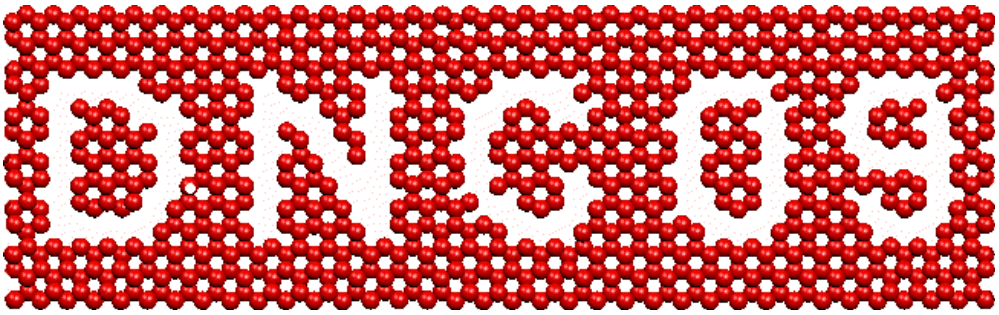

REPORT

On workshop

"Computational Studies of Defects in Nanoscale Carbon Materials,"

May 11-13, 2009,
CECAM-HQ-EPFL, Lausanne, Switzerland

CECAM Home Page: http://www.cecam.org/workshop-0-313.html

MSU Home Page: http://nanotube.msu.edu/dnc09/

Organizers:

***Arkady Krasheninnikov**, University of Helsinki and Helsinki University of Technology*

***Savas Berber**, Gebze Institute of Technology, Turkey*

***David Tomanek**, Michigan State University, USA*

Supported by: ***CECAM (Euro 7,500), Psi-K (Euro 4,000) and Springer (Euro 500)***

Summary

The workshop "Computational Studies of Defects in Nanoscale Carbon Materials"(DNC09) took place in CECAM-HQ-EPFL, Lausanne, Switzerland, in May 2009. The workshop was followed by another workshop on a very close subject "Carbon and Inorganic Nanotubes", (CINN09). In fact one day was common, so that the presentations on the common day dealt with the scientific matters relevant to both workshops. The DNC09 workshop was attended by 39 participants (including the organizers) from all over the world. The financial support from CECAM (Euro 7,500), Psi-K (Euro 4,000) and Springer (Euro 500) made it possible to invite a considerable number of world-renown experts working on defects in nanoscale carbon materials. As the main idea behind this workshop was to bring together representatives of solid-state physics and materials science communities who use computational tools to discuss the state of our understanding of defects in carbon nanostructures, most speakers had theoretical background and concentrated on the theoretical progress. In addition to the theoretical advances, recent progress in the experiment was covered by several speakers. As detailed below, the latest and most important results in the field were presented by the speakers and by other participants during the poster session. In addition to the already published results, a considerable amount of new unpublished data was presented. The central point was the detrimental and beneficial roles of defects in the behavior

of carbon nanosystems and related issues such as the production of defects under electron and ion irradiation, the characterization of defects by various techniques, and the engineering of the properties of carbon nanosystems by controllable introduction of defects through irradiation and by chemical methods. Such a combination of complementary topics (theory/experiment, theoretical method development/applications etc.) resulted in interesting and productive scientific discussion which should have a strong impact on the development of the field and could eventually give rise to new collaborations. Based on the enthusiastic feedback we have received from the participants of the workshop, we believe the event was a success. It should also be pointed out that the workshop attracted a considerable number of students and young postdocs, so that the event was also important in the context of young researcher training.

Scientific content of the workshop

As mentioned in the workshop proposal, defects in nanoscale carbon materials, such as nanotubes and graphene, may fully govern their mechanical and electronic properties. Moreover, defects may cause intriguing behavior including magnetism. Presence of defects in solids is in general believed to be mostly detrimental. This is also true for carbon nanomaterials: indeed, defects reduce the mechanical toughness and electronic conductance. However, there are beneficial effects of defects, including stiffening of loosely-connected nanotube networks or nucleation sites for structural transformations, which have been mostly overlooked. Be vice or virtue, defects in carbon nanomaterials require complete understanding at the microscopic level. The aim of the workshop was to bring together representatives of solid-state physics and materials science communities who use atomistic computer simulations to understand the role of defects in carbon nanostructures at the microscopic level, and discuss recent progress in our understanding of the role of defects. Besides this, several experts gave an overview of the state-of-the-art in the experiments.

The following main topics were addressed:

1. The types and abundance of point defects in nanostructured carbon materials, such as graphene, nanotubes, fullerenes, etc, identification of defects.
2. Effect of defects on the electronic and mechanical properties of nano-structured carbon materials.
3. Production of defects in carbon nanotubes and graphene under irradiation.
4. Defect-mediated magnetism in nanostructured carbon materials.
5. Experimental studies of native and irradiation-induced defects in carbon nanosystems.

Although the main stress of the workshop was on simulations, the last topic was very important for establishing links between the simulation and experimental results and for finding out new simulations challenges.

Topic 1: The types and abundance of point defects in nanostructured carbon materials

This issue was addressed in the presentation by Florian Banhart, University of Strasbourg, France, who gave an overview of new experimental developments with a particular stress on graphene. He presented new results of experimental studies on point defects in carbon nanomaterials carried out in an aberration-corrected transmission electron microscope (TEM). Additional experimental information on the signatures of native and irradiation-induced defects in scanning tunneling microscopy (STM) images of carbon nanotubes was given by Oliver Groening, Swiss Federal Laboratories for Materials Testing and Research, Switzerland. They spoke about point defects such as vacancies and interstitials and their signatures in TEM and STM images. It was pointed out that due to high energetic barriers separating different atomic configurations in carbon nanomaterials the concentration of defects may be nonequilibrium under certain conditions.

From the viewpoint of theory, the discussion was continued by Steven Louie who spoke on density functional theory (DFT) simulations of defects in graphene nanoribbons and nanotubes and on how defects influence electronic transport in these materials. Oleg Yayzev, Swiss Federal Institute of Technology, Lausanne, Switzerland, gave further details of first-principles simulations of defects in nanocarbons, including defects in double-layer graphene and graphite. The overview of point defects was also given in the presentations of the workshop organizers, S. Berber, D. Tomanek and A. Krasheninnikov. Formally their presentations were in the CINN09 workshop, but as the talks were given on the "common" day, these presentations can be discussed in the context of the topics addressed at the DNC09 workshop. It was pointed out that sp^2-bonded carbon nanomaterials have a unique ability to heal defects such as vacancy clusters by forming new bonds and mending the "holes" trough non-hexagonal rings.

Extended defects were discussed in the presentation by Irene Suarez-Martinez, Institut des Matériaux Jean Rouxel, France, and in part by Laszlo Forro, Ecole Polytechnique Fédérale de Lausanne, Switzerland. Carbon nanotube intramolecular junctions were addressed by Andres Ayuela, University of San-Sebastian, Spain. Such junctions, which normally give rise to interface states, are typically made of topological defects arising from the connection between tubes of different chiralities. As pointed out in the presentation, although interface states are commonly regarded as a drawback in device performance, they may actually provide a means of achieving diode behavior at the nanoