Towards Novel Boron Nanostructured Materials: Theoretical Predictions and Experimental Confirmations.

Technische Universität Dresden
Chair Material Science and Nanotechnology

April 30, 2009
Conventional Approach

New Materials

• Quasicrystals (Shechtman 1984)
• Fullerenes (Kroto & Smally 1985)

Experiment

New Properties & Methods

• Femtochemistry (Ahmad Zewail 1999)
• Superconductivity MgB\(_2\) (Nagamatsu 2001)

Theory
Opposite Approach

New Materials
- Planarity of Boron Clusters, Boustani 1994
- Boron-Nitride Nts, Rubio & Cohen 1994
- Boron NTs, Boustani & Quandt 1997

New Properties
- Aromaticity
- Hardness, Softness
- (Super) Conductivity

Experiment → Theory
Observation → Prediction
Measurement → Simulation
Survey of the Talk

- **Outlines**
  - Why Boron
  - Solid Boron
  - Boron Clusters

- **Theoretical Methods**
  - Basic Concepts
  - Ab Initio Methods
  - Geometry Optimization

- **Novel Boron**
  - Clusters & Cages
  - Sheets & Nanotubes
  - Nanoribbons

- **Applications**
  - Nanotechnology
  - Space Industry
  - Medicine
Motivations

• **Mass Spectra of Boron Clusters:**
  - Geometrical Structures
  - Electronic Properties

• **Search for New Materials with definite properties:**
  - Superlight
  - Superhardness
  - Anti-Corrosion
  - Manufacturable
  - High Temperature
  - (Semi) Conductive

• **Computationally Applicable**
  - Lightweight Atoms
  - at Nanoscale Sizes
Atomic properties

- Electron deficient
- Short covalent radius
- More Orbitals than Valence Electrons

Special properties

- High melting point
- Thermal conductive
- Semi-, Superconductor
- Hardness close to Diamond
Crystalline Rhombohedral $\alpha$-Boron

- 2-center bonds
- 3-center bonds
- Multi-center bonds
- Inverse umbrella bonding (along edges of unit cell)

Density of States: Semiconductor with Bandgap of 1.57 eV
Crystalline $\beta$-Boron
Widom et al., PRB 77, 064113 (2008)

Metal-Hexaborides & Diboredes

Doped $\alpha$-Boron,
Bylander & Kleinman
PRB 43, 1487 (1991)

$\beta$-Boron viewed along the rhombohedral 111 axis
Novel Crystall: $\gamma$-Boron

A R Oganov et al, *Nature*, 2009, DOI:10.1038/nature07736

At 19 GPa $\alpha$-$B_{12}$ transforms to $\gamma$-$B_{28}$

At 89 GPa $\gamma$-$B_{28}$ transforms to $\alpha$-Ga

$\gamma$-$B_{28}$ is at 200 GPa an insulator with a bandgap of 1.25 eV
Mass Spectra of Boron Clusters
Hanley, Whitten and Anderson JPC 92, 8503, 1988

Figure 2. Typical mass distribution of $B_n^+$ from the laser ablation source.
3D Boron Clusters


2D Boron Clusters

Prediction of Quasi-planar Boron Clusters
Boustani, IJQC 52, 1081 (1994)
Theoretical Methods

\[ \Psi(r) \quad \rho(r) \]

- Born-Oppenheimer approximation
- Hohenberg-Kohn theorems

**HARTREE-FOCK**
- LCAO approximation
- orbital approximation

**ROOTHAN**
- approximation on Hamiltonian

**AB INITIO SCF**
- treatment of correlation

**SEMI-EMPIRICAL MODELS:**
- AM1, PM3, CNDO, INDO, MNDO...
- HÜCKEL, EHT, EH-TB\(^4\)

**DENSITY FUNCTIONAL THEORY**
- Kohn-Sham (KS) development

**KS-LDA(LSD) METHODS**
- non-LCAO
- Mixed
- LCAO

- **PW-PP\(^1\), APW**
- **OPW, LMTO\(^2\), MS-X\(\alpha\)...**
- **FP-LAPW\(^3\)**
- **LCGTO-LSD, FPLO, KKR...**

**KS NON-LDA (GGA) METHODS:**
- BP86, B3LYP, PBE...

- treatment of exchange-correlation
- treatment of excited states

- **TD-DFT**

\(^1\)VASP, \(^2\)LMTO-ASA, \(^3\)WFCN-2k, \(^4\)Yaehmop
Novel Boron

CitationIndex 2008
Ihsan Boustani

Clusters, Sheets & Nanotubes
Gu, J. Comp. Chem. 19, 203, 1997
Fowler, JPC A 104, 397, 2000
Cao, J. Cond. M. 13, 5065, 2000
Shvartsburg, JPCA104, 9448, 2000

