B* **1990**, *42*, 9033–9039.

(8) Prasad, D. L. V. K.; Balakrishnarajan, M. M.; Jemmis, E. D. *Phys. Rev. B* **2005**, *72*, 195102.

(9) Masago, A.; Shirai, K.; Katayama-Yoshida, H. *Phys. Rev. B* **2006**, *73*, 104102.

(10) van Setten, M. J.; Uijttewaal, M. A.; de Wijs, G. A.; de Groot, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 2458–2465.

(11) Shang, S.; Wang, Y.; Arroyave, R.; Liu, Z.-K. *Phys. Rev. B* **2007**, *75*, 092101.

(12) Widom, M.; Mihalkovic, M. *Phys. Rev. B* **2008**, *77*, 064113.

10.1021/ja807622w CCC: $40.75

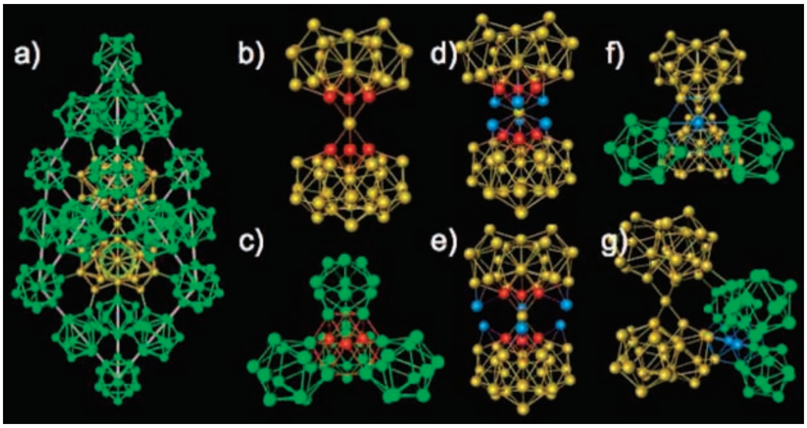

Figure 1. Building blocks of β-rhombohedral boron: (a) icosahedral B_{12} units (green spheres) are located at the corners and the middle edges of the rhombohedral unit cell. Two B_{28} units and an interstitial atom (gold spheres) are located in the middle of the unit cell. In panels b−g, the locations of the partially occupied sites (POS) are represented by red and blue spheres, with the same naming scheme used in ref 3. (b) B13 sites form trimers in the B_{28} units (red spheres); (c) B16 sites are located at the center of the hexagonal rings connecting B_{12} units (red spheres). (d) B17 sites and (e) B18 sites (blue spheres) next to and surrounding the B13 sites are shown. (f) B19 sites and (g) B20 sites (blue spheres) located at the middle of the hexagonal rings connecting B_{12} and B_{28} units are shown.

and it was concluded that α-boron is more stable than β-boron at zero temperature.[8,9,11] However, two recent investigations indicate that it is possible to find an arrangement of POS in β-boron that makes it more stable than the α-phase.[10,12] Due to the astronomical number of possible combinations of POS configurations, in all of the theoretical investigations that have appeared so far, the choice and occupation of POS have been based on semiempirical electron counting rules, experimentally measured occupation rates, or ab initio studies on small gas-phase boron clusters. The lack of a systematic, nonempirical optimization has so far prevented a microscopic description of the mechanisms by which defects (i.e., POS) may stabilize β-boron and ultimately an understanding of why such an unusual, complex state should be energetically favored.

In this paper, we used a combination of lattice model Monte Carlo techniques and ab initio DFT total energy calculations to carry out the first global configuration space search of POS occupations in β-boron. The results of this optimization procedure allowed us to identify a series of β-boron structures nearly degenerate in energy and more stable than α-boron at zero T. These are disordered structures with intrinsic self-doping, exhibiting localized electronic levels within the optical gap. The presence of POS enables the conversion of conventional two-center bonds, present in nondefective β-boron, into three-center bonds characteristic of many boron compounds.[13,14] In addition, we computed the thermodynamic properties of the ab initio Ising model used to describe the partial occupancy of β-boron and found that it exhibits macroscopic residual entropy, with no indication of a transition to an ordered POS distribution down to near zero T,[15,16] suggesting that elemental boron is a frustrated system, analogous to ice[17,18] and spin ice.[19]

Computational Approach

Unless otherwise noted, the ab initio DFT codes GP[20] and Qbox[21] were used for all the structural optimizations and the total energy calculations. To obtain all the ab initio results presented here, we used DFT[22] with the local density approximation (LDA).[23] We employed optimized norm-conserving nonlocal pseudopotentials[24] to represent the ionic core of boron, and the electronic wave functions were expanded in plane waves with a cutoff energy of 30 Ry. For all of the supercell calculations, we only used the Γ-point to sample the Brillion zone of the supercell; however, fine k-point grids were used for calculations used to compare total energies of different structures, that is, α- and β-rhombohedral boron phases (see Supporting Information sections 1 and 2). The phonon density of states (DOS) of α- and β-rhombohedral boron were calculated by ab initio linear response theory, as implemented in the computer package PWSCF, version 2.1.5, distributed at www.pwscf.org. The phonon DOS was used to estimate the quantum zero point motion of nuclei in the different phases of boron, which was included in the computation of total energies shown in Figure 2. The maximally localized Wannier functions shown in Figure 3 were calculated with the Wannier90 computer program,[25] distributed at www.wannier.org, from electronic wave functions optimized with the PWSCF code. A detailed discussion of the choice of parameters, calculation procedures, and an assessment of the accuracy (including comparison with previous first-principles studies and with experiments) is provided in the Supporting Information.

In order to carry out an optimization of the β-boron structure including all of the POS, an efficient global configuration space search scheme is needed, as there are $\left[{504 \atop 92}\right]$ possible POS configurations for the 1280-atom supercell used in this work.[26] We have developed a generalized Ising model parametrized from first principles and have performed simulated annealing to obtain stable POS occupation configurations[27−29] (see Supporting Information

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(13) Although the three-center bond of boron might seem unusual, the bonding scheme was first explained in terms of a simple linear combination of atomic orbitals description more than 40 years ago. For isolated trimer configurations, see ref 14. For more general cases, including extended systems, see ref 42.

(14) Durrant, P. J.; Durrant, B. *Introduction to Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1962; Chapt. 5.

(15) Ogitsu, T.; Gygi, F.; Reed, J.; Udagawa, M.; Motome, Y.; Schwegler, E.; Galli, G. Manuscript in preparation.

(16) The replica Exchange Monte Carlo simulations have been performed down to 0.001 meV (or ∼10 mK) with no evidence of a phase transition.

(17) Pauling, L. *J. Am. Chem. Soc.* **1935**, *57*, 2680–2684.

(18) Giauque, W. F.; Stout, J. W. *J. Am. Chem. Soc.* **1936**, *58*, 1144–1150.

(19) Bramwell, S. T.; Gingras, M. J. P. *Science* **2001**, *294*, 1495–1501.

(20) Gygi, F. *GP 1.24.0*, A General Ab Initio Molecular Dynamics Program; Lawrence Livermore National Laboratory: Livermore, CA, 2003.

(21) Gygi, F. *Qbox*, a large-scale parallel implementation of first-principles molecular dynamics, http://eslab.ucdavis.edu/.

(22) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136*, B864–B871. Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133–1138.

(23) Ceperley, D. M.; Alder, B. J. *Phys. Rev. Lett.* **1980**, *45*, 566–569. Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048–5079.

(24) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993–2006.

(25) Mostofi, A. A.; Yates, J. R.; Lee, Y.-S.; Souza, I.; Vanderbilt, D.; Marzari, N. *Comput. Phys. Commun.* **2008**, *178*, 685–699.

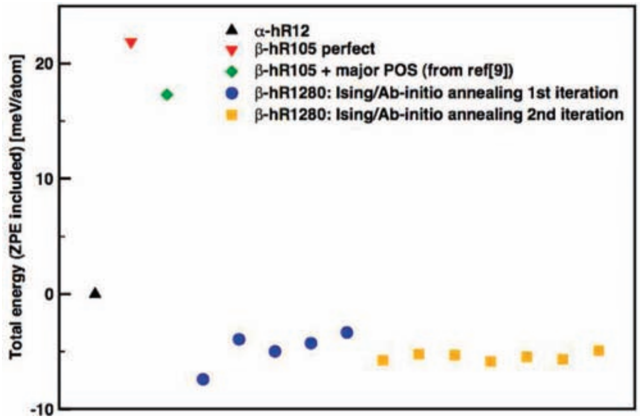

Figure 2. Relative ab initio DFT total energies, including zero-point energy contributions, of α-rhombohedral boron (black triangle), perfect β-rhombohedral boron (red triangle, 105 atoms in the rhombohedral unit cell), β-rhombohedral boron with only B13 and B16 POS from ref 9 (green diamond). Blue circles and yellow squares are the ab initio DFT total energies of hR1280 systems obtained in steps iv and v of the CEMC/ab initio procedure (see text). Each symbol corresponds to the total energy of a single hR1280 structure (not an averaged value).

