Disorder and defects are not intrinsic to boron carbide

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A unique combination of useful properties in boron-carbide, such as extreme hardness, excellent fracture toughness, a low density, a high melting point, thermoelectricity, semi-conducting behavior, catalytic activity and a remarkably good chemical stability, makes it an ideal material for a wide range of technological applications. Explaining these properties in terms of chemical bonding has remained a major challenge in boron chemistry. Here we report the synthesis of fully ordered, stoichiometric boron-carbide \( \text{B}_{13}\text{C}_2 \) by high-pressure–high-temperature techniques. Our experimental electron-density study using high-resolution single-crystal synchrotron X-ray diffraction data conclusively demonstrates that disorder and defects are not intrinsic to boron carbide, contrary to what was hitherto supposed. A detailed analysis of the electron density distribution reveals charge transfer between structural units in \( \text{B}_{13}\text{C}_2 \) and a new type of electron-deficient bond with formally unpaired electrons on the \( \text{C–B–C} \) group in \( \text{B}_{13}\text{C}_2 \). Unprecedented bonding features contribute to the fundamental chemistry and materials science of boron compounds that is of great interest for understanding structure-property relationships and development of novel functional materials.

Boron carbide is one of the hardest substances, surpassed only by diamond and boron nitride1. The high mechanical and thermal stability, low density and low costs of fabrication have made boron carbide the prime choice in a series of technological applications2–7. Boron carbide preserves the same structure for a range of compositions, and details of this crystal structure have been discussed in terms of chemical disorder of boron and carbon atoms as well as the presence of vacancies8–11. Electronic-structure calculations suggest that the properties of boron carbide depend on the stoichiometry and the details of the disorder12–14.

Experimentally, chemical bonding can be accessed through single-crystal x-ray diffraction. Reliable information on the distribution of the electron density in the unit cell can be obtained only for good-quality single crystals with minimal structural disorder14. Synthesis of defect-free material is the most challenging task in boron-carbide chemistry. We have succeeded in growing small single crystals of the stoichiometric composition \( \text{B}_{13}\text{C}_2 \) by high-pressure–high-temperature techniques (see Methods). The material is transparent with a dark red or maroon color, indicating an insulator or a large-band-gap semiconductor. This is in agreement with some literature data15, but it is inconsistent with the relatively high electrical conductivity reported for boron carbide1. To the best of our knowledge, dark red transparent boron carbide has not been reported before.

A multipole (MP) model has been obtained for the crystal structure of \( \text{B}_{13}\text{C}_2 \) by refinement against accurately measured intensities of Bragg reflections (see Methods and Supplementary Information Section S1)14. The excellent fit to the diffraction data with \( R = 0.0197 \) provides strong evidence for the stoichiometry of \( \text{B}_{13}\text{C}_2 \), in agreement with the composition obtained by Energy-dispersive x-ray (EDX) analysis (see Methods). The excellent fit furthermore indicates the absence of disorder: \( \text{B}_{13}\text{C}_2 \) is composed of \( \text{B}_{12} \) icosahedral clusters and CBC linear chains (Fig. 1 and Supplementary Information Section S2). Lattice parameters and values of atomic displacement parameters (ADPs) fall within a range previously assigned to the composition \( \text{B}_{13}\text{C}_2 \),†, 8–10. The possibility of different compositions was investigated by additional MP refinements with small amounts of carbon at the \( \text{B}_3 \) site, corresponding to \( \text{B}_{12-x}\text{C}_{3+x} \) stoichiometries with \( x = 0.44 \) and \( x = -0.11 \), respectively (see Supplementary Information Section S1 for details). Both models gave a slightly worse fit to the diffraction data than the \( \text{B}_{13}\text{C}_2 \) model. More importantly, the number of valence electrons of \( \text{C} \) at the \( \text{B}_3 \) site refined to zero, thus showing that the MP refinement has effectively removed carbon from the \( \text{B}_3 \) site, providing further support for the ordered

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stoichiometric character of the investigated crystal. Interestingly, a refinement of the independent atom model (IAM) including the site occupancy factors of C at the BP and BE sites resulted in 19% occupancy of the BP site by carbon (x = −0.11). Contrary to the MP model (R1 = 0.0197), the IAM with disorder (R1 = 0.0287) leads to only a small improvement of the fit to the data (Table S4). These results suggest that the charge transfer towards BP in the MP model is mimicked in the disordered IAM by a fractional occupancy of the BP site by C.

