Electron-Deficient and Polycenter Bonds in the High-Pressure $\gamma$-B$_{28}$ Phase of Boron

Swastik Mondal,$^1$ Sander van Smaalen,$^{1,*}$ Andreas Schönebleber,$^1$ Yaroslav Filinchuk,$^{2,4}$ Dmitriy Chernyshov,$^2$
Sergey I. Simak,$^3$ Arkady S. Mikhailushkin,$^3$ Igor A. Abrikosov,$^3$ Evgeniya Zarechnaya,$^4$
Leonid Dubrovinsky,$^4$ and Natalia Dubrovinskaia$^1$

$^1$Laboratory of Crystallography, University of Bayreuth, 95440 Bayreuth, Germany
$^2$Swiss-Norwegian Beam Line, ESRF, 38043 Grenoble, France
$^3$Theory and Modeling Division, IFM, Linköping University, 581 33 Linköping, Sweden
$^4$Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany

(Received 29 November 2010; revised manuscript received 20 April 2011; published 25 May 2011)

The peculiar bonding situation in $\gamma$ boron is characterized on the basis of an experimental electron-density distribution which is obtained by multipole refinement against low-temperature single-crystal x-ray diffraction data. A topological analysis of the electron-density distribution reveals one-electron–two-center bonds connecting neighboring icosahedral B$_{12}$ clusters. A unique polar-covalent two-electron–three-center bond between a pair of atoms of an icosahedral cluster and one atom of the interstitial B$_2$ dumbbell explains the observed charge separation in this high-pressure high-temperature polymorph of boron.

DOI: 10.1103/PhysRevLett.106.215502
PACS numbers: 61.50.Ks, 61.44.Fw, 61.66.Fn

The peculiar bonding situation in $\gamma$ boron is characterized on the basis of an experimental electron-density distribution which is obtained by multipole refinement against low-temperature single-crystal x-ray diffraction data. A topological analysis of the electron-density distribution reveals one-electron–two-center bonds connecting neighboring icosahedral B$_{12}$ clusters. A unique polar-covalent two-electron–three-center bond between a pair of atoms of an icosahedral cluster and one atom of the interstitial B$_2$ dumbbell explains the observed charge separation in this high-pressure high-temperature polymorph of boron.

The element boron is known for its polymorphism, although many reported allotropes might actually be boron-rich compounds, which are stabilized by the presence of impurities [1]. The existence as true polymorphs of boron has been established for rhombohedral $\alpha$ boron [2], rhombohedral $\beta$ boron [3,4], and the recently discovered orthorhombic high-pressure modification $\gamma$ boron [5–7]. All three modifications can be obtained at ambient conditions by quenching. While $\gamma$ boron is the stable polymorph at conditions of high pressure and high temperature, it is not certain whether $\alpha$ boron or $\beta$ boron is the stable polymorph at ambient conditions [1].

Characteristic for the crystal structures of boron and boron-rich compounds is the presence of triangular B$_3$ units that are condensed in polyhedra of various sizes [1]. In particular, an icosahedral, quasimolecular cluster of 12 boron atoms is the building block of all allotropes of boron as well as of many boron-rich solids. $\alpha$ boron exclusively comprises B$_{12}$ icosahedral clusters which are arranged in a distorted cubic closest packing of spheres. The crystal structure of orthorhombic $\gamma$-B$_{28}$ can be described as a distorted cubic closest packing of B$_{12}$ clusters with B$_2$ pseudopair units (dumbbells) placed at the octahedral sites (Fig. 1) [5,6]. Chemical bonding in these solids has been rationalized in terms of polycenter bonds on the B$_{12}$ closo cluster and two-electron–two-center ($2e2c$) and two-electron–three-center ($2e3c$) bonds between the clusters [1]. The ubiquitous occurrence of the B$_{12}$ cluster has incited the notion that boron would form molecular solids containing molecularlike icosahedral clusters [8]. However, those properties of boron polymorphs and boron-rich compounds which make them interesting for materials science and technology (extreme chemical stability associated with high hardness and low compressibility) are highly unusual for molecular solids. Explanation of this phenomenon requires a detailed analysis of chemical bonding between boron atoms [8,9]. Based on calculated electronic band structures, a partial ionic nature of bonding has been proposed for $\alpha$ boron [10] and—more recently—for the high-pressure polymorph $\gamma$-B$_{28}$, suggesting a charge separation between the icosahedral cluster and the dumbbell [5]. On the other hand, there is now a general agreement that bonding in $\gamma$-B$_{28}$ is predominantly covalent [5,7,11–13].

