Metal-Nonmetal Transition in the Boron Group Elements

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Structural competition in boron group elements has been studied by means of *ab initio* calculations. For boron we predict a structural change α-B $\rightarrow$ α-Ga accompanied by a nonmetal-metal transition at a pressure of about 74 GPa. For Al and Ga we find an icosahedron based elemental modification (α-B) 0.22 and 0.05 eV/atom, respectively, higher in energy than the corresponding metallic ground state structures. In particular, the low energy difference for Ga raises expectations into the experimental feasibility of new modifications for these elements, especially in nanosized systems.

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Because of the fast development in nanoscience the possibilities to manipulate structures and properties are rapidly increasing. Therefore elements exhibiting competing crystal structures become of particular interest due to the relative ease with which they can transform from one phase to another. Elemental boron exhibits a unique structural physics based on icosahedral entities which are linked together in a variety of ways. Little is known about the relative stability between the various polymorphs [1] and even the actual ground state modification of boron is debated [2]. In α-rhombohedral B [3], which is the modification with the simplest structure, B_{12} icosahedra are arranged as in a cubic close packing of spheres, joined by two-electron three-center bonds within the layers and connected by two-electron two-center bonds between them [4]. Complex β-rhombohedral B, which is the most commonly found modification, represents a framework of 105 atoms in the primitive cell (hR105) in which icosahedra are linked by two-electron two-center bonds and sharing common faces. Most important, several partially occupied sites stuffing this framework add additionally 1.7 B atoms per unit cell and give rise to remarkable structural defects in β-B [5]. The modifications α-B and β-B are semiconductors with band gaps of 2.0 eV and 1.6 eV, respectively [6]. When proceeding to the next element of the boron group, Al, an abrupt change of the bonding properties occurs. Al has a high electrical conductivity and displays just one elemental modification which has the simple face-centered cubic (fcc) structure typical of metals. Most recently two striking and at a first glance not at all connected experimental findings were made. First, Eremets *et al.* reported on a nonmetal-superconductor transition in boron at high pressures. However, no structural model for metallic boron was presented [7]. Second, Klemp *et al.* succeeded in the preparation of compounds $Al_{22}X_{20}$ ($X =$ Cl, Br) with an unforeseen neutral icosahedral Al cluster core and raised the intriguing question whether such clusters could be intermediates towards novel icosahedron based elemental structures of Al [8].

In the present work we explored the nature of the nonmetal-metal transition in boron and the most exciting possibility that its heavier congeners Al and Ga will attain an icosahedral, perhaps semiconducting, elemental modification. In particular, we investigated the structural stability of B, Al, and Ga over a wide range of volumes by means of *ab initio* calculations employing pseudopotentials and a plane wave basis set [9] in the framework of the density functional theory (DFT). As competing structures we considered the α-B structure (as a representative for an icosahedral structure), the α-Ga structure, and the body-centered tetragonal (bct) structures with a variable c/a ratio (i.e., covering the Bain path), thus including the fcc and body-centered cubic (bcc) structures. With this selection we considered all important structures occurring for the boron group elements [1,12]. First we point out the special role of gallium. Ga adopts a peculiar ground state structure with a local $(1 + 6)$ coordination for each Ga atom. There is in fact a close relationship to the icosahedral boron structures where the shortest distances occur between the two-electron two-center linked icosahedra [local $(1 + 5)$ coordination] [13]. As a consequence, α-B can be considered as a two-dimensional metal and thus its structure represents a natural candidate for the observed high-pressure metallic boron modification.

Figures 1 and 2 summarize our results concerning the high-pressure behavior of boron. According to our energy vs volume calculations [Fig. 1(a)] α-boron will transform to the α-Ga structure at 74 GPa, which remains more stable than the bct structures until the extremely high pressure of 790 GPa where a transition into fcc takes place. At the transition pressure of the first structural transition the calculated band gap of α-B has been reduced from 1.6 eV [14] at the ground state volume $V/V_0 = 1$ to ≈ 0.3 eV at $V/V_0 = 0.765$ [Figs. 1(c) and 2(a)]. The electronic density of states (DOS) of B in the

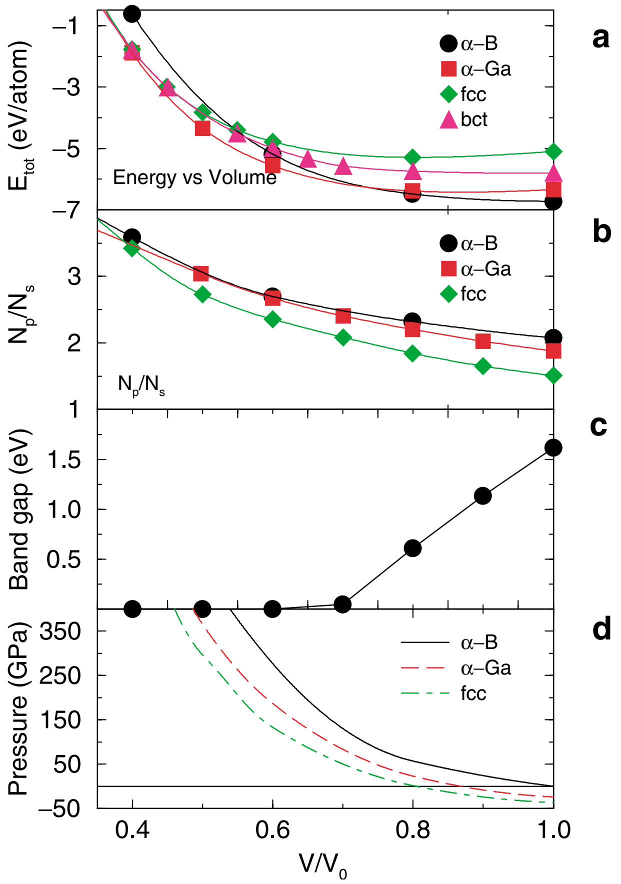

FIG. 1 (color). (a) Calculated energy vs volume for B in the structure types α-B, α-Ga, fcc, and bct. (b) The ratio of the number of valence p and s states (N_p/N_s) for B in the structure types α-B, α-Ga, and fcc as a function of volume. (c) Evolution of the calculated (GGA) band gap of B in the α-B structure as a function of volume. (d) Equation of states of B in the structure types α-B, α-Ga, and fcc.

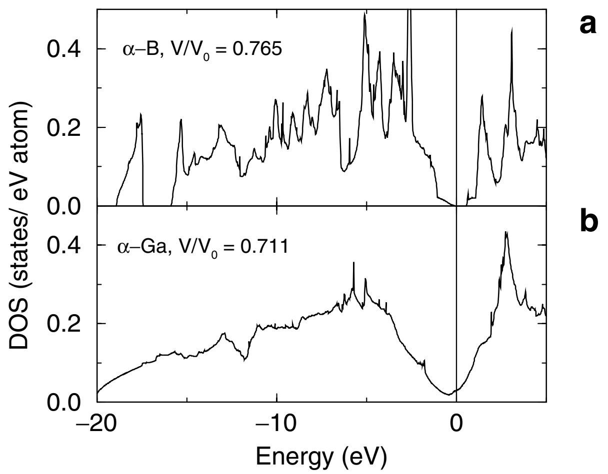

FIG. 2. (a) DOS of B in the α-B structure at transition pressure ($p = 74$ GPa, $V/V_0 = 0.765$). (b) DOS of B in the α-Ga structure at transition pressure ($p = 74$ GPa, $V/V_0 = 0.711$).

competing α-Ga structure has no real band gap but a pronounced pseudogap with an extremely low value of the density of states (0.018 states/eV atom) at the Fermi level [Fig. 2(b)]. Thus, the structural transition α-B $\rightarrow$ α-Ga in boron corresponds to a nonmetal-metal transition. However, B in the α-Ga structure is a very poor metal. Compared to the theoretical calculations by Mailhiot *et al.* [15] who predicted the nonmetal-metal transition in boron at around 210 GPa (α-B $\rightarrow$ bct) the inclusion of the α-Ga structure shifts this transition to considerably lower pressures. Interestingly, we find that the sequence of high-pressure structural transitions in boron follows the principle of optimizing s-p mixing. We quantify s-p mixing or hybridization of the s and p valence bands by the ratio between the total number of p and s states (N_p/N_s) [16]. N_p/N_s mirrors to a good approximation the high-pressure stability ranges of the structure types α-B, α-Ga, and fcc [Fig. 1(b)]. The most stable structure at a particular volume attains the highest value of N_p/N_s, i.e., expresses the highest degree of s-p mixing. Optimizing s-p mixing has also a remarkable significance for structural stability of the heavier boron group elements (i.e., Al, Ga, In, Tl). In particular, it was found that the optimization of s-p hybridization governs the stability of the ground state structures of those elements as well as the high-pressure transitions of Ga and In [17,18].

