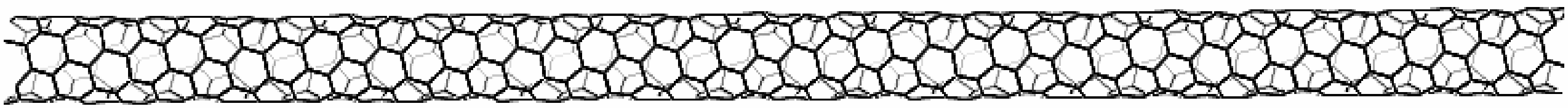
Applications of Nanostructured Materials



ITAMIT Workshop

Aug 6, 2004

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Outline

- Motivation
- Computational Methods
- Thermal Contraction of Nanotubes
- Microfastening System: *NanoVelcro*
- Hydrogen Storage
- Summary and Conclusions

Motivation

- Demands for high performance composites with ***near-Zero Thermal Expansion***
  - Thermally contracting materials: *Nanotubes?*
- Demands for ***Super Glues*** in NEMS and other systems
  - Self-assembled, mechanical bonds: *NanoVelcro?*
- Demands for ***Hydrogen Fuel*** in future hydrogen economy: ***Hydrogen Storage***
  - New materials based on physisorption: *Carbon materials (nanotubes)? If not?*

Computational Methods

- Density Functional Theory
  - Pseudopotential method
  - Atomic orbitals basis
  - LDA & GGA
- Parametrized LCAO Formalism
  - Parameters based on density functional theory
  - Recursion technique: O(N)
- Molecular Dynamics Simulations
  - Hellmann-Feynman forces
  - Microcanonical MD
  - Canonical MD: Nose-Hoover formalism
- Adsorption Theory
  - van't Hoff equation
  - Langmuir isotherm

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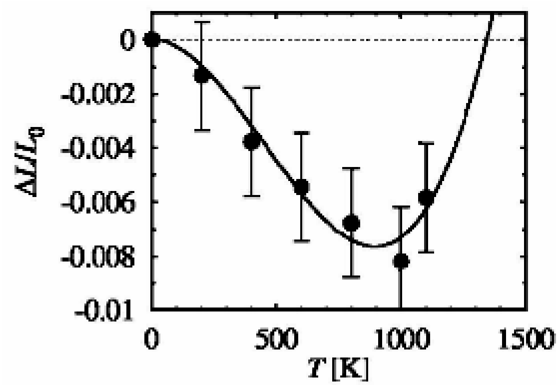
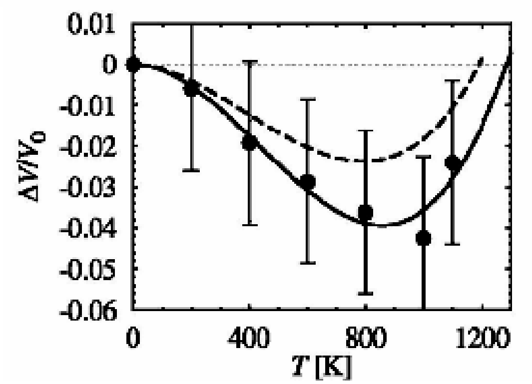
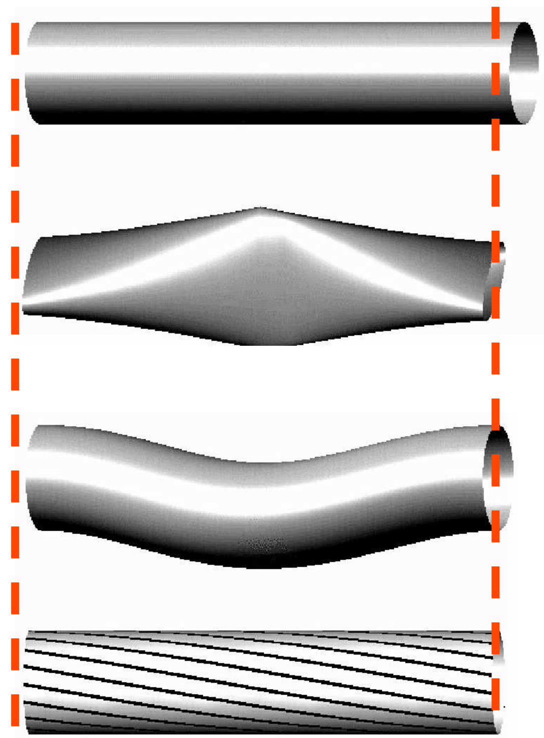
Thermal Contraction of Nanotubes

Length



Volume





$$\alpha = \frac{1}{L}\frac{\partial L}{\partial T}$$ length

$$\beta = \frac{1}{V}\frac{\partial V}{\partial T}$$ volume

- Nanotubes ***contract*** rather than expand up to ~800 K
- Dominant modes: pinch and bend (length); pinch (volume)

[PRL **92**, 015901 (2004)]

