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Structure of Boron

Determination of Phase Stability of Elemental Boron**

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***Abstract:** Boron is an important element, used in applications from superhard materials to superconductors. Boron exists in several forms (allotropes) and, surprisingly, it was not known which form (α or β) is stable at ambient conditions. Through experiment, we quantify the relative stability of α-boron and β-boron as a function of temperature. The ground-state energies of α-boron and β-boron are nearly identical. For all temperatures up to 2000 K, the complicated β-boron structure is more stable than the simpler α-boron structure at ambient pressure. Below 1000 K, β-boron is entropically stabilized with respect to α-boron owing to its partially occupied sites, whereas at higher temperatures β-boron is enthalpically stabilized with respect to α-boron. We show that α-boron only becomes stable on application of pressure.*

Many materials exhibit more than one polymorph, such as calcium carbonate (progressively less thermodynamic stability for calcite, aragonite, vaterite, and amorphous $CaCO_3$[1]), ice,[2] and elements such as carbon, tin, and phosphorous. For all these examples, the relative stability of different polymorphs is well-established. Such is not the case for boron. Boron is never found in its elemental form in nature, but boron compounds are well-known, including borax for cleaning, thermally shock-resistant borosilicate glass, and ultrahard cubic boron nitride. Boron has some unusual features, such as three-center two-electron bonds. Superconductivity in magnesium diboride[3] was a surprise. The remarkable all-boron fullerene, B_{40}, has recently been observed.[4] The discovery of a novel superhard high-pressure allotrope in which some boron atoms form cationic clusters, while other form anionic clusters,[5] highlighted a significant knowledge gap:[6] which boron allotrope is stable at ambient conditions? For good reason, boron has been called "arguably the most complex element in the Periodic Table".[7]

The allotropes in competition for stability at standard conditions are α-boron and β-boron. The former has rhombohedral symmetry (space group $R\bar{3}m$), with twelve boron atoms in an icosahedral configuration in the unit cell.[8,9] The structure of β-boron has the same space group but is far more complex;[10–13] the unit cell contains four icosahedra at the edges and the corners of the unit cell, and an inverted pair of triply fused icosahedra connected by an interstitial boron occupies the center of the unit cell. Interestingly, the number of atoms in this idealized unit cell is 105 ($=4\times12+2\times28+1$), which is significantly lower than the value of 106.67 from the experimental density.[13] After painstaking experimental and theoretical investigations over several decades,[9] it is now understood that many crystallographic sites in β-boron are only partially occupied,[13] to satisfy the chemical bonds of boron.[6] This is a unique feature among known elements: macroscopic numbers of interstitial sites and vacancies are needed to form the closed-shell electronic structure of β-boron. The corresponding structures are shown in Figure 1. For details, see recent reviews of boron structures and properties.[14,15]

Recent experimental investigations of the phase diagram of boron at high pressure show that α-boron is stable with respect to β-boron at low temperatures and high pressures; linear extrapolation of the *P*-*T* boundary predicts α-boron to

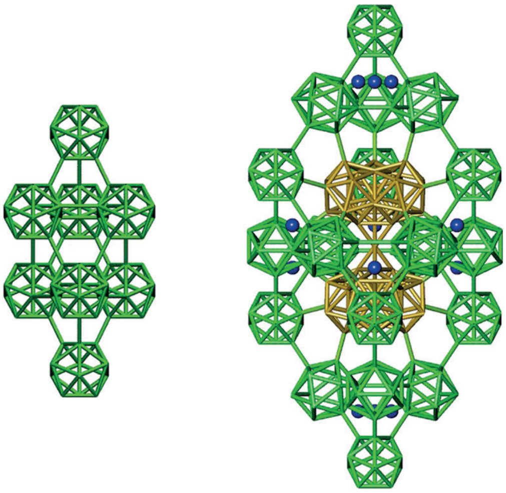

Figure 1. Left: Structure of α-boron. Icosahedra are located at the corners of the rhombohedral cell, and each has six 2c–2e bonds with icosahedra of neighbouring layers and six 3c–2e bonds to icosahedra within its own layer. Right: Structure of β-boron, showing B_{12} icosahedra (green), two (B_{28})B clusters (triply-fused icosahedra, gold), and one B partially occupied interstitial site (B16, blue). All the icosahedra and fused-icosahedra are bonded by 2c–2e bonds, while the B16 interstitial atoms are bonded to surrounding icosahedra by 3c–2e bonds.