It is most interesting to relate our results with the experimental findings of Eremets *et al.* who investigated the pressure dependence of the resistance of β-B at room temperature [7]. Up to 170 GPa boron remained semiconducting but at approximately 175 GPa the conductivity finally changed to metallic behavior. However, the value of the conductivity was just close to that of minimum metallic conductivity (around 500 $\Omega^{-1}\,\mathrm{cm}^{-1}$). Additionally, at 175 GPa the material was found to be superconducting with a T_c of 6 K. The value of T_c increased with pressure and reached 11 K at 250 GPa which was the maximum pressure applied. The authors estimated the onset of superconductivity to be around 130 GPa and further observed a pronounced kink in the pressure dependence of T_c at $\approx$ 180 GPa (i.e., close or corresponding to the pressure where the material exhibits metallic conductivity). The former result was attributed to the actual metallization of boron, the latter to a structural transition. We notice a large difference between the calculated pressure for a structural transition α-B $\rightarrow$ α-Ga and the experimental pressure for a suggested transition β-B $\rightarrow$ metallic structure. To explain a considerably higher pressure for a transition β-B $\rightarrow$ α-Ga compared to α-B $\rightarrow$ α-Ga one could assume that β-B actually is essentially more stable than α-B. This, however, is not supported from our relative stability investigation of α-B and hR105 framework of β-B [19]. It is more reasonable to assume that generally high-pressure structural transitions in B may appear considerably delayed at ambient temperature because the destruction of tightly bonded B_{12} clusters in the icosahedral structures should represent a very high barrier towards a possible metallic high-pressure structure. Therefore, we interpret the experimental onset of superconductivity (the actual metallization) in B at 130 GPa by the band gap closure [14] in β-B at this pressure. This is perfectly reasonable when comparing with the evolution of the calculated band gap in α-B with pressure [Fig. 1(c)]. The band gap closure in α-B occurs at a calculated pressure of 141 GPa which would compare well with an experimental band gap closure in β-B at 130 GPa considering the somewhat smaller band gap of the latter at ambient conditions. Further, we propose the α-Ga structure as a structural model for a metallic high-pressure modification of B after a phase transition of either semiconducting icosahedral α-B or β-B. This is supported by the fact that boron in the α-Ga structure would match well the experimentally found high-pressure conductivity properties of B in the range between 180 and 250 GPa, i.e., being a poor metal because of an extremely low value of the density of states at the Fermi level (for a wide range of volumes) and being a superconductor [21].

We now turn to the situation of the higher boron congeners Al and Ga. The results are summarized in Figs. 3 and 4, respectively. According to the energy vs volume calculations we find for Al that the icosahedral α-B structure type becomes most stable at volumes larger than $V/V_0 = 1.4$ [Fig. 3(a)]. The minimum energy difference between the α-B type and the ground state fcc structure is 0.22 eV/atom. For comparison, the energy differences between elemental polymorphs in the neighboring carbon group [22] range from 0.02 eV/atom (graphite/diamond, α-Sn/β-Sn) up to 0.4 eV/atom (diamond/C_{60}). Furthermore, the interatomic distances within the icosahedra are in a range between 2.67 and 2.72 Å, which compares well with the range of 2.65–2.76 Å found within the neutral Al icosahedra in the clusters $Al_{22}X_{20}$ ($X =$ Cl, Br) prepared by Klemp *et al.* [8]. Interestingly, for Al the α-Ga structure should not represent an intermediate structural solution between the fcc ground state and α-B, because at volumes below $V/V_0 = 1.2$ the *Cmca* α-Ga structure is unstable with respect to the fcc structure [23]. Thus, if considering a structural transition at negative pressure (expanded volumes) a direct transition fcc → α-B would occur. For Ga the competition between the α-Ga and the α-B structure is very close with a minimum energy difference of just 0.05 eV/atom [Fig. 4(a)]. The most stable configuration of the α-B structure type corresponds to an expanded volume of about $V/V_0 = 1.2$. At this volume the range of interatomic distances within the icosahedra is 2.68–2.78 Å. Thus, Ga appears to be close to realizing an icosahedral elemental structure.

Importantly, according to the DOS [Figs. 3(b) and 4(b)] neither Al nor Ga in the icosahedral α-B structure would correspond to semiconductors (as boron) but remain metals. The reason is that in Al and Ga with the α-B structure the two-electron three-center connected icosahedra within the hexagonal layers are considerably closer packed compared to B. As a matter of fact, in Al and Ga the intercluster bond lengths in the layers approach the lengths of the intracluster ones, whereas the intercluster two-electron two-center contacts between the icosahedra of adjacent layers are considerably shorter.