Discrepancies between the present values of the lattice parameters and ADPs and those reported in the literature18–20 for the same composition may be the result of different degrees of disorder and defects between different samples. The single MP refinement16 reported previously for B13C2 gave a much worse fit to their XRD data (R1 = 0.0440), which questions the reliability of that model. The single MP refinement17 for B12C3 also led to a substantially worse fit to their XRD data (R1 = 0.0250) than we have obtained for our model against the present XRD data (R1 = 0.0197). Thus, a highly precise MP refinement refutes recent less accurate diffraction studies13 and theoretical electronic-structure calculations21, where a disorderly replacement by carbon of a certain fraction of the boron atoms of the B12 clusters was considered as absolutely essential for the stability of B13C2.

The MP model extends the independent atom model (IAM) of spherical atoms by parameters describing the reorganization of electron density due to chemical bonding. Previous electron-density studies on boron carbide18,19 have been restricted to a discussion of the qualitative features of the electron densities. Quantitative information about chemical bonding can be extracted from the static electron density of the MP model through its topological properties according to Bader’s quantum theory of atoms in molecules (QTAIM)20,21. Critical points (CPs) are defined as the positions where the gradient of the electron density is zero \( \nabla \rho(r) = 0 \). They are classified according to the number of positive eigenvalues of the Hessian matrix of second derivatives as local maxima (3 positive eigenvalues), bond critical points BCPs (2), ring critical points RCPs (1) and local minima (0 positive eigenvalues)20.

All atomic positions of the present MP model can be identified with local maxima in the static electron density, while additional local maxima do not exist. BCPs and RCPs have been found between the atoms of the B12 cluster in a similar pattern as for \( \alpha \)-boron21, and with comparable values for the electron densities and Laplacians (Table 1). Together, these features indicate similar bonding by molecular-type orbitals on the B12 clusters in B13C2 and \( \alpha \)-boron21. According to Wade’s rule22, this bonding involves 26 of the 36 valence electrons of the twelve boron atoms of this closo-cluster, thus leaving for each boron atom one orbital but only 5/6 electrons for exo-cluster bonding21,22.

The crystal structure of B13C2 comprises four crystallographically independent atoms. CBC chains contain the carbon atom and a boron atom denoted as C: the B12 cluster is made of six polar and six equatorial atoms, denoted as BP and BE, respectively (Fig. 1). According to the QTAIM20, bonding between a pair of atoms exists, if the electron density possesses a BCP between those atoms. For B13C2, we have found BCPs between pairs of BP atoms from neighboring clusters. The distance BP–BP is slightly larger and the magnitudes of the electron density, \( \rho_{\text{BCP}} \), and Laplacian, \( \nabla^2 \rho_{\text{BCP}} \), are slightly smaller than those of the corresponding inter-cluster bonds in \( \alpha \)-boron23 and \( \gamma \)-boron24 (Table 1). The high value of \( \rho_{\text{BCP}} \) together with a negative value of \( \nabla^2 \rho_{\text{BCP}} \) of large magnitude indicate a strong covalent interaction between these atoms20. The similarities with bonding in \( \alpha \)-boron23 (Table 1) allow this bond to be classified as a 2-electron-2-center (2e2c) bond. Further evidence for this interpretation comes from the QTAIM theory, which assigns a charge to each atom by integration of the electron density over the atomic basins. A charge of −0.21 electrons has been obtained by integrating the experimental static electron density over the atomic basin of BP (Table 2). This value is in good agreement with electron counting. With 5/6 electrons per boron atom available for exo-cluster bonding, a formal charge of −0.17 is obtained for BP involved in a 2e2c BP–BP exo-cluster bond.