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be more stable than β-boron at ambient conditions.[16,17] On the other hand, theoretical studies based on density functional theory (DFT) indicate that β-boron is more stable than α-boron at $P = 0$ GPa and $T = 0$ K when all the experimentally observed partial occupancies are taken into consideration.[6,18,19] However, the calculated difference in ground-state energies of α-boron and β-boron was very small, on the order of 0.1 kJ mol^{-1}. A later theoretical study has suggested that the contradiction between theory and experiments may not be as great if the uncertainty in the theoretical estimate of quantum zero point motion energy of β-boron (ZPE_β) is taken into account;[20] however lack of direct experimental evidence on the relative thermodynamic stability of α- and β-boron at low pressure and temperature has left the question of the ground-state structure of elemental boron unanswered.

Generally, such a stability competition can be resolved unambiguously through consideration of a cycle such as that shown in Figure 2, taking advantage of the fact that enthalpy, entropy, and Gibbs energy are all state functions. Definitive values of the enthalpy, entropy, and Gibbs energy differences (ΔH, ΔS, and ΔG, respectively) could be determined if accurate experimental data were available. In particular, values of molar heat capacities at constant pressure ($C_{\mathrm{P,m}}$) would be required to very low temperature, allowing an accurate extrapolation to $T = 0$ K, along with further thermodynamic information for reactions (steps 3 and 4 in Figure 2) or high-temperature extrapolation (steps 5 and 6) and conversion (step 7). Such information would allow calculation of thermodynamic changes at $T = 0$ K (step 8), via closure of the cycle, and experimentally derived data for ΔH, ΔS, and ΔG for the allotropic conversion at all temperatures could follow.

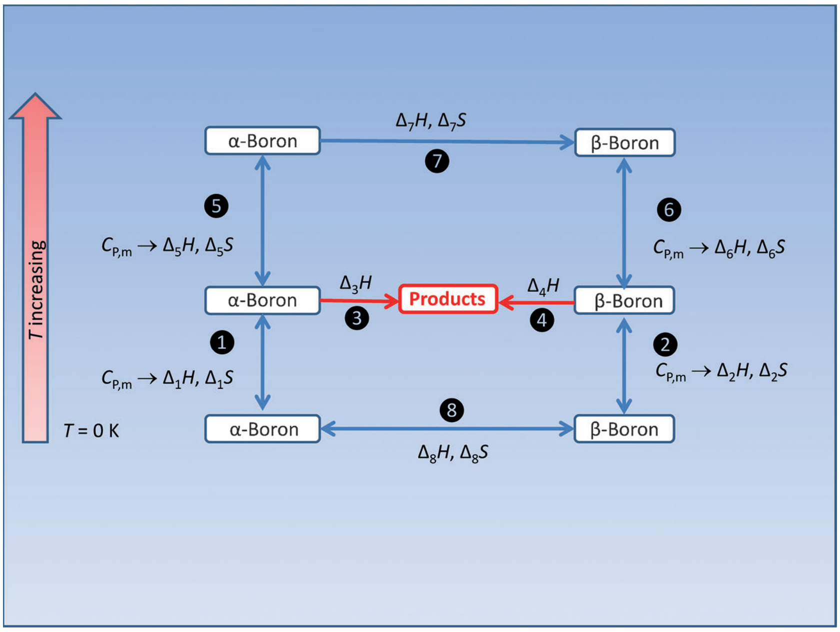

Figure 2. Thermodynamic cycle to determine relative stability of α- and β-boron. The enthalpy difference between α-boron and β-boron at $T = 0$ K, Δ_8H, can be calculated if values for the other steps in a cycle (1, 3, 4, and 2, or 1, 5, 7, 6, and 2) are known.

Why has a thermodynamic cycle analysis not been reported for the α-boron/β-boron competition? In part it stems from lack of accessibility to α-boron. While β-boron is commercially available and well-studied, providing (mostly) accurate data for steps 2, 4, and 6,[21] α-boron is neither commercially available nor easy to synthesize. Furthermore, until recently, gram quantities were required for thermodynamic property determination, especially steps 1 and 2 (Figure 2).

However, state-of-the-art experimental techniques make it possible to accurately determine heat capacities of a few mg of a solid; we also developed a synthesis of α-boron to determine its $C_{\mathrm{P,m}}$ with high accuracy from 1.8 K to 300 K.[21]

The cycle for ΔH could be completed via steps 1, 2, 3, and 4. The enthalpy changes for steps 3 and 4 require reactions with well-characterized products, but boron is exceptionally unreactive. The only feasible boron reaction is fluoridation; results have been reported for β-boron to give Δ_4H,[22] but not for α-boron (Δ_3H). Fluorine bomb calorimetry is now a lost art, thwarting attempts to complete the enthalpy cycle by a chemical reaction approach.

However, at high temperature, α-boron converts into β-boron.[23] The transformation is not reversible (that is, $\Delta_7G < 0$) and thus experiment provides only Δ_7H and a lower limit on Δ_7S (see below). High-temperature heat capacity data for steps 5 and 6 are available,[21] allowing the complete thermodynamic cycle to reveal Δ_8H, that is, the enthalpy change for the β→α conversion at $T = 0$ K. This approach deals with small differences between large numbers;[21] the result is $\Delta H(\alpha\rightarrow\beta, T = 0\ \mathrm{K}) = 0.24 \pm 0.30$ kJ mol^{-1}. In other words, the experimentally determined ground state energy difference between α-boron and β-boron is very small, zero within its uncertainty. (By comparison, the graphite/diamond and ice polymorph differences in enthalpy are 1.9 kJ mol^{-1},[24] and ca. 10 kJ mol^{-1},[25] respectively.) The reported theoretical values for boron were $\Delta H_{\mathrm{DFT}}(\alpha\rightarrow\beta, T = 0\ \mathrm{K}) = -0.29$ kJ mol^{-1},[16] -0.083 kJ mol^{-1},[20] and -0.72 kJ mol^{-1},[6] in agreement with experiment. It should be noted that the value from reference [20] does not include ZPE, while the others[6,16] do. As discussed in reference [20], the calculations of ZPE_β in reference [6] involved an approximation in the dynamical matrix elements to avoid increase of computational cost associated with the presence of partial occupancy, which likely underestimates ZPE_β. It was shown that the best choice of ZPE_β correction parameter which puts the theoretical α–β phase boundary in a position consistent with the high-pressure experimental data,[16] would still favor β-boron over α-boron as the ground state by a mere 0.23 kJ mol^{-1}.[20]

The temperature-dependent thermodynamic properties of the boron allotropes also allow the calculation of $\Delta H(\alpha\rightarrow\beta)$ as a function of temperature; the results indicate little

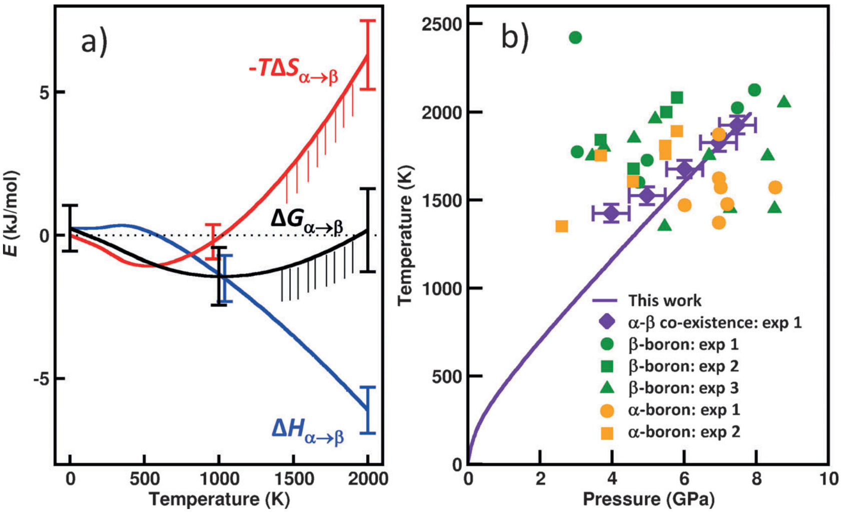

Figure 3. Stability of α-boron relative to β-boron. a) Results of the experimentally based analysis of the transformation of α-boron to β-boron as a function of temperature at atmospheric pressure. The enthalpy change (ΔH) values were derived here as described in the text; error bars indicate uncertainty from experiments. The entropy change, represented as $-T\Delta S$, and values of ΔG are upper bounds. In particular, note that $\Delta G<0$ at $T\approx2000$ K because independent information[23] shows that α→β spontaneously at this temperature. b) Phase diagram for elemental boron for $P<10$ GPa. The α–β phase line was calculated based on the EOS model of α- and β-boron described in Ref. [20], where $\Delta G(\alpha\rightarrow\beta,\ T=0\ \mathrm{K})\approx0$ (kJ mol^{-1}), obtained in this work, and the α-β-γ triple point, $T=1923$ K and $P=7.5$ GPa, reported in Ref. [16] was used for additional constraints. Symbols correspond to (P,T) points where α- or β-boron were directly observed in high-pressure experiments. Exp 1 to 3 correspond to experimental results from Refs. [16,17,5b], respectively.

difference in enthalpy between the two forms for $T<500$ K, but a large enthalpic stabilization of β-boron for $T>500$ K (Figure 3).

At high temperature (step 7 in Figure 2), α-boron and β-boron are not in equilibrium. Rather, α→β spontaneously, so $\Delta_7G<0$ and it follows that $\Delta_7S>\Delta_7H/T$ (Δ_7H from reference [23]), yielding $\Delta_7S>-3.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$. From the cycle of Figure 2 and the experimental data for steps 1, 5, 7, 6, and 2, we find that $\Delta S(\alpha\rightarrow\beta,\ T=0\ \mathrm{K})>2.2\pm0.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$. With the justified assumption that α-boron is fully ordered at $T=0$ K, we can conclude that the residual entropy for β-boron, $S_0(\beta)$, is $>2.2\pm0.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The value of $S_0(\beta)$ is reasonable considering theoretical estimates of $0.327\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for the Ising model for partial occupancy of β-boron and $4.157\ \mathrm{J\,K^{-1}\,mol^{-1}}$ based on an AF Ising model on a Kagome lattice.[26]

As for $\varDelta H(\alpha\rightarrow\beta)$, we can calculate ΔS as a function of temperature, except that we know only a lower bound on $S_0(\beta)$, and thus a lower bound on $\Delta S(\alpha\rightarrow\beta)$ and a resulting upper bound on $-T\Delta S(\alpha\rightarrow\beta)$; see Figure 3 for the result. (Note that an upper bound on $S_0(\beta)$ of the AF Ising model on a Kagome lattice would reduce the value of $-T\Delta S(\alpha\rightarrow\beta)$ by about $4\ \mathrm{kJ\,mol^{-1}}$ at $T=2000$ K, less at lower temperatures.)

The most important finding is the Gibbs energy difference between α- and β-boron. Data for ΔH and the bound on values of $-T\Delta S(\alpha\rightarrow\beta)$ lead to an upper bound on $\Delta G(\alpha\rightarrow\beta)$. As shown in Figure 3, clearly β-boron is favored over α-boron at ambient pressure and all temperatures below about 2000 K. At lower temperatures ($T<$ ca. 1000 K), the stability of the β allotrope is largely entropy-driven (since $-T\Delta S(\alpha\rightarrow\beta)<0$), and can be attributed in part to the residual entropy of β-boron owing to its partially occupied sites. At $T=300$ K, about 90% of the $-T\Delta S(\alpha\rightarrow\beta)$ value is configurational arising from the non-zero $S_0(\beta)$.[21] However, at higher temperature, the higher heat capacity of α-boron increases its contribution to the $\int C_\mathrm{P}\,\mathrm{d}\ln T$ term in $T\Delta S(\alpha\rightarrow\beta)$, and the heat capacity term dominates over the residual entropy difference, leading to a favorable entropic stabilization of α-boron at high temperature, more than compensated by enthalpic stabilization of β-boron, as we discuss below.

From the enthalpy perspective, below about 500 K, $\Delta H(\alpha\rightarrow\beta)\approx0$. However, at higher temperature the higher heat capacity of α-boron leads to $\Delta H(\alpha\rightarrow\beta)<0$, and β-boron is enthalpically stabilized relative to α-boron, and $\Delta G(\alpha\rightarrow\beta)<0$.

High-pressure experiments linearly extrapolated to $P=0$ suggested β→α at $T\approx1000$ K, predicting that α-boron is stable at ambient conditions.[16] However, those experiments were confined to very high pressures, $P>4$ GPa, and extrapolation to $P=0$ was subject to considerable uncertainty. For β-boron to be stable at all temperatures at $P=0$, the α–β equilibrium line must have $(\mathrm{d}P/\mathrm{d}T)\approx0$ for $P\rightarrow0$. On the basis of the Clapeyron equation,[21] this implies that $\Delta H(\alpha\rightarrow\beta)\approx0$ at low temperature and pressure, as we have shown from the thermodynamic cycle, in agreement with theory.[5] See Figure 3.