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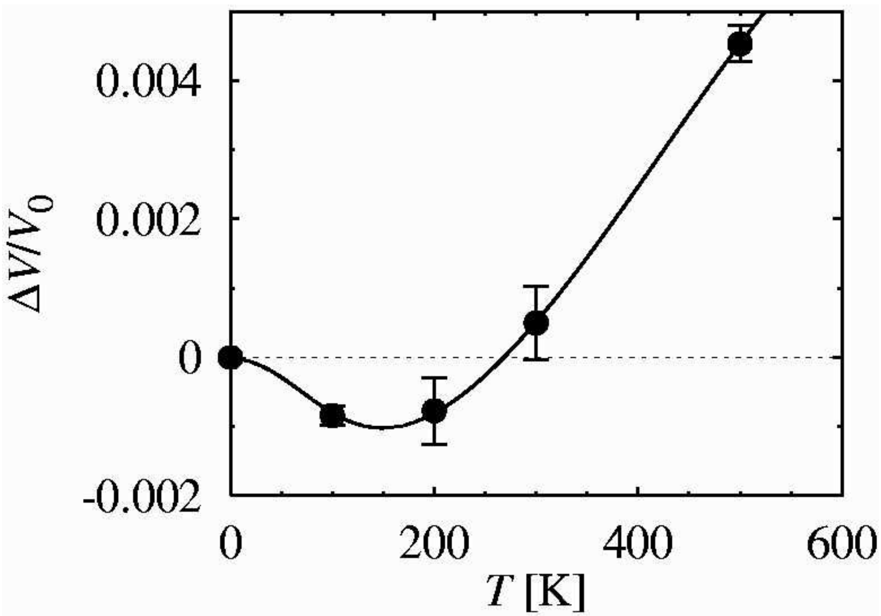
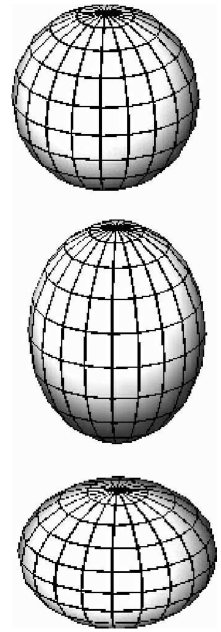
Volumetric contraction of fullerenes

Volume





$$\beta = \frac{1}{V}\frac{\partial V}{\partial T} \quad \text{volume}$$

- Fullerenes contract up to ~150 K
- Volumetric contraction is dominated by quadrupolar deformations at low temperatures
- Physical origin: volume contraction due to a gain in configurational and vibrational entropy

[PRL **92**, 015901 (2004)]

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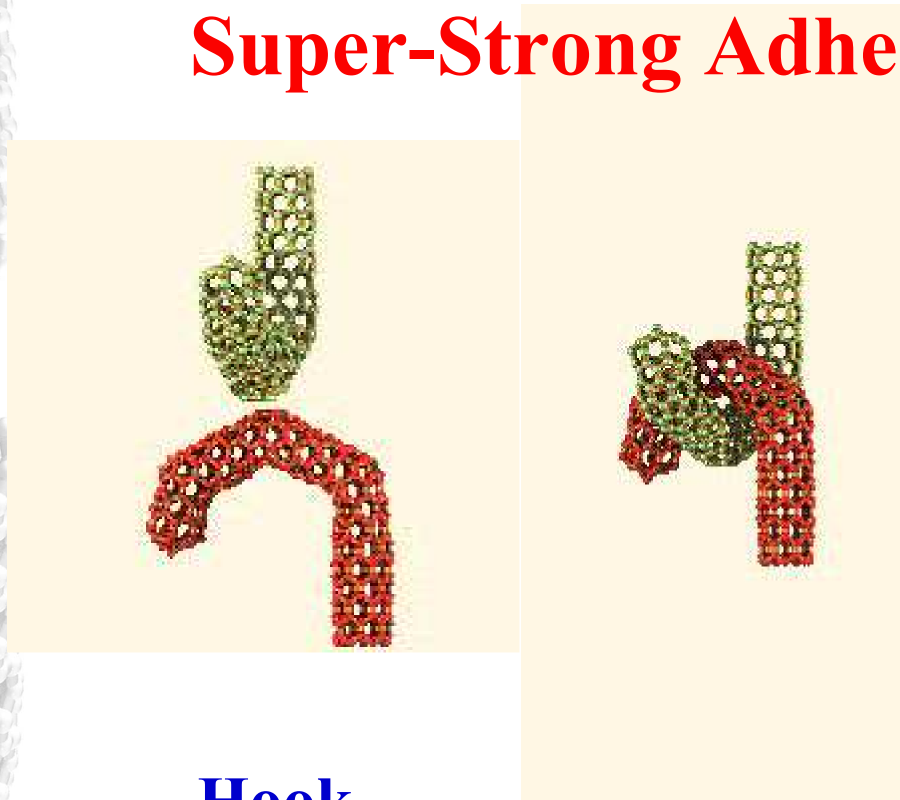
Curly Nanotubes and Nano-Velcro™

- Can Crooked Nanotubes be Used as **Super-Strong Adhesives**?



Hook (closing)

Unhook (opening)

- Mating nanotube hook elements
  - Extremely strong bonds
  - Self-repairing bonds
  - Chemically inert and non-toxic
  - Thermally stable
  - Good thermal and electrical conductors
  - U.S. Patent pending

[PRL **91**, 165503 (2003)]

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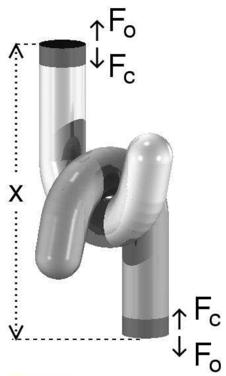
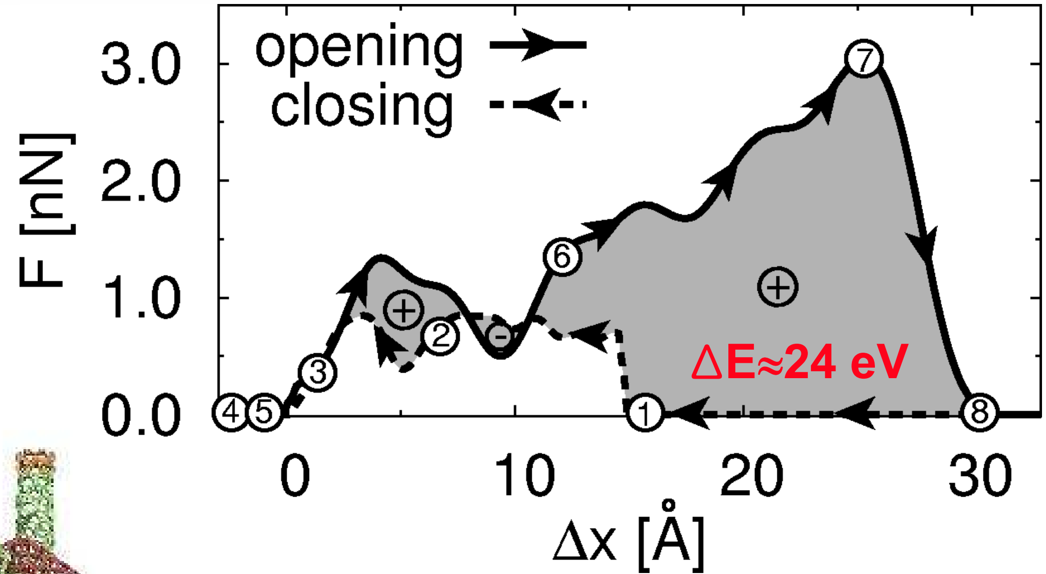
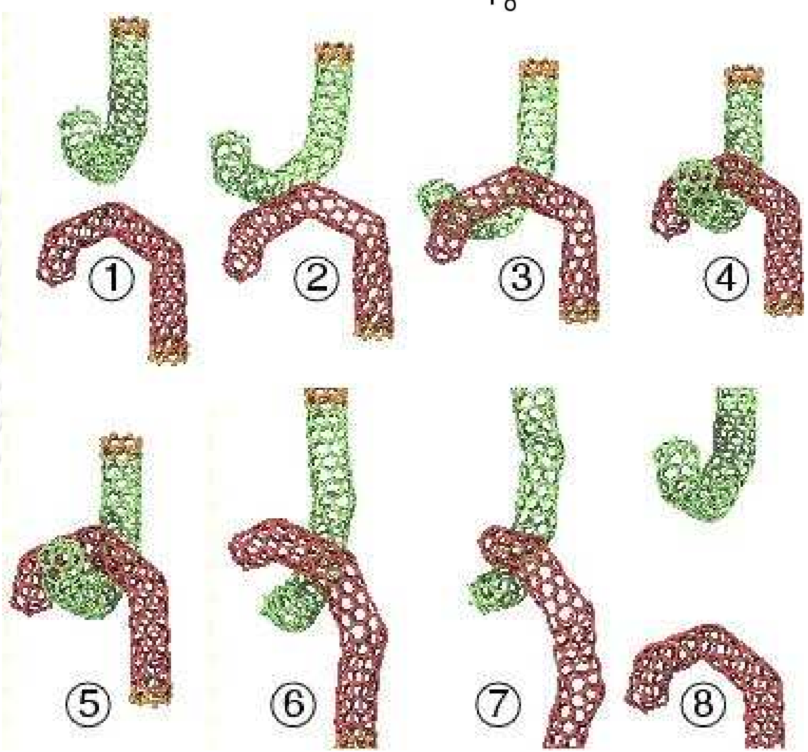
Toughness of Nano-Velcro







- Average closing force = 0.9 nN
- Average opening force = 1.7 nN
- Toughness of (7,0) nano-velcro = 30 eV
- Stability of (7,0) nano-velcro = 24 eV
- Cleavage energy of (7,0) CNT = 15.4 eV
- Ultimate strength up to 3 GPa