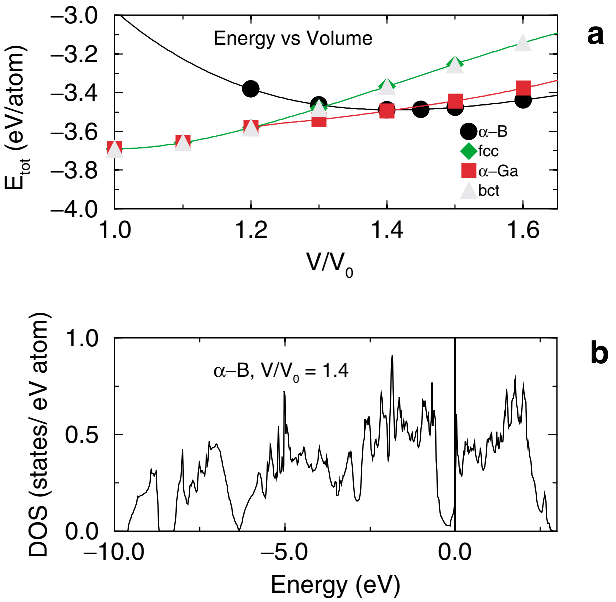

FIG. 3 (color). (a) Calculated energy vs volume for Al in the structure types α-B, fcc, α-Ga, and bct. (b) DOS of Al in the α-B structure at equilibrium volume ($V/V_0 = 1.4$).

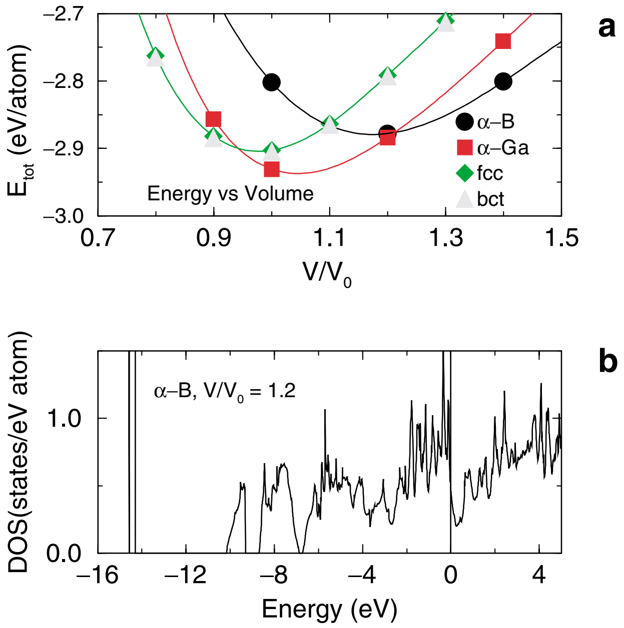

FIG. 4 (color). (a) Calculated energy vs volume for Ga in the structure types α-B, α-Ga, fcc, and bct. (b) DOS of Ga in the α-B structure at equilibrium volume ($V/V_0 = 1.2$).

This situation is also found for α-B when compressed above the point of band gap closure. Thus, one can think of the hexagonal layers of icosahedra in Al and Ga with the α-B structure as polymerized, metallic conducting aggregates. In conclusion we find that the idea of metastable novel icosahedra based modifications of Al presented by Klemp *et al.* is well taken, but from a thermodynamic point of view Ga appears to be even more promising. The disproportionation reactions of monovalent Al and Ga halides performed by this group [24] could indeed provide a route for the synthesis of new elemental Al and Ga modifications. If "naked," neutral Al_{12} and Ga_{12} icosahedra can form from the disproportionation process, these units may arrange into larger aggregates provided the disproportionation reactions are directed towards the formation of nanoparticles using metal coordinating surfactants. The process of nanocrystal formation from the solution phase is often kinetically controlled which leads to the trapping and growth of metastable phases.

In summary, we have described structural competition and electronic relationships between icosahedral open-packed and metallic close-packed modifications for B, Al, and Ga. We reveal a nonmetal-metal transition of boron from α-B to α-Ga at a pressure of about 74 GPa. For Al and Ga we find an icosahedron based modification (α-B) just slightly higher in energy than the corresponding metallic ground state structures. This raises expectations into the experimental feasibility of new modifications for these elements, especially in nanosized systems.

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