From our experimental studies we answer the question of boron phase stability: the stable form of boron at ambient pressure is the complex, partially disordered allotrope β-boron from about 2000 K down to below ambient temperature (ca. 100 K), and likely to $T=0$ K, given that our estimate of $\Delta G(\alpha\rightarrow\beta,T)$ is an upper limit. The ordered α-form of boron only becomes stable when pressure is applied. The present work shows that at ambient pressure the partially disordered structure (β-boron) is more stable than the more "normal" ordered structure (α-boron) of this element, a highly unusual finding.

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[1] L. Kabalah-Amitai, B. Mayzel, Y. Kauffmann, A. N. Fitch, L. Bloch, P. U. P. A. Gilbert, B. Pokroy, *Science* **2013**, *340*, 454–457.
[2] R. J. Hemley, *Annu. Rev. Phys. Chem.* **2000**, *51*, 763–800.
[3] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, *Nature* **2001**, *410*, 63–64.

[4] H.-J. Zhai et al., *Nat. Chem.* **2014**, *6*, 727–731.
[5] a) A. R. Oganov, J. Chen, C. Gatti, Y. Ma, Y. Ma, C. W. Glass, Z. Liu, T. Yu, O. O. Kurakevych, V. L. Solozhenko, *Nature* **2009**, *457*, 863–868; b) E. Yu. Zarechnaya et al., *Phys. Rev. Lett.* **2009**, *102*, 185501.
[6] T. Ogitsu, F. Gygi, J. Reed, Y. Motome, E. Schwegler, G. Galli, *J. Am. Chem. Soc.* **2009**, *131*, 1903–1909.
[7] A. R. Oganov, V. L. Solozhenko, *J. Superhard Mater.* **2009**, *31*, 285–291.
[8] L. V. McCarty, J. S. Kasper, F. H. Horn, B. F. Decker, A. E. Newkirk, *J. Am. Chem. Soc.* **1958**, *80*, 2592–2592.
[9] B. F. Decker, J. S. Kasper, *Acta Crystallogr.* **1959**, *12*, 503–506.
[10] D. E. Sands, J. L. Hoard, *J. Am. Chem. Soc.* **1957**, *79*, 5582–5583.
[11] R. E. Hughes, C. H. L. Kennard, D. B. Sullenger, H. A. Weakliem, D. E. Sands, J. L. Hoard, *J. Am. Chem. Soc.* **1963**, *85*, 361–362.
[12] J. L. Hoard, D. B. Sullenger, C. H. L. Kennard, R. E. Hughes, *J. Solid State Chem.* **1970**, *1*, 268–277.
[13] G. A. Slack, C. I. Hejna, M. F. Garbauskas, J. S. Kasper, *J. Solid State Chem.* **1988**, *76*, 52–63.
[14] B. Albert, H. Hillebrecht, *Angew. Chem. Int. Ed.* **2009**, *48*, 8640–8668; *Angew. Chem.* **2009**, *121*, 8794–8824.
[15] T. Ogitsu, E. Schwegler, G. Galli, *Chem. Rev.* **2013**, *113*, 3425–3449.
[16] G. Parakhonskiy, N. Dubrovinskaia, E. Bykova, R. Wirth, L. Dubrovinsky, *Sci. Rep.* **2011**, *1*, 96.
[17] V. L. Solozhenko, O. O. Kurakevych, *Sci. Rep.* **2013**, *3*, 2351.
[18] M. J. van Setten, M. A. Uijttewaal, G. A. de Wijs, R. A. de Groot, *J. Am. Chem. Soc.* **2007**, *129*, 2458–2465.
[19] M. Widom, M. Mihalkovič, *Phys. Rev. B* **2008**, *77*, 064113.
[20] T. Ogitsu, E. Schwegler, *Solid State Sci.* **2012**, *14*, 1598–1600.
[21] See Supporting Information for details.
[22] G. K. Johnson, H. M. Feder, W. N. Hubbard, *J. Phys. Chem.* **1966**, *70*, 1–6.
[23] T. G. Dzhandieri, G. I. Kalandadze, P. D. Kervalishvili, *Inorg. Mater.* **1988**, *24*, 1702–1704.
[24] M. W. Chase, NIST JANAF Thermochemical Tables 4th ed., J. Phys. Chem. Ref. Data Monograph **1998**, *9*.
[25] B. Santra, J. Klimeš, D. Alfè, A. Tkatchenko, B. Slater, A. Michaelides, R. Car, M. Scheffler, *Phys. Rev. Lett.* **2011**, *107*, 185701.
[26] T. Ogitsu, F. Gygi, J. Reed, M. Udagawa, Y. Motome, E. Schwegler, G. Galli, *Phys. Rev. B* **2010**, *81*, 020102.