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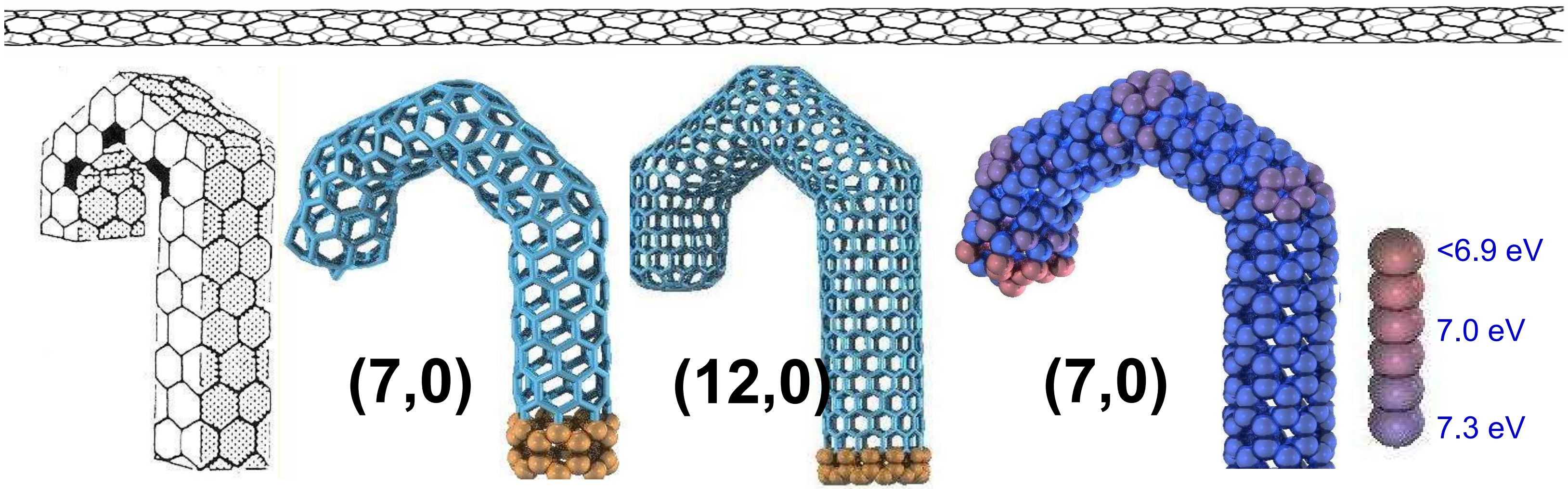
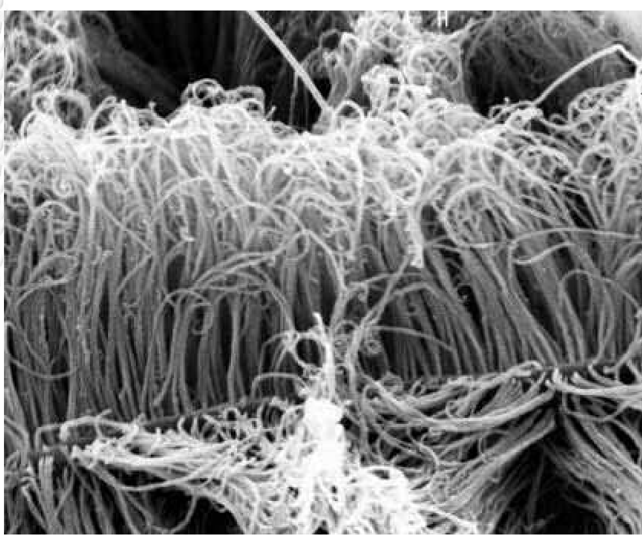
Nano-Velcro

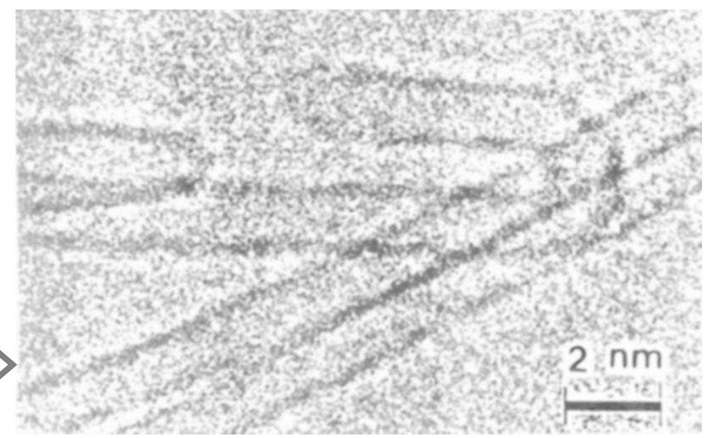


Just a Science Fiction or Theoretical Imagination?



SEM of curly nanotubes (Nanomix)

HRTEM of a nanohook (S. Iijima)



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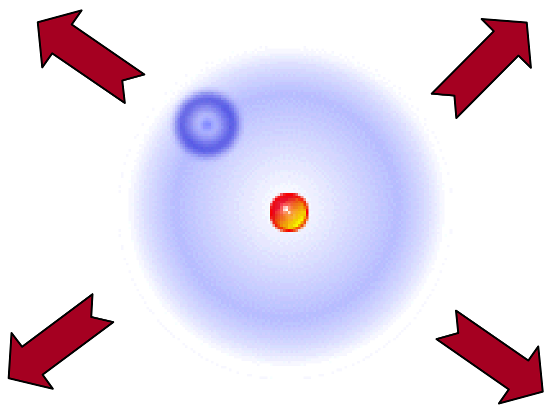
Hydrogen Storage Alternatives

- Are there any Materials that **Store Hydrogen** more than **6.5% by Weight**?

high pressure H_2 gas
(5K-10K psi)

cryogenic H_2 liquid
(20K temperature)



nanostructures
(low temperature physisorption)

- **Activated carbon (Eb~60meV)**
- **Nanotubes (controversial, but..)**
- **New materials**
  - **high binding energy**
  - **high surface area**

metal hydrides
(high temperature chemisorption)

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BES Hydrogen Studies

Reported by M. Dresselhaus & others

Universal Finding:

The Hydrogen Economy Requires Breakthrough Basic Research to Find New Materials and Processes
$\Rightarrow$ Define a new state of the art

Paths to Increase Binding Energy

- **Graphene/Nanotubes**

  $E_b \approx$ 60meV / 80 meV

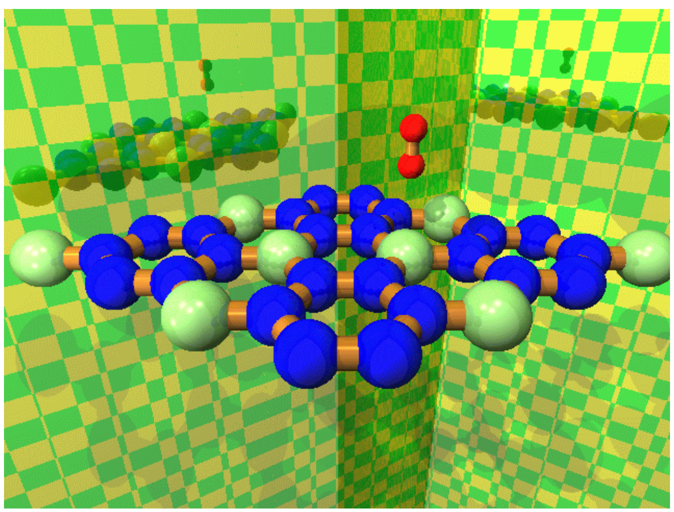
- **Inside C_{60} / (5,5) tubes**

  $E_b \approx$ 0.2 eV

- **Substitutional doping**

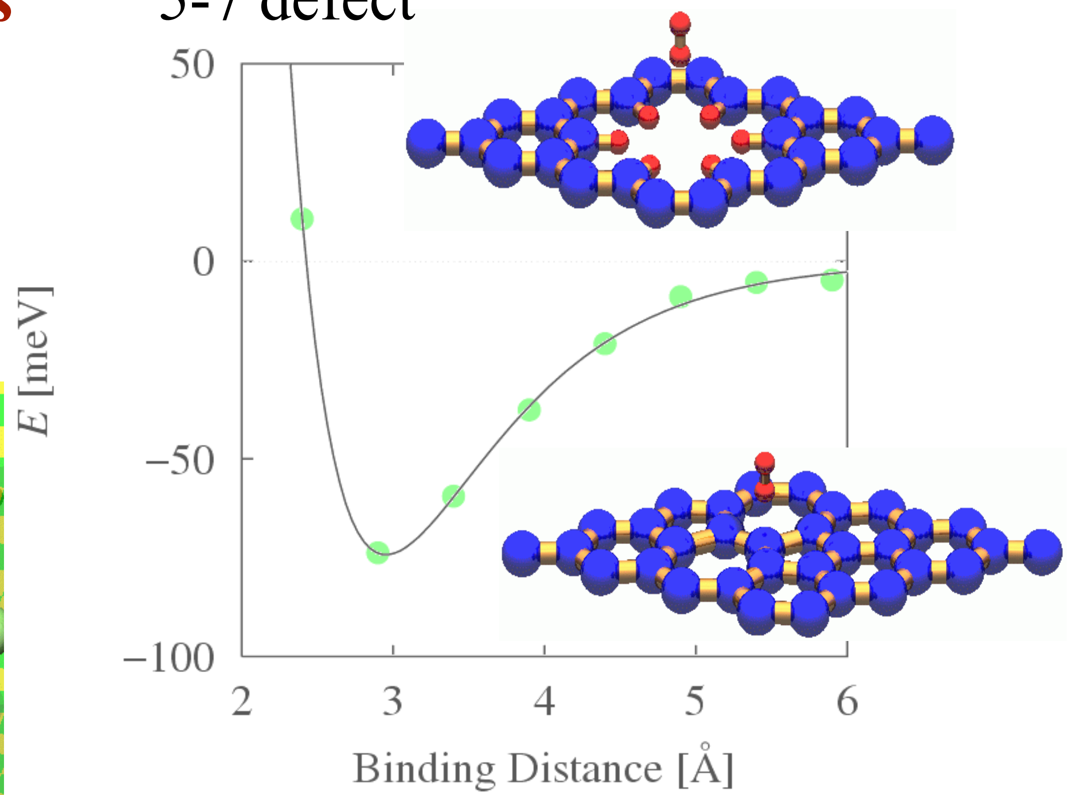
  Boron-doped graphene

  $E_b \approx$ 80 meV



- **Structural efects**

  Vacancy
  5-7 defect → **20 %** ↑



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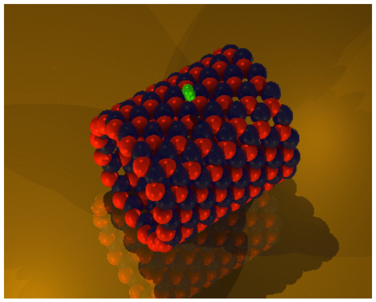