Electron-density studies by means of high-quality, low-temperature x-ray diffraction data provide important experimental information about chemical bonding in crystalline solids [14], including the identification of bonding...
interactions, ionicity vs covalency of bonds, and an estimate about the strength of interactions. Among all boron phases, experimental charge-density studies have been reported only for α boron [8,15,16], but all these studies have refrained from a quantitative interpretation of the charge density. Here we report the results of an experimental charge-density study of γ-B_{28}. A quantitative interpretation according to a topological analysis of the charge density [17] has revealed the unexpected peculiarities of chemical bonding, and it has identified the mechanism for charge separation in this covalently bonded solid.

High-resolution, single-crystal x-ray diffraction data of γ-B_{28} have been collected at a temperature of 85 K at the Swiss-Norwegian beam line BM01A of the European Synchrotron Radiation Facility (ESRF). A multipole refinement [14] has been carried out with the computer program xd [18], resulting in an excellent fit to the observed Bragg reflections with \( R_F = 0.0120 \) [19]. The starting point was the set of atomic coordinates of the five crystallographically independent atoms as taken from the literature [5–7]. The purity of the sample has been established previously [7] and also follows from the excellent fit to the diffraction data.

A topological analysis of the static electron density has been performed according to Bader’s quantum theory of atoms in molecules [17]. The quantum theory of atoms in molecules defines a bond critical point (BCP) as the point of minimum density along the bond path between two atoms (saddle point of the electron density). Similarly, ring critical points (RCPs) characterize closed paths of bonded atoms. Bonding interactions require the presence of a BCP and/or RCP, and values of the density and its Laplacian at BCPs and RCPs correlate with properties of chemical bonds [17]; e.g., densities and negative Laplacians of increasing magnitudes indicate covalent bonds of increasing strength. The present experimental static electron density reveals BCPs for all bonds as well as RCPs for three-center (3c) and polycenter bonds (Table I and Fig. 1). The arrangement of BCPs and RCPs is in agreement with the following interpretation of bonding in γ-B_{28}.

BCPs are found for all triangular faces of the B_{12} group (B1-B1-B4, B1-B2-B3, B1-B2-B4, B1-B3-B4, B2-B4-B4, and B3-B4-B5). They indicate polycenter bonds on this closo cluster (Table I). Three of the four two-center (2c) bonds (B3-B3, B2-B5, and B5-B5) have electron densities (\( \rho_{BCP} \)) and negative Laplacians (\( \nabla^2 \rho_{BCP} \)) of large magnitudes at the BCPs. Therefore, they should be considered as 2e2c bonds. The value of \( \rho_{BCP} \) of these bonds is comparable to \( \rho_{BCP} \) for the single intercluster bond in α boron [8], suggesting the similar character of the 2e2c bonds in these two boron allotropes. However, we do not find any evidence for an anomalous electron-density distribution in 2e2c bonds of γ boron (Fig. 2) as opposed to the bent character reported for the single intercluster bond in α boron [8]. The unconventional distribution of electron density reported for this bond of α boron might be an artifact of the maximum entropy method possibly caused by the overlap of Bragg peaks in the powder diffraction data of Ref. [8], which is not an issue for the present single-crystal diffraction experiment.

The fourth 2c bond (B1-B4) is substantially longer (\( d = 1.83 \) Å) and has significantly smaller magnitudes of \( \rho_{BCP} \) and \( \nabla^2 \rho_{BCP} \). Ab initio calculations also suggest a concentration of electrons at the B1-B4 bond that is lower than on other 2c bonds [19]. Considering the electron-deficient nature of boron, these features are indicative of an one-electron–two-center (1e2c) bond. The existence of 1e2c bonds in electron-deficient systems is well established in chemistry and, in fact, has originally been explained by the example of a boron hydride but has never been proposed for elemental boron [20,21].

Finally, an RCP is found in the triangle B4-B4-B5, outside the B_{12} cluster. Together with BCPs between the two B4 atoms and between B4 and B5—the latter coinciding

<table>
<thead>
<tr>
<th>Bond</th>
<th>( d_{BCP} ) (Å)</th>
<th>( \rho_{BCP} ) (eÅ(^{-3}))</th>
<th>( \nabla^2 \rho_{BCP} ) (eÅ(^{-5}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-center bonds, BCPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B3-B3</td>
<td>0.830, 0.830</td>
<td>1.165</td>
<td>−10.404</td>
</tr>
<tr>
<td>B2-B5</td>
<td>0.901, 0.772</td>
<td>1.193</td>
<td>−11.677</td>
</tr>
<tr>
<td>B5-B5</td>
<td>0.862, 0.862</td>
<td>1.134</td>
<td>−10.189</td>
</tr>
<tr>
<td>B1-B4</td>
<td>0.865, 0.979</td>
<td>0.782</td>
<td>−4.402</td>
</tr>
<tr>
<td>Three-center bonds, RCPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1-B1-B4</td>
<td>⋯</td>
<td>0.620</td>
<td>0.115</td>
</tr>
<tr>
<td>B1-B2-B3</td>
<td>⋯</td>
<td>0.744</td>
<td>−0.464</td>
</tr>
<tr>
<td>B1-B2-B4</td>
<td>⋯</td>
<td>0.719</td>
<td>−0.671</td>
</tr>
<tr>
<td>B1-B3-B4</td>
<td>⋯</td>
<td>0.699</td>
<td>−0.234</td>
</tr>
<tr>
<td>B2-B4-B4</td>
<td>⋯</td>
<td>0.697</td>
<td>−0.049</td>
</tr>
<tr>
<td>B3-B4-B4</td>
<td>⋯</td>
<td>0.739</td>
<td>−0.539</td>
</tr>
<tr>
<td>B4-B4-B5</td>
<td>⋯</td>
<td>0.508</td>
<td>0.688</td>
</tr>
</tbody>
</table>

FIG. 2. (a) Static electron density and (b) Laplacian in the mirror plane containing the atoms B2, B3, and B5 (compare Fig. 1). Contour lines of equal density are at 0.05 eÅ\(^{-3}\) up to 2.0 eÅ\(^{-3}\). Contour lines in the Laplacian map are at ±(2, 4, 8) × 10\(^{-5}\) eÅ\(^{-5}\) (−3 ≤ n ≤ 3) with solid lines for positive and dashed lines for negative contours.
TABLE II. Experimental atomic charges (this work; number of electrons) compared to charges obtained from a theoretical density [5].

<table>
<thead>
<tr>
<th>Atom</th>
<th>Experiment</th>
<th>Theory [5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>+0.0571</td>
<td>+0.0029</td>
</tr>
<tr>
<td>B2</td>
<td>−0.1386</td>
<td>+0.0636</td>
</tr>
<tr>
<td>B3</td>
<td>+0.0011</td>
<td>+0.0255</td>
</tr>
<tr>
<td>B4</td>
<td>−0.1943</td>
<td>−0.1680</td>
</tr>
<tr>
<td>B5</td>
<td>+0.4138</td>
<td>+0.2418</td>
</tr>
</tbody>
</table>

with valence shell charge concentrations—this indicates a 3c bond on B4-B4-B5 (Fig. 3). The absence of a BCP for B1-B5 and of an RCP for B1-B4-B5 provides strong evidence against a 3c bond on B1-B4-B5, as it has been proposed by Rulis, Wang, and Ching [22].