Nanowires & Belts
Ribbons & Rings
Ruoff, JACS 124, 4564, 2001
Wang, CPL 367, 495, 2002
Rühle, APL 80, 4228, 2002

PRL, Nature, JACS, Nano Letters, PRB ...

Over 1000 papers

Hirsch-Index 20
Prediction of Quasi-planar Boron Clusters
Boustani, IJQC 52, 1081 (1994)

2D Clusters

3D Clusters

Convex

Quasiplanar

(Open) Spheres

Hexagonal Pyramide

Pentagonal Pyramide
Highly stable *Boron Clusters and Spheres* can be constructed from *two* basic units: $\text{B}_6$ & $\text{B}_7$, while *Boron Sheets & Nanotubes* only from *one* basic unit: $\text{B}_7$

The Aufbau starts by consecutively adding atoms to $\text{B}_7$ forming new *hexagonal pyramids* generating *Sheets or Nanotubes.*
Theoretical Confirmation I
Curiously Stable Quasiplanar $B_{13}^+$


Similar to Benzene, Cationic $B_{13}$ is Aromatic
Theoretical Confirmation II of Quasiplanar Clusters

J. Aihara, JPC A
105, 5486 (2001)

J. Aihara, JACS
127, 13324 (2005)

π-MOs with six \( \pi \) electrons

Aromaticity of Planar Clusters is confirmed
Experimental Confirmation of Quasiplanarity I

Vertical Electron Detachment  B_n Clusters  \( \pi \)-MOs  Aromatic Boron Clusters
Experimental Confirmation of Quasiplanarity II


<table>
<thead>
<tr>
<th>Cluster size</th>
<th>Number</th>
<th>Symmetry/ state label</th>
<th>( \Delta E ) [eV]</th>
<th>( \Omega_{\text{calc}} ) [( \text{Å}^2 )]</th>
<th>( \Omega_{\text{exp}} ) [( \text{Å}^2 )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>I</td>
<td>( C_1^2 A'' )</td>
<td>0</td>
<td>62.8*</td>
<td>63.6 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>( D_{2h}^2 A_u )</td>
<td>0.48</td>
<td>58.6</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>I</td>
<td>( C_{2v} )</td>
<td>0</td>
<td>66.7*</td>
<td>66.7 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>( C_{2v} )</td>
<td>0.84</td>
<td>58.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>( C_{2v} )</td>
<td>0.89</td>
<td>59.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IV</td>
<td>( C_2 )</td>
<td>1.04</td>
<td>66.9</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>I</td>
<td>( C_{2h}^2 B_u )</td>
<td>0</td>
<td>89.1</td>
<td>83.2 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>( C_1^2 A' )</td>
<td>0.08</td>
<td>81.7*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>( C_1^2 A' )</td>
<td>1.13</td>
<td>90.2</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>I</td>
<td>( C_{2h}^2 B_u )</td>
<td>0</td>
<td>91.4</td>
<td>84.9 ± 1.8</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>( C_1^2 A' )</td>
<td>0.48</td>
<td>90.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>( C_1^2 A' )</td>
<td>0.89</td>
<td>84.6*</td>
<td></td>
</tr>
</tbody>
</table>

Collision Cross Sections

**Clusters**

| 12  | Cs   | 62.8 |
| 13  | \( C_{2v} \) | 66.7 |
| 14  | \( C_{2v} \) | 68.3 |
| 15  | Cs   | 72.1 |

| Collision Cross Sections |

| 63.6 ± 1.9 | 66.7 ± 0.9 | 69.0 ± 1.8 | 69.4 ± 2.6 |
Transition from Quasiplanar to Cylindrical Structure


Transition between Quasi-Planar and Cylindrical Structures at B_{16}
Transition from Quasiplanar to Cylindrical Structure II

\( B_{20} \) as the embryo of SWBNTs
Kiran et al., PNAS 102, 964 (2005)

Structural Transition via Optical Absorption
Marques & Botti, JCP 123, 014310 (2005)

The tubular \( B_{20} \) cluster may be viewed as the embryo of the thinnest boron nanotube, with a diameter of 5.2 Å.
On the Strong Ring Currents in B20 and neighboring Boron Toroids


| TABLE 2: Integrated Induced Currents for Selected Molecules in nA/T¹ |
|-----------------|------------|---------|---------|----------|
| sym             | total current | diamagnetic | paramagnetic | NICS     |
| B_{16}          | D_{6d}      | 31       | 33       | −1       | −33      |
| B_{20}          | D_{10d}     | 42       | 43       | −1       | −40      |
| B_{24}          | D_{12d}     | 50       | 51       | −1       | −35      |
| B_{18}          | C_{2h}      | −117     | 11       | −128     | +62      |
| B_{22}          | C_{1}       | −121     | 8        | −130     | +90      |
| B_{12}          | C_{3v}      | 25       | 25       | 0        | −30      |
| C_{60}^{10+}    | I_{h}       | 60       | 81       | −21      | −82      |
| C_{6}H_{6}      | D_{5h}      | 12       | 17       | −5       | −8       |
Boron Fullerenes

Ihsan Boustani © FB C - Theoretische Chemie, Bergische Universität Wuppertal, Germany

B. I. Yakobson et al., PRL 98, 166804 (2007)
Boron Fullerene-like Nanospheres

Stuffing Improves the Stability of Fullerene-like Boron Clusters
Prased and Jemmis, PRL 100, 165504 (2008)
Boron fullerenes: from \( \text{B}_{80} \) to hole doped boron sheets
Amy Lui et al., PRB 79, 161403 (2009)

Boron Fullerenes become metallic around \( n=4-5 \)
Their \( 60n^2 \) carbon cousins are semiconductors.
Probing Properties of Boron α-Tubes by Ab Initio Calculations
Yakobson et al., Nanoletters, 8, 1314 (2008)

Table 1. Calculated Stiffness (C), Poisson Ratio (ν), and Radial Breathing Mode Frequencies (f_{RBM}) of Boron α-Tubes

<table>
<thead>
<tr>
<th>nanotubes</th>
<th>diameter (Å)</th>
<th>C (N/m)</th>
<th>ν</th>
<th>f_{RBM} (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5,5)</td>
<td>8.13</td>
<td>209.4</td>
<td>0.18</td>
<td>238.9</td>
</tr>
<tr>
<td>(9,0)</td>
<td>8.63</td>
<td>206.7</td>
<td>0.21</td>
<td>224.8</td>
</tr>
<tr>
<td>(6,6)</td>
<td>9.93</td>
<td>202.1</td>
<td>0.26</td>
<td>195.9</td>
</tr>
<tr>
<td>(12,0)</td>
<td>11.31</td>
<td>204.6</td>
<td>0.21</td>
<td>170.6</td>
</tr>
<tr>
<td>(7,7)</td>
<td>11.37</td>
<td>215.2</td>
<td>0.20</td>
<td>173.7</td>
</tr>
<tr>
<td>(8,8)</td>
<td>13.13</td>
<td>214.0</td>
<td>0.21</td>
<td>150.2</td>
</tr>
<tr>
<td>(18,0)</td>
<td>16.50</td>
<td>217.5</td>
<td>0.15</td>
<td>119.2</td>
</tr>
</tbody>
</table>
The total energy of B$_{80}$ fcc solid is 0.23 eV/atom lower than the isolated B$_{80}$ fullerene
Boron Sheets

Kunstmann & Quandt 2008

Double Layers

Single Layer

Infinite Sheet

Multi Layers

Band Structure, Electron Density, DOS : metallic
2D Boron Sheets
2D Boron Sheets with Hexagonal Motives
2D Boron Sheets with Hexagonal Motives

Highest stability occurs when $E_f$ places precisely at the zero-point of In-Plan PDOS filling all available in-plane bonding states and none of the anti-bonding ones.
Single Wall Boron Nanotubes

Boustani & Quandt, EPL 1997, JCP 1999

Metallic

DOS

24

32

450

150
Control the Radius & Chirality of BNTs
Kunstmann, Quandt & Boustani, Nanotechnology 18, 155703 (2007)
The boron sheet is a metal and the nanotubes can be either metals or semiconductors gap 0.1–0.8 eV dependent on diameter & chirality.
The boron nanoribbons with different edges are metals. The H-terminated nanoribbons are semi-conductors with a Band gap of 0.5 eV
Structure and stability of Mg-intercalated boron nanotubes and crystalline bundles
Double Wall Boron Nanotubes