section 3 for more details). This approach, usually referred to as cluster expansion Monte Carlo (CEMC), has been used to successfully identify the ground state of intermetallic compounds such as AlNi, CuRh, CuPd, CuPt, and CuAu[27] and the observed ordered vacancy phases in Li_xCoO_2.[29] In our case, we mapped the POS occupation numbers onto a spin Hamiltonian and expressed the total energy of the β-phase as a linear combination of correlations in occupancy between different sets of POS. The coefficients of such an expansion were fitted to ab initio total energy data obtained for a large set of configurations. Our optimization strategy consists of the following steps: (i) We considered rhombohedral cells with both 106 and 107 atoms (hR106 and hR107, respectively, corresponding to 318 and 321 atom/hexagonal cells, thus bracketing the number of atoms/cell proposed experimentally, ∼320). The total number of possible configurations (∼150 million in the case of hR107) was restricted to symmetrically independent and physically relevant ones, thus reducing their number to 2591. (ii) Using the correlation coefficients obtained by fitting these 2591 total energies, we constructed a spin Hamiltonian for supercells containing 1280 atoms (referred to as hR1280 hereafter). (iii) Monte Carlo simulated annealing cycles with the Metropolis algorithm were then performed for this Hamiltonian. (iv) The most stable hR1280 structures obtained by the MC annealing procedure were further optimized by ab initio methods, by relaxing both atomic positions and cell parameters.[30] (v) The new ab initio results were inserted back into the database fit to improve the model, and further iterations of steps iii and iv were carried out. At the end of the fitting procedure, the accuracy of model Hamiltonian to the DFT energy reached roughly within a few millielectronvolts per atom for the low-energy structures. We now turn to the discussion of the results obtained in our optimization procedure, but first we discuss the features of β-rhombohedral boron known experimentally.

Results and Discussion

Figure 1 illustrates the building blocks of β-boron. The main backbone can be viewed as 20 B_{12} icosohedra located at the corners and edges of a rhombohedral cell, with two B_{28} clusters connected by an interstitial atom in the center. Within this backbone there are 15 inequivalent sites (i.e., sites not related by symmetry operations), which we refer to as B1−B15, following the notation of previous works.[2,3] The B13 site, which is located in the B_{28} clusters next to the interstitial atom (see Figure 1b), is a vacancy-type POS, known from experiment to have an occupation of approximately 75%.[2,3] If all of the B13 sites were fully occupied, β-boron would be a perfect crystal with 105 atoms in a rhombohedral unit cell (commonly referred as hR105). In addition to those on the main backbone, five additional inequivalent sites B16−B20 (see Figure 1c−g) have been identified as POS by experiment.[31] It is interesting to note that in all of the previous ab initio studies where β-boron was found to be higher in energy than α-boron, the atomic density was an approximation of the experimental value, and the B17−B20 POS were not taken into account;[32] on the other hand, in the two ab initio studies[10,12] where β-boron was found to be more stable than α-boron, the B17−B20 POS occupations were studied, though only a very limited number of occupation configurations were considered.[33]

As shown in Figure 2, by using the ab initio CEMC method described in the previous session, we obtained a family of (meta-)stable structures with very similar DFT total energies (within a few millielectronvolts per atom of each other), suggesting a nearly degenerate character of the β-boron phase. These energies are several millielectronvolts per atom lower than that of α-boron (the total energy of the most stable one is 7.5 meV/atom below that of α-boron). All total energies were computed by including the zero-point energy (ZPE) contribution evaluated from ab initio full phonon dispersion calculations.[34]

In all stable hR1280 structures found by our optimization procedure, there are specific sets of POS that are always occupied, and the POS occupation configurations exhibit clear short-range correlations responsible for structural stabilization. For example, B17 and B18 POS are always present in the lowest energy structures (see Table S3.1 in Supporting Information) and they always appear in a paired configuration next to two B13 vacancies, similar to previous predictions by Slack et al.[3] However, in our stable structures the configurations of the B13 vacancies are different from those suggested in ref 3; we find

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(26) The number of possible configurations is calculated as follows: The 1280 atom supercell contains 12 rhombohedral cells. In the rhombohedral cell, the positions of 99 atoms correspond to fully occupied sites. This number is obtained by adding the total number of sites for B1−B12, B14, and B15. The number of each site can be found in ref 3. Note that the numbers reported in the literature are for the hexagonal cell, so one should divide by 3 to obtain the numbers used here. In the 1280-atom supercell, 99 × 12 = 1188 atoms have coordinates corresponding to fully occupied sites. Therefore, 1280−1188 = 92 atoms have coordinates corresponding to POS. The total number of possible POS in the 1280-atom supercell is (6 + 6 + 6 + 6 + 6 + 12) × 12 = 504. Finally, the 92 POS atoms can be distributed over the 504 sites, which corresponds to $\left[{504 \atop 92}\right]$ possible configurations.