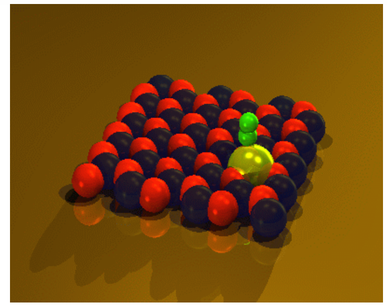
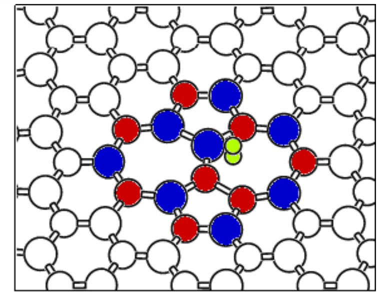
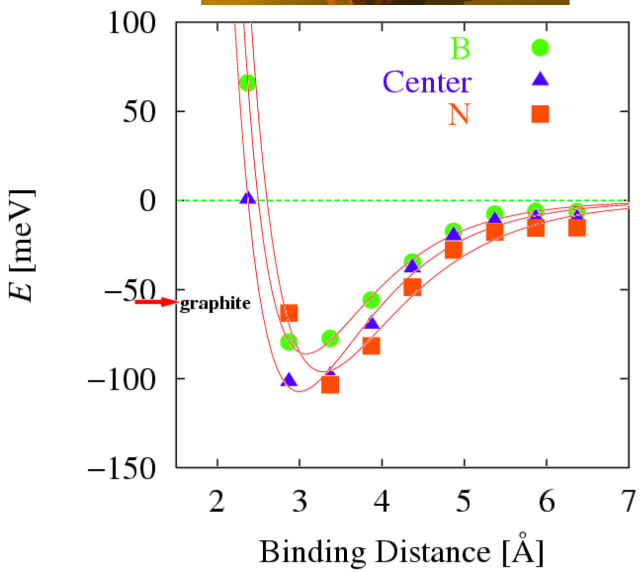
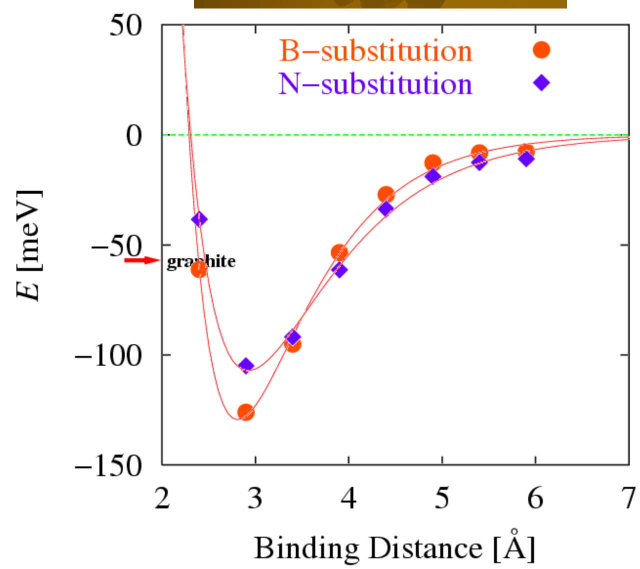
Hydrogen on Boron Nitride (BN)











Doping/defects:
10-30 % increase

➢ Binding is stronger than on carbons!

[PRB **69**,245407 (2004)]

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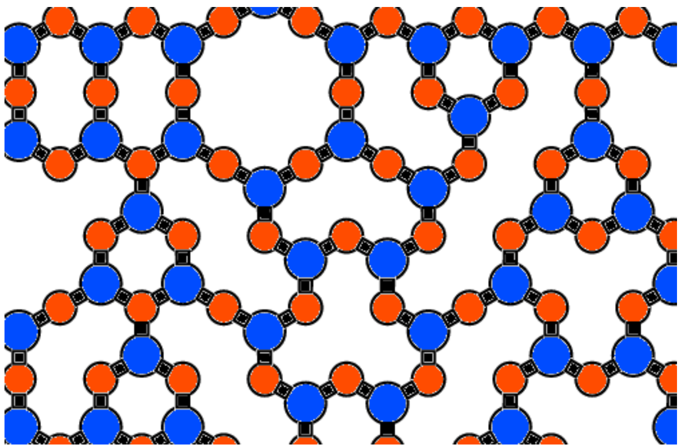
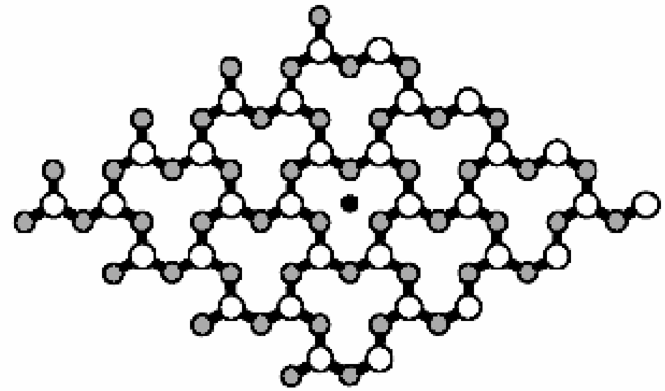
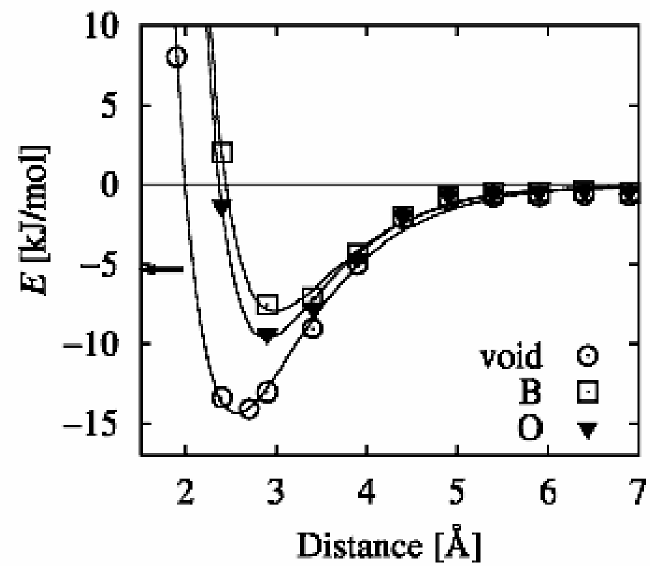
New H_2 Storage Material: B_2O_3