- **Armchair** \((2\times12 + 2\times24)\)

- **Zigzag** \((4\times12 + 4\times24)\)
Double Wall Boron Nanotubes

Band structure and density of states DOS of s-band and p-bands of zigzag and armchair DWBNTs
Experimental Confirmation of Single-Walled Boron Nanotubes

**Theory:** Boustani & Quandt, Europhys. Lett. 39, 527 (1997)

**Experiment:**
Experimental Developments of boron Nanostructures I

Theory

Boustani & Quandt et al.
JCP 110, 3176 (1999)

Nanowires
13, 1701 (2001)

Nanoribbons
Ruoff et al. Nano Lett.
124, 4564 (2002)

Experiment

Nanobelts
Kimura et al. J. Vac. Sci.
B 23, 2510 (2005)

Nanorods
Otten et al., JACS
124, 4564 (2002)
Experimental Developments of boron Nanostructures II

Yoke Khin Yap, Michigan TechnicaL University (MTU), 2008

- **Nanobelts**
- **Nanocups**
- **Nanobats**
- **Nanoyarns**
Potential Applications

**Boron Clusters:**
- Boron Chemistry
- Hydrogen Storage
- Propulsion & Energetic
- Embedding & Implantation

**Boron Sheets and Nanotubes:**
- Semiconductors
- Nanotechnology
- Superconductors
- Neutron Absorber, Fieldemission

**Doped α-Boron**
- Thermoelectric Devices
- Coating & Ceramics
- High-Temperature Devices
- Electro-Optics & Corrosion

**Boron Cages (Nanotubes !):**
- Liquid Crystals
- Inorganic Chemistry
- Nuclear Medicine (BNCT)
Materials needed for hydrogen storage are chemically non-dissociatively binding hydrogen molecules.

Window (0.2-0.6 eV/H₂) necessary for efficient reversible H-Storage at room T and moderate pressures for onboard automotive applications.
One more electron is transferred from each Sc atom to the corresponding pentagon, which enhances both the Sc-C46B12 binding and the hydrogen storage capacity.
Hydrogen Storage II
Physisorption on Boron Sheets and Nanotubes
Cabria, Lopez and Alonso, Nanotechnology 17, 778 (2006)
Hydrogen Storage

- 0.03-0.06 eV/H₂
- 0.3 eV/H₂

Chemisorption

Metal Hydride

Physisorption

CH₄
Nanotechnology

• Nanotubular Network

• Basic Layout for nanodevices
Electron Transport in Boron Nanotubes

Schematic model of (6,0) SWBNT between two gold electrodes

I-V characteristics and the transmission spectra of the system.
Elektron Transport in Boron Fullerenes

Schematic model of $B_{80}$ Sphere between two gold electrodes

Current-voltage curves for $B_{80}$ and $C_{60}$ molecular systems.
Conclusions

• We established a new fullerene-like researchfield called *Boron Nanomaterials*.

• Theory is able to predict nanostructures and the experimentally observed boron clusters and nanotubes are the best evidence.

• The planarity (aromaticitiy) of small boron clusters is *unique* between all atomic clusters known up to date.

• Boron Nanomaterials have (in opposite to carbon) potential applications in nanotechnology & medicine.
What is missing!

- **Theory**: Mech., Optical, Therm. and Electronic Properties, the Nature of 2e-3c Bonds, and the Aromaticity of the Most Boron Nanostructures, Simulation of Proteins@Natotubes!
- Chemical Reaction of Boron Nanostructures with small molecules (H₂, O₂, HF, CO, CO₂ ...) → H-Storage, Sensoric!
- **Experiment**: Synthesis and Production of Boron Nanotubes & Fullerenes → New Synthesis-Method are required
- Development the Chemistry of Boron Clusters & Fullerenes → Benefit of the Planarity and Aromaticity.
- Synthesis and Production of Boron Nanosheets & Thinfilms, → Does exist a Boron-Graphene or New Boron Phases!
- Can BNanoflakes&Sheets replace expensive c-BN-Coating!
- Synthesis of Boron Nanomaterials for BNCT.
- Thermoelectric & Magnetic BNTs (Doping with TM & RE)
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