Electron-Deficient and Polycenter Bonds in the High-Pressure γ-B_{28} Phase of Boron

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The peculiar bonding situation in γ 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 α boron [2], rhombohedral β boron [3,4], and the recently discovered orthorhombic high-pressure modification γ boron [5–7]. All three modifications can be obtained at ambient conditions by quenching. While γ boron is the stable polymorph at conditions of high pressure and high temperature, it is not certain whether α boron or β 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. α boron exclusively comprises B_{12} icosahedral clusters which are arranged in a distorted cubic closest packing of spheres. The crystal structure of orthorhombic γ-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 α boron [10] and—more recently— for the high-pressure polymorph γ-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 γ-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
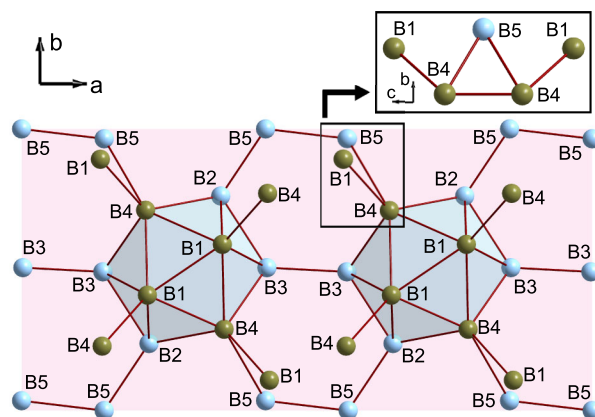

FIG. 1 (color online). Perspective view of γ-B_{28}. Atoms B2, B3, and B5 are on the crystallographic mirror plane (indicated by light red shading). Atoms B1–B4 form the B_{12} group; atom B5 forms the dumbbell [7,19]. The box shows the B1-B4-B5-B4-B1 region, perpendicular to the mirror plane.

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 Baders' 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}.

RCPs 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-B4). 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 (ρ_{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 ρ_{BCP} of these bonds is comparable to ρ_{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

TABLE I. Topological properties of the experimental static electron density at BCPs and RCPs for $2c$ and $3c$ bonds. d_{BCP} is the distance between the atoms and the BCP.

Bond	d_{BCP} (Å)	ρ_{CP} (eÅ^{-3})	$\nabla^2 \rho_{CP}$ (eÅ^{-5})
Two-center bonds, BCPs			
B3-B3	0.830, 0.830	1.165	-10.404
B2-B5	0.901, 0.772	1.193	-11.677
B5-B5	0.862, 0.862	1.134	-10.189
B1-B4	0.865, 0.979	0.782	-4.002
Three-center bonds, RCPs			
B1-B1-B4	$\cdots$	0.620	0.115
B1-B2-B3	$\cdots$	0.744	-0.464
B1-B2-B4	$\cdots$	0.719	-0.671
B1-B3-B4	$\cdots$	0.699	-0.234
B2-B4-B4	$\cdots$	0.697	-0.049
B3-B4-B4	$\cdots$	0.739	-0.539
B4-B4-B5	$\cdots$	0.508	0.688

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 ($d \approx 1.83$ Å), and it has significantly smaller magnitudes of ρ_{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
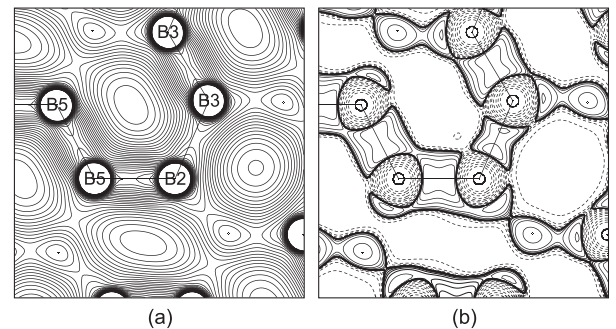

FIG. 2. (a) Static electron density and (b) Laplacian in the mirror plane containing the atoms B2, B3, and B5 (compare Fig. 1). Contour lines of equal density are at 0.05 eÅ^{-3} up to 2.0 eÅ^{-3}. Contour lines in the Laplacian map are at $\pm(2, 4, 8) \times 10^n$ eÅ^{-5} ($-3 \le n \le 3$) with solid 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].

Atom	Experiment	Theory [5]
B1	+0.0571	+0.0029
B2	−0.1386	+0.0636
B3	+0.0011	+0.0255
B4	−0.1943	−0.1680
B5	+0.4138	+0.2418

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 B_{12} *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
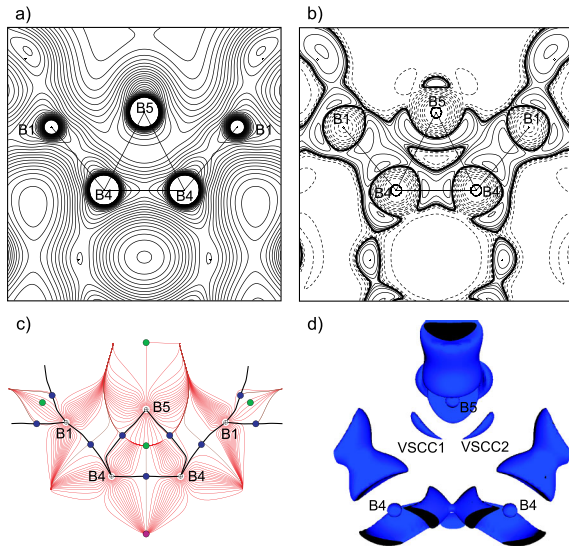

FIG. 3 (color online). Properties on the plane containing B4-B4-B5, perpendicular to the mirror plane. (a) Static electron density; contour lines at 0.05 up to 2.0 $e/Å^{-3}$. (b) Laplacian; contour lines at $\pm(2, 4, 8) \times 10^n\ e/Å^{-5}$ ($-3 \le n \le 3$); solid line = positive and dashed line = negative contours. (c) Gradient trajectories of the electron density with BCPs (blue), RCPs (green), and cage critical points (purple) indicated. (d) Laplacian at $-2.6\ e/Å^{-5}$ iso level, showing the valence shell charge concentrations with two features near B5.

the three valence electrons of B5. Perfect accounting for all valence electrons by $2c$ and $3c$ bonds suggests that bonding in γ-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 $\nabla^2 \rho_{RCP}$ and small ρ_{RCP} 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 ρ_{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 γ-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 γ-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 intraicosahedral bonds, and the structures of boron and boron-rich compounds are controlled by individual two- and three-center bonds between boron atoms.

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