- Predicted Binding Energy: 0.13 eV
- Material is very cost effective
- Material physics is complex
- Patent pending

[Solid State Commun. **129**, 769 (2004)]

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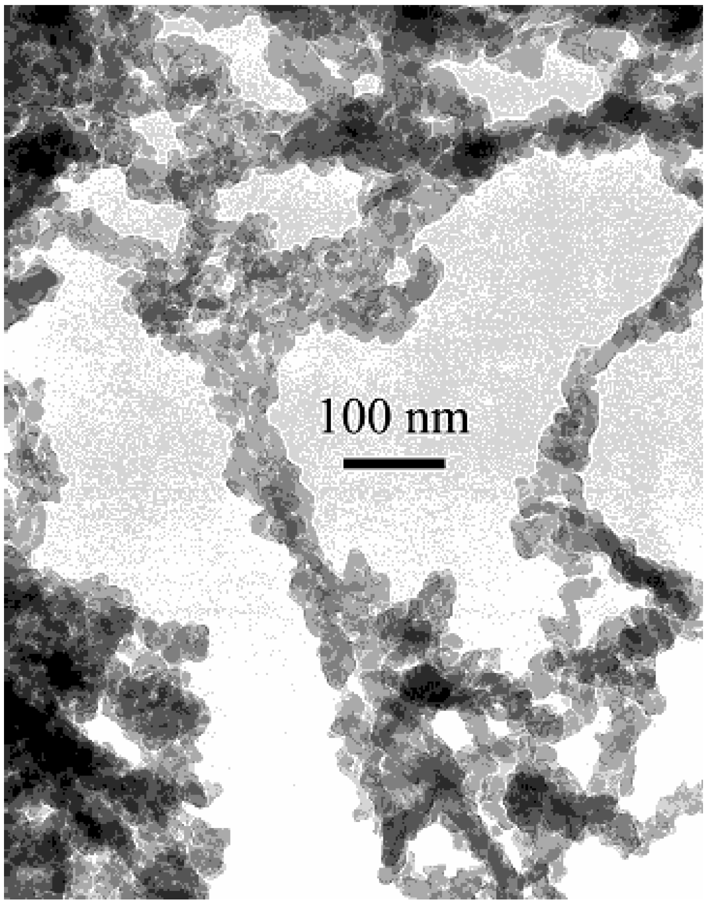
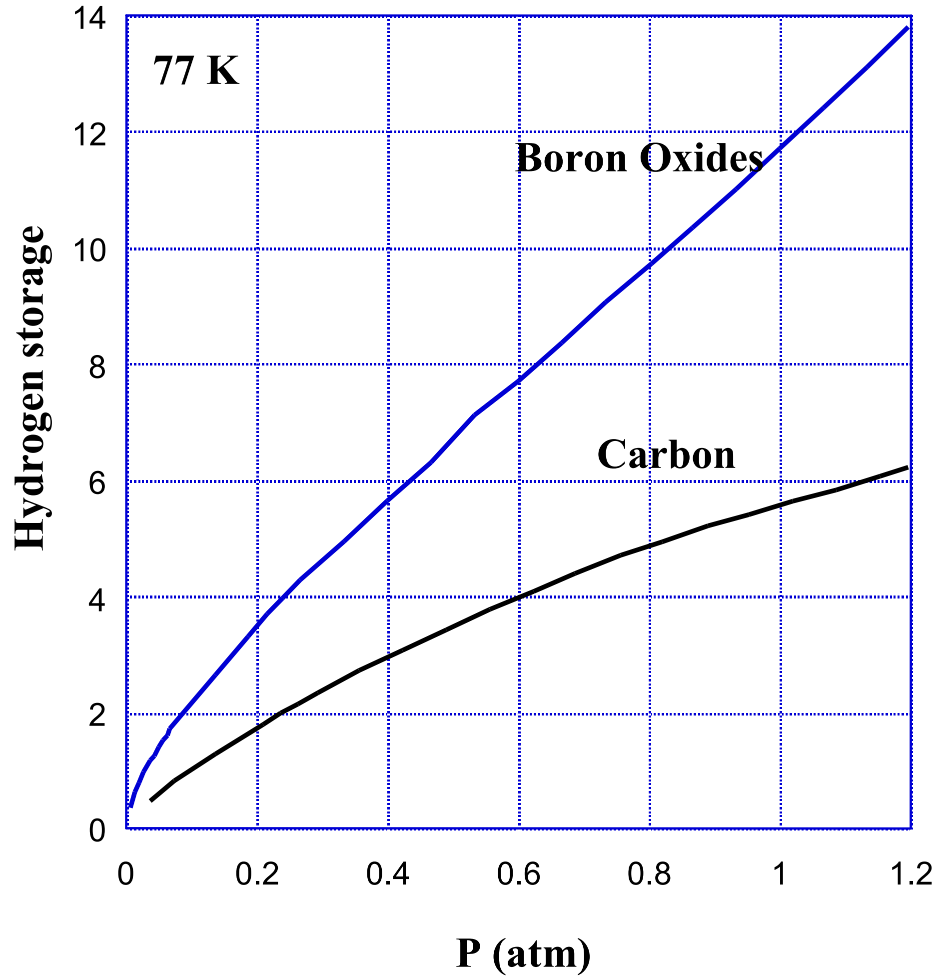
New H_2 Storage Material: B_2O_3