According to Wade’s rule [23,24], covalent bonding within the $\gamma$-B$_{28}$ closo cluster involves 26 of its 36 valence electrons. The bonding interactions described above show that four more electrons are used for two 2e2c bonds with neighboring icosahedral clusters (B3-B3) and two 2e2c bonds with the B$_2$ units (B2-B5). Another four electrons are used for eight 1e2c bonds to neighboring icosahedral clusters lying below and above the mirror plane. Each of the remaining two electrons is combined with one electron from a dumbbell (a B5 atom) for the formation of a non-icosahedral 2e3c bond on B4-B4-B5. Together with the B2-B5 and B5-B5 2e2c bonds, this model also accounts for the three valence electrons of B5. Perfect accounting for all valence electrons by 2c and 3c bonds suggests that bonding in $\gamma$-B$_{28}$ is predominantly covalent in nature.

Atomic charges have been obtained by integration over the atomic basins in the experimental charge density (Table II). They confirm a charge transfer between boron atoms, but numerical values are different from those obtained from the theoretical density [5]. Combined with the positive $\nabla^2 \rho_{BCP}$ and small $\rho_{BCP}$ of B4-B4-B5 (Table I), they suggest the following mechanism of charge transfer which primarily involves the atoms B4 and B5 and which is in agreement with a simple electron count. The pair of B4 atoms and the single B5 atom each contribute one electron to the 2e3c bond. Since each atom in a symmetric 2e3c bond should contribute equally to the bond, a redistribution of charge is induced that removes 1/3 electron from B5 and assigns an additional 1/6 electron to each B4 atom. The latter value is close to the observed negative charge of this atom (Table II).

A charge transfer of secondary magnitude can be envisaged between the B5 and B2 atoms. The large magnitudes of $\rho_{BCP}$ and the negative $\nabla^2 \rho_{BCP}$ demonstrate the accumulation of charge in the bonding region, and they stress the covalent character of this interaction. The location of the BCP away from the midpoint of the B2-B5 bond (Table I) is responsible for the apparent charge transfer between these atoms.

The local character of charge transfer is furthermore evidenced by the observation that the B1 and B3 atoms—not involved in bonding to the B$_2$ dumbbell—remain almost neutral. The appropriate description of bonding in $\gamma$-B$_{28}$ thus involves 2e2c and 2e3c polar-covalent bonds rather than an explicit charge transfer between B$_{12}$ and B$_2$ clusters as proposed by Oganov et al. [5].

In summary, a quantitative analysis of the experimental charge density has revealed the bonding situation of the high-pressure polymorph $\gamma$-B$_{28}$ of boron. As is evident, covalent polycenter bonds exist on the B$_{12}$ clusters. Neighboring clusters are bonded to each other by 2e2c and electron-deficient, 1e2c bonds. Strong 2e2c bonds exist within the B$_2$ dumbbells and between the dumbbell and icosahedral groups. Finally, a unique polar-covalent 2e3c bond has been identified between a pair of atoms of one B$_{12}$ group and one atom of the dumbbell. It is proposed that the charge transfer originates in this peculiar 2e3c bond, to which the three boron atoms contribute unequal amounts of electrons. The present results explain why boron and boron-rich compounds containing quasimolecular icosahedral B$_{12}$ clusters acquire physical properties unusual for molecular solids. While these clusters geometrically mimic molecules, intericosahedral chemical bonds are of equal or higher strength than intricosahedral bonds, and the structures of boron and boron-rich compounds are controlled by individual two- and three-center bonds between boron atoms.

![FIG. 3 (color online). Properties on the plane containing B4-B4-B5, perpendicular to the mirror plane.](image-url)
Financial support has been provided by the German Science Foundation (DFG), VR, and SSF. Electronic structure calculations have been performed at SNIC resources. N. D. thanks the DFG for financial support through the Heisenberg program.

*smash@uni-bayreuth.de
†Present address: Institute of Condensed Matter and NanoScience, University of Louvain, 1348 Louvain-la-Neuve, Belgium.
‡http://www.crystal.uni-bayreuth.de