(27) Lu, Z. W.; Wei, S.-H.; Zunger, A. *Phys. Rev. B* **1991**, *44*, 512–544.

(28) Garbulsky, G. D.; Ceder, G. *Phys. Rev. B* **1995**, *51*, 67–72.

(29) Wolverton, C.; Zunger, A. *Phys. Rev. Lett.* **1998**, *81*, 606–609.

(30) The deviation of the cell-parameters from rhombohedral symmetry was negligibly small in all of our simulations.

(31) The B16 POS was first reported in ref 2, and the rest of the POS, B17−B20, were first reported in ref 3.

(32) In refs 8 and 9, the atomic density was fixed at 105 atoms/rhombohedral cell, while in ref 11, atomic densities corresponding to 104, 105, 106, and 111 atoms/cell were examined. However, only the occupations of B13 and B16 POS in their simplest possible configurations were considered. For example, with 106 atoms/cell, they considered only one POS configuration where all B13 sites and one B16 site were occupied.

(33) van Setten et al.[10] derived their stable structures with 106 atoms in the rhombohedral cell by proposing candidate structures based on previous experimental work as well as intuition. Widom and Mihalkovic[12] considered only 22 possibilities out of over a million possible configurations within 214 atoms in the supercell consisting of a 2 × 1 × 1 rhombohedral cell. None of them systematically explored the POS configuration space within the hexagonal cell (or a larger supercell) at the experimental atomic density.

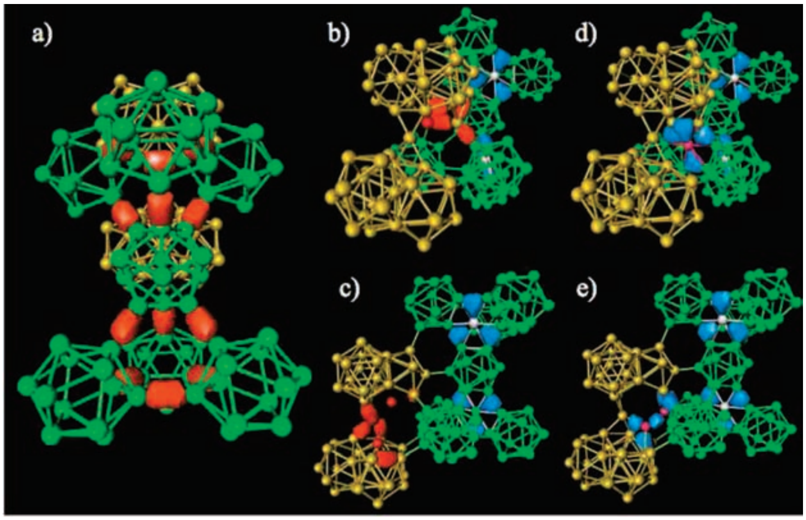

Figure 3. Isosurfaces of the square of maximally localized Wannier functions (MLWFs),[25,39] where the color represents the occupation (η): blue, $1 \geq \eta \geq 0.95$, and red, $\eta < 0.95$. The occupation of MLWF is calculated from the occupation of eigenstates and the unitary transformation, which define the relationship between eigenstates and MLWFs. Red isosurfaces correspond to electron-deficient bonds, while blue ones correspond to fully occupied bonds. The isosurface value is set at half the maximum value of the square of the MLWF. Structure a corresponds to the perfect hR105. The center of the hexagonal ring coincides with the B16 POS. The red sphere denotes the location of a B13 vacancy in structure b or the B19 atom (occupied) in structure d. The two red spheres correspond to the location of the B13s in structure c or the B17−B18 pair in structure e. Structures b and c are made from structures d and e by removing B19 and B17−B18 atoms, respectively, to show the role of those POS atoms. Therefore, structures b and c do not represent the stable POS occupation configurations, while structures d and e represent the stable POS occupation configurations.

the inclusion of two B13 vacancies on the same B_{28} cluster to be highly unfavorable, as compared to distributing them on opposite sides of the interstitial atom linking two B_{28} clusters (see Figure 1b). We note that the occupation of B19 or B20 POS takes place only when there is a single B13 vacancy nearby. A clear explanation for these favored short-range correlations (except for the B17−B18 pairing) can be expressed in the language of the spin model Hamiltonian: *antiferromagnetic correlation*, that is, occupied−unoccupied correlations. The origin of antiferromagnetic correlation will be discussed later.