Bond-critical points are also found between a BP atom and the closest C atom. Large magnitudes of \( \rho_{\text{BCP}} \) and the negative Laplacian \( \nabla^2 \rho_{\text{BCP}} \) indicate a strong covalent interaction and a 2e2c C–BP bond. An equal split of these

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**Figure 1. Crystal structure of B13C2.** (a) Perspective view highlighting the environment of the icosahedral B12 cluster. Each B12 cluster is bonded by BP–BP bonds to three B12 clusters in each of the two neighboring close-packed planes, and to six CBC chains by C–BE bonds. (b) Perspective view highlighting the environment of the CBC chain. Each carbon atom is bonded to three B12 clusters within a single close-packed plane. Color code: BP is blue, BE is green, BC is red, and C is grey.
have been observed at much lower concentrations in boron carbides of different compositions. One explanation of the effect of pressure on the electrons in lithium metal.

The low chemical reactivity follows from the electron-deficient character of this bond. The internal pressure has squeezed out most of the electrons of BC, reminiscent of the presence of carbon atoms at a small fraction of the BP sites.

Stoichiometric B13C2 is a form of boron carbide with compositions on the carbon-rich side of B12C3 and which reduces the number of unpaired spins. On the other hand, the itinerant character of the electron states or localization as bipolarons may be in agreement with low concentrations of unpaired spins.

In summary, we have synthesized stoichiometric boron carbide B13C2, which is free of intrinsic disorder, and which lies in chemical disorder and vacancies, which are necessarily present for other compositions than stoichiometric B13C2, which reduce the number of unpaired spins. On the other hand, the itinerant character of the electron states or localization as bipolarons may be in agreement with low concentrations of unpaired spins.

Table 1. Geometries and topological properties of the experimental static electron density for 2-center exo-cluster bonds in B13C2. d is the bond-length and dBCP is the distance between a BCP and each of the two constituent atoms of that bond. \( \rho_{BCP} \) is the electron density at the BCP and \( \nabla^2 \rho_{BCP} \) is its Laplacian. Topological properties for the inter-cluster B–B bonds in \( \alpha \)-boron and in \( \gamma \)-boron are also given.

| Bond | d (Å) | dBCP (Å) | \( \rho_{BCP} \) (e/Å3) | \( \nabla^2 \rho_{BCP} \) (e/Å5) |
|------|-------|-----------|---------------------|---------------------|
| Bonds in B13C2 | | | | |
| C–BC | 1.6037(2) | 1.082/0.523 | 1.097 | −8.289 |
| C–BB | 1.4324(5) | 0.938/0.494 | 1.556 | −8.985 |
| Bp–BP | 1.7131(4) | 0.857/0.857 | 1.030 | −6.463 |
| Inter-cluster bonds in \( \alpha \)-boron | | | | |
| B1–B1 (2e2c) | 1.6734(3) | 0.837/0.837 | 1.104 | −9.572 |
| Inter-cluster bonds in \( \gamma \)-boron | | | | |
| B3–B3 (2e2c) | 1.6599(5) | 0.830/0.830 | 1.165 | −10.404 |
| B1–B4 (1e2c) | 1.8275(2) | 0.865/0.979 | 0.782 | −4.002 |

Table 2. Atomic basins (volume \( V_{basin} \)) and ionic charges for the four crystallographically independent atoms in B13C2 along with their multiplicity in the unit cell.

| Atom | Multiplicity | \( V_{basin} \) (Å3) | Charge (e) |
|------|-------------|---------------------|-----------|
| Bp   | 6           | 7.808               | −0.210    |
| BP   | 6           | 5.176               | +0.703    |
| C    | 2           | 14.571              | −2.610    |
| BC   | 1           | 1.936               | +2.298    |

electrons between C and Bp again gives a formal charge of −0.17 for Bp, and it would result in a \( \text{B}_{12}^{2-} \) group. However, carbon is more electronegative than boron and should attract most of the bonding electrons. Indeed, the integration of the electron density over the atomic basins leads to a positive charge of BE and a strongly negative \( \text{C}^- \). The latter value is the result of the extremely small volume of the atomic basin of \( \text{C}^- \). The former value is the result of the extremely small volume of \( \text{BC} \).