[Solid State Commun. **129**, 769 (2004)]

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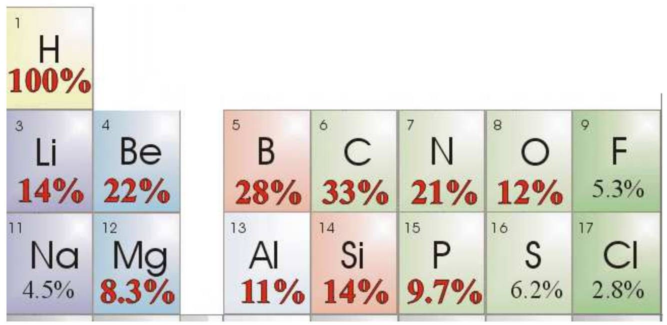
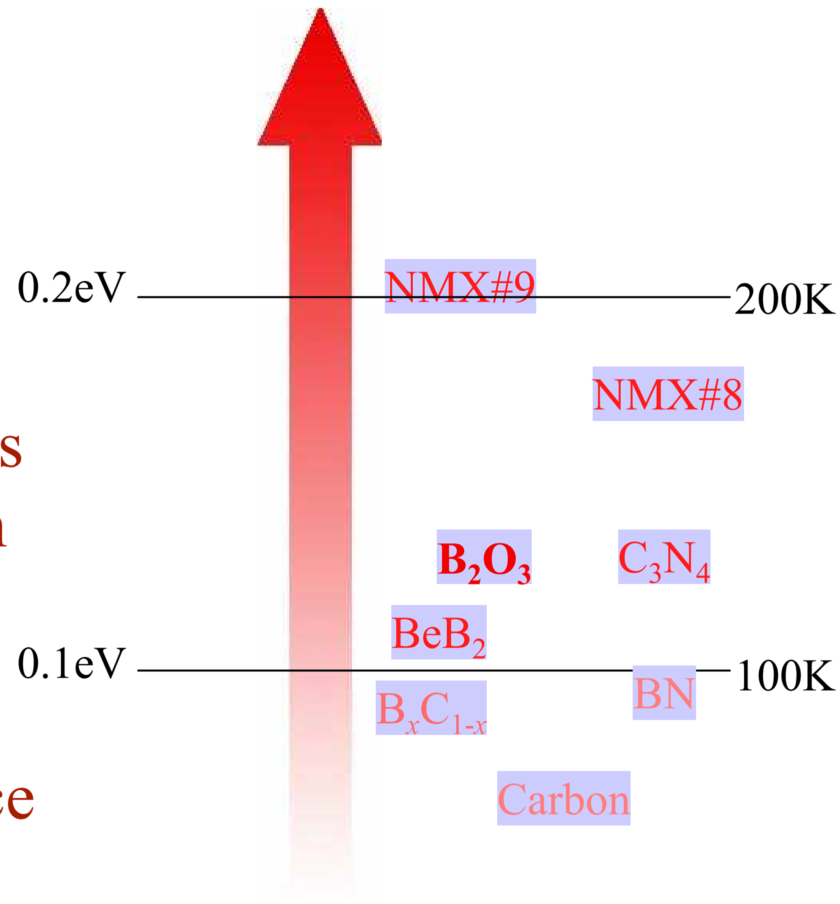
Path to Improved Hydrogen Storage



- Evaluation of new materials using computational design
- Synthesis and test of predicted materials
- Increase of available surface area by forming nanostructure

US Patent # 6,672,077



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Summary and Conclusions

- Nanotubes and fullerenes contract thermally at low temperatures, and expand at high temperatures.
- Contraction is caused by gain in configurational and vibrational entropy.
- Nanotube-based composites may exhibit zero thermal expansion.
- Nano*VELCRO* based on crooked nanotubes may be used to interconnect NEMS device components.
- Nano*VELCRO* bond is tough, self-repairing, withstands high temperatures, conducts heat and electricity well.
- Introduction of defects (e.g., chemical doping or structural defects) enhances hydrogen binding energy
- Heteropolar or ionic characters are important for increasing hydrogen binding energy
- Search for new hydrogen storage materials that operate at ambient conditions should continue

Acknowledgments

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- Seung-Hoon Jhi, NanomixUCB
- Steven G. Louie, UCB/Nanomix
- David Tománek, MSU
- Alex Zettl, UCB/Nanomix

The End