We have found that the presence of defects does stabilize the β-boron structure, which is lower in energy than the ordered α-phase, but there remains an open question about a possible transition to an ordered configuration of POS at low temperature. We have addressed this question by studying the thermodynamic properties of the cluster expansion Hamiltonian (a generalized Ising model) used here to describe β-boron. In particular, we have performed thermodynamic integration using the replica Exchange Monte Carlo method[35] to calculate the entropy as a function of temperature, which shows that the model Hamiltonian possesses a macroscopic amount of entropy[15] at the lowest temperatures that could be numerically investigated.[16] The presence of residual entropy is characteristic of frustrated systems, such as ice,[17,18] spin ice,[19] and antiferromagnetic Ising models on triangular[36,37] (or kagome[38]) lattices. The surprisingly similar thermodynamic properties of the nearest-neighbor Ising model to that of a real system has played an important role in understanding the nature of frustration in real systems.[19] However, we note that the observed residual entropies at very low temperature in real systems turns out to be due to equilibrium fallout,[19] while a nearest-neighbor Ising model can be shown to have a rigorously degenerate and disordered ground state.[36−38] Here we suggest, on the basis of our simulation results, that β-boron is a frustrated element, analogous to ice[17,18] and spin ice[19] compounds.

We now turn to analysis of the bonding properties of β-boron in terms of maximally localized Wannier functions (MLWF)[39] (Figure 3). These functions are analogous to the Boys orbitals commonly used in quantum chemistry to investigate bonding properties of compounds (see Supporting Information section 5 for more details). Our analysis allowed us to identify two distinct stabilization mechanisms in β-boron: one involves the conversion of two-center to three-center bonds, localized near B16, B19, and B20 sites; in particular, the relatively high occupation rate of B16 sites diminishes the electron deficiency imbalance between B_{12} and B_{28} units (such an imbalance was pointed out also by Jemmis et al.[40] in the case of boron clusters). The second mechanism is related to B17−B18 pairing next to B13 vacancies, which is accompanied by a saturation of dangling bonds on B_{28} units.

A comparison between Figure 3 structures a and c indicates that switching between B13 and B16 POS occupation saturates the electron deficiency of B_{12}−B_{12} interconnects, at the expense of forming dangling bonds in the B_{28} clusters. The electron-

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(34) The ZPE of both α- and β-boron were calculated from the full phonon dispersion by use of the linear response theory implemented in the PWSCF code. Additional details can be found in Supporting Information section 4. For β-boron, the perfect hR105 system was used, and its ZPE was 8.2 meV/atom lower than that of α-boron. The impact of POS occupation was estimated by the sums of Γ-point phonon frequencies of the two most stable hR107 systems. This yielded a difference of 3 meV/atom, with respect to the energy of the perfect hR105. Therefore, we expect that the use of the hR105 structure to compute the ZPE (instead of hR107) has no impact on our conclusions regarding the relative stability of β- and a-boron. Note: The lower symmetry of hR107 would prohibitively increase the computational cost of the full phonon calculations.

(35) Hukushima, K.; Nemoto, K. *J. Phys. Soc. Jpn.* **1996**, *65*, 1604–1608.

(36) Wannier, G. H. *Phys. Rev.* **1950**, *79*, 357–364.

(37) Husimi, K.; Syozi, I. *Prog. Theor. Phys.* **1950**, *5*, 177–186.

(38) Syozi, I. *Prog. Theor. Phys.* **1951**, *6*, 306–308.

(39) Souza, I.; Marzari, N.; Vanderbilt, D. *Phys. Rev. B* **2002**, *65*, 035109−13.

(40) Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. *J. Am. Chem. Soc.* **2001**, *123*, 4324–4330.

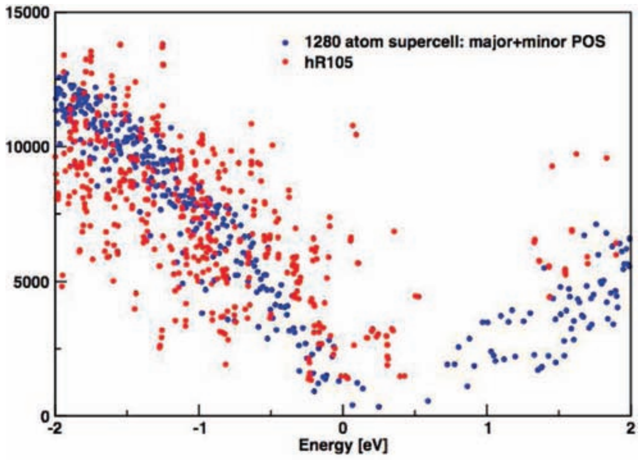

Figure 4. Participation functions of eigenstates from one of the 1280-atom supercells of β-boron and the hR105 perfect β-boron. The participation function, defined as $\zeta_i = \int_V 1/|\Psi_i(r)|^4 \, dr$, where $\Psi_i(r)$ is the ith eigenstate of the system and V is the volume of the supercell, represents the localization volume of the electronic eigenstate.

deficient bonds linking two B_{12} units around the B16 sites (see Figure 3c) are not simply saturated; they are transformed from two-center bonds (cocoon-shape isosurfaces) into three-center bonds (triangular-shape isosurfaces). If one assumes that the most electron-deficient bonds are likely to be the most chemically active, then it is reasonable to expect that the POS near the electron deficient bonds will be preferentially occupied. This is precisely what we observe in the optimized, stable hR1280 configurations: When one B13 vacancy is present in a $(2B_{28})B$ unit, the closest B19 POS is occupied. In this case, the formation of three-center bonds around the B19 atom is clearly observed (Figure 3d), and simultaneously, all the electron-deficient bonds in the B_{28} unit are now fully saturated (compare Figure 3 structures b and d). Essentially the same trends in the electronic structure are found when the B20 site closest to a B13 vacancy is occupied. When two B13 vacancies are present in a $(2B_{28})B$ cluster, the nearby B17−B18 paired sites are occupied, and saturation of the electron-deficient bonds occurs (compare Figure 3 structures c and e). However, the formation of unambiguous three-center bonding is not as clear.

Jemmis et al.[40] pointed out two important facts about bonding in solid boron, derived from empirical *mno* rules and confirmed by ab initio total energy calculations on the isolated B_{12} and $(2B_{28})B$ clusters. They found that B_{12} clusters are more electron-deficient than B_{28} (this can also be seen in Figure 3a) and that the full occupation of B13 is energetically unfavorable in B_{28} clusters, which we confirmed with our solid-phase calculations. The relatively high occupation rate of B16 is clearly related to the electron-deficiency imbalance between B_{12} and B_{28}, while the smaller B17−B20 occupations are controlled by the number of available B13 vacancies.

These electronic effects due to the presence of POS can be interpreted in terms of self-doping, as they are accompanied by an adjustment of the Fermi level to the electronic excitation gap.[41] Recently, Tang and Ismail-Beigi[42] studied the stable forms of boron in 0-D (clusters) and 2-D (sheets) using DFT total energy calculations and found that their most stable 0-D and 2-D structures have certain ratios of three- and two-center bonds leading to a full occupation of in-plane bonding states (with no occupied antibonding orbitals). This is essentially the same mechanism that we have found to occur in the presence of POS sites in the 3-D β-boron structure, with the exception of B17−B18 pair formation, for which a perfect filling of bonding states (valence band) cannot be realized at the experimental atomic density due to the increased number of bonding states. To summarize, our analysis indicates two important properties of boron: (i) Antiferromagnetic correlations in POS occupancy in β-boron (that are at the origin of frustration in this material) are related to the suppression of dangling bonds created by the presence of B13 vacancies, which originates in the instability of the B_{28} units. (ii) The highly favorable B17−B18 pairing introduces an additional bonding state, resulting in the presence of intrinsic hole states in β-boron.

Although boron is the only element whose stable solid structure is composed of icosahedral building blocks, we note that other third-group elements exhibit a well-known tendency to form icosahedral quasicrystal compounds, such as aluminum−magnesium−zinc[43] or gallium−magnesium−zinc.[44] It is generally believed that the Hume−Rothery mechanism plays an important role in the stabilization of these systems,[45−48] where the presence of midrange ordering leads to an opening of a pseudo gap in the free electronlike density of states of an aperiodic intermetallic compound; this in turn causes a preference for stoichiometries where the Fermi level coincides with the minimum of the pseudo gap.[46] An analogy with quasicrystals can be found in the electronic stabilization mechanisms we have identified here for β-boron; however, in the present case it is the conversion of bond types (from two- to three-center), which enables an additional POS atom to raise the Fermi level without changing the number of the bonding state, that leads to the Fermi level adjustment.