A 3e3c C–BC–C bond contains one unpaired electron per formula unit B13C2. Experimentally, unpaired spins have been observed at much lower concentrations in boron carbides of different compositions. One explanation lies in chemical disorder and vacancies, which are necessarily present for other compositions than stoichiometric B13C2, and which reduce the number of unpaired spins. On the other hand, the itinerant character of the electron states or localization as bipolarons may be in agreement with low concentrations of unpaired spins.

The presence of an unsaturated bond on the CBC chains should result in a high chemical reactivity of this bond. However, we have found that BC is extremely small and well shielded from the outside by C atoms and bulky B12 clusters. Steric effects hindering access to reactive sites is known to stabilize radicals. High temperatures can overcome these barriers, and a high reactivity at elevated temperatures toward oxidizing agents has been described for boron carbide. Recently, amorphisation of boron carbide B12C3 has been explained on the basis of the presence of carbon atoms at a small fraction of the Bp sites. Stoichiometric B13C2 is a form of boron carbide that lacks this detrimental property of technical boron carbide with compositions on the carbon-rich side of B12C3.

In summary, we have synthesized stoichiometric boron carbide B13C2, which is free of intrinsic disorder, and is built of B12 icosahedral clusters and C–B–C chains. Unlike band-structure calculations on fully ordered B13C2, the ordered stoichiometric compound is an insulator or large band-gap semiconductor. An experimental electron–density study by X-ray diffraction conclusively determines that B13C2 is an electron-precise material. The electron-deficient character is explained by Bp being stripped of two of its valence electrons and the existence of a unique, electron deficient 3e3c bond on the C–B–C chains. The low chemical reactivity follows from the extremely small volume of Bp.
Methods summary

Crystal growth. Single crystals of boron-carbide were grown at high pressures of 8.5–9 GPa and high temperatures of 1873–2073 K using a 1200-ton (Sumitomo) multi-anvil hydraulic press at the Bayerisches
Geoinstitut. Energy-dispersive x-ray (EDX) analysis has been employed to determine the composition as $B_{51(12)}C$, in agreement with stoichiometric $B_{13}C_2$. The presence of other elements could be excluded.

**X-ray diffraction experiment for and electron density analysis.** A single crystal of boron-carbide of dimensions $0.09 \times 0.08 \times 0.05 \text{ mm}^3$ was chosen for an x-ray diffraction experiment with synchrotron radiation at beamline F1 of HASYLAB, DESY in Hamburg, Germany. The sample was kept at a temperature of 100 K, while a complete data set of accurate intensities was measured for Bragg reflections up to $\sin(\theta)/\lambda = 1.116 \AA^{-1}$. The diffraction data were integrated using the computer program EVA. Structure refinements have been performed with the software XD2006. A topological analysis of the static electron density has been performed by the modules TOPXD and XDPROP of the computer program XD2006. Two-dimensional density maps have been generated by the module XDGRAPH. See the Supplementary Information for details on procedures and the MP model.

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Author Contributions
S.v.S. planned and coordinated the study. N.D. and G.P. grew the single crystals. S.M., E.B. and L.D. selected the crystal by single-crystal x-ray diffraction. S.M., S.D. and S.I.A. collected diffraction data for the electron-density analysis. S.M. performed the electron-density study. S.v.S. and S.M. wrote the paper. All authors contributed to the discussion.

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