We now compare our findings on the electronic structure of β-boron with experimental observations. The comparison is qualitative for the following reason. Since experimentally β-boron is usually prepared from the melt, and due to the large energy barrier between different POS configuration as a covalent system, it is highly likely that an actual β-boron sample freezes into a metastable POS configuration while the sample is cooling down from its high-T equilibrium state. Our ab initio molecular dynamics simulations suggest that the onset of diffusion of the POS atoms occurs at roughly 1000 K. The electronic structure of the hR1280 systems sampled in our MD simulations varies significantly, in particular near the Fermi level, even in the case of the most stable, nearly degenerate structures found in our optimization procedure. However, there are some general trends that can be identified. The most stable structures tend to have the largest gap with the fewest number of intrinsic hole states, while the higher energy structures tend to have a large number of gap levels (see Supporting Information section 6). Most of the experimental reports indicate the presence of some

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(41) The perfect hR105 has 5 hole states per rhombohedral cell in the valence band. If one assumes that the number of valence bands does not change upon the introduction of POS atoms, the hole states would be perfectly filled at an atomic density of $106\,^{2}/_{3}$ per rhombohedral cell (the experimental value). Our finding is that the stable hR1280 systems nearly satisfy this condition, except for the small deviation originating from the presence of B17−B18 pairs. See Supporting Information sections 5 and 6 for additional details.

(42) Tang, H.; Ismail-Beigi, S. *Phys. Rev. Lett.* **2007**, *99*, 115501–4.

(43) Takeuchi, T.; Murasaki, S.; Matsumuro, A.; Mizutani, U. *J. Non-Cryst. Solids* **1993**, *156−158*, 914–917.

(44) Ohashi, W.; Spaepen, F. *Nature* **1987**, *330*, 555–556.

(45) Bancel, P.; Heiney, P. A. *Phys. Rev. B* **1986**, *33*, 7917–7922.

(46) Friedel, J. *Helv. Phys. Acta.* **1988**, *61*, 538–556.

(47) Smith, A. P.; Ashcroft, N. W. *Phys. Rev. Lett.* **1987**, *59*, 1365–1368.

(48) Fujiwara, T.; Yokokawa, T. *Phys. Rev. Lett.* **1991**, *66*, 333–336.

gap levels.[49,50] Our most stable hR1280 structure has an electronic band gap of 0.8 eV, which is smaller than experiment (1.5−1.6 eV).[49,50] However, when the possible uncertainty in the structure of real β-boron samples at finite T and the well-known tendency of the local density approximation to underestimate gaps are considered, this level of agreement is reasonable. It has been reported that β-rhombohedral boron is an intrinsic p-type semiconductor[51,52] that has variable-range hopping-type transport properties.[52,53] The measured conductivity within the impurity free limit is on the order of 10^{-8} $[1/\Omega \cdot \mathrm{cm}]^3$. We have calculated the participation function, which is a measure of the localization volume of electronic eigenstates (see Figure 4). This analysis clearly shows that the gap levels are localized compared to the eigenstates in the valence and conduction bands. As was mentioned before, all of our stable hR1280 structures have hole states originating from B17−B18 pairing that lead to p-type semiconducting transport properties. We have also computed the optical conductivity of representative hR1280 structures within the Kubo−Greenwood formalism.[54,55] Indeed, the estimated DC conductivity at $T = 300$ K is low, 50 ± 50 $[1/\Omega \cdot \mathrm{cm}]$,[56] reflecting the localized character of gap levels (Figure 4). The overall transport properties of β-boron emerging from our simulations, a p-type semiconductor with poor conductivity due to localized gap levels, is qualitatively in good agreement with the experimental observations[3,49−53]

Finally, we discuss the prospects of finding the true ground state of elemental boron, which is presumably an ordered structure. Ice and spin ice compounds are the few well-characterized frustrated systems, for which the mechanism that breaks degeneracy is understood. For example, in these two prototypical systems, long-range dipole−dipole interactions are believed to be responsible for lifting the ground-state degeneracy, leading to ordered structures at low temperature. For the spin ice system, this scenario is supported by results obtained by an advanced Monte Carlo method on the dipole spin Ising model,[57−59] although the presence of an ordered phase in the corresponding pyrochlore materials has not been confirmed by experiments.[60] For ice, the low-temperature ordered phase at ambient pressure (commonly called ice XI) was first found by experiments, where KOH impurity doping was used to unlock the system from the metastable disordered phase.[61] It was confirmed by first-principles total energy calculations, where the statistical sampling of hydrogen-bonding configurations was performed by graph invariants, that the proton-ordered phase (ice XI) has a lower internal energy than that of a proton-disordered phase (ice Ih), and the calculated transition temperature between ice Ih and ice XI was found to be in reasonable agreement with experiment.[62] Finding the true ground state of a frustrated system has proved to be a very challenging problem, as it involves finding the global minimum out of a macroscopic number of nearly degenerate metastable states. The existing work on ice and spin ice suggests that there are two key ingredients that will be needed to fully determine the ground state of boron: (i) an experimental approach to find a perturbation that unlocks the POS atoms from a metastable configuration, and (ii) theoretical work to identify the mechanism that lifts the ground-state degeneracy. As such, we leave the precise determination of the ground-state structure of boron to future investigations.

Conclusions

In conclusion, we have performed a global configuration search on the partial occupancy of β-boron using the generalized Ising model fitted to first-principles DFT total energies. Our results indicate that the ground state of elemental boron is likely to be the β-rhombohedral phase, which is a nearly degenerate semiconductor with self-doping sites. The Ising model of β-boron turned out to have macroscopic residual entropy, which is characteristic of a frustrated system similar to ice and spin ice compounds. These are unique properties, not shared by any other element in the periodic table. The origin of frustration, described as the antiferromagnetic correlations on the complex lattice structure of β-rhombohedral boron, originates in the following: (i) The B_{28} unit has intrinsic instability leading to B13 vacancies that creates dangling bonds. (ii) B17−B20 occupations terminate the dangling bond created by B13 vacancies. The highly favored short-range correlation, B17−B18 pair, is found to introduce a hole state, suggesting that the presence of hole states is an intrinsic property of β-rhombohedral boron.

Ever since the first reports in the 1930s,[17,18] the physics of frustration has attracted broad interest in the scientific community. Originally this interest was motivated by the potential conflict with the third law of thermodynamics, and more recently by the expectation that frustration might be intimately related to exotic phenomena, such as high T_c superconductivity[63] or magnetic monopoles.[64] The complex form of frustration present in β-boron suggests that there may be exciting, novel properties of boron and boron-based compounds yet to be discovered.

Acknowledgment. We thank Livermore Computing for providing us with a significant amount of dedicated computer time as well as with visualization support. We thank Dr. Jonathan Yates (Corpus Christi College, U.K.) and Professor Ivo Souza (UC Berkeley) for stimulating discussions on Maximally Local-

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(49) Golikova, O. A.; Kazanin, M. M.; Samatov, S.; Khomidov, T. *Sov. Phys. Semicond.* **1982**, *16*, 479–480.

(50) Werheit, H.; Laux, M.; Kohlamann, U. *Phys. Status Solidi B* **1993**, *176*, 415–432.

(51) Majni, G.; Prudenziati, M. *Phys. Status Solidi A* **1971**, *5*, K129–K132.

(52) Szadkowski, A. *Phys. Status Solidi A* **1979**, *53*, 95–104.

(53) Werheit, H.; Leis, H. G. *Phys. Status Solidi* **1970**, *41*, 247–256.

(54) Kubo, R. *J. Phys. Soc. Jpn.* **1957**, *12*, 570–586.

(55) Greenwood, D. A. *Proc. Phys. Soc. (London)* **1958**, *71*, 585–596.

(56) As the Kubo−Greenwood formula does not account for inelastic electron−phonon scattering, our estimate should be considered as an upper bound.

(57) Siddharthan, R.; Shastry, B. S.; Ramirez, A. P.; Hayashi, A.; Cava, R. J.; Rosenkranz, S. *Phys. Rev. Lett.* **1999**, *83*, 1854–1857.

(58) Siddharthan, R.; Shastry, B. S.; Ramirez, A. P. *Phys. Rev. B* **2001**, *63*, 184412.

(59) Melko, R. G.; den Hertog, B. C.; Gingras, M. J. P. *Phys. Rev. Lett.* **2001**, *87*, 067203.

(60) Due to extremely slow dynamics at such a low temperature (sub-Kelvin), bringing a system into equilibrium is extremely challenging. Therefore, it is generally assumed that the spin ice systems freeze into a metastable state and do not exhibit the expected phase transition to an ordered phase at low temperature (see ref 19).

(61) Tajima, Y.; Matsuo, T.; Suga, H. *Nature* **1982**, *299*, 810–812.

(62) Singer, S. J.; Kuo, J.-L.; Hirsch, T. K.; Knight, C.; Ojamae, L.; Klein, M. L. *Phys. Rev. Lett.* **2005**, *94*, 135701.

(63) Si, Q.; Abrahams, E. Preprint at http://arxiv.org/abs/0804.2480v2.

(64) Castelnovo, C.; Moessner, R.; Sondhi, S. L. *Nature* **2008**, *451*, 42–45.

ized Wannier Function analysis. T.O. also thanks Professor Roderich Moessner (MPI Dresden) for invaluable advice on the physics of frustration. Part of this work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Support from DOE/Scidac Grant DE-FG02-06ER46262 is gratefully acknowledged.

Supporting Information Available: Six sections of text, three tables, and nine figures as described in the main text. This material is available free of charge via the Internet at http://pubs.acs.org.

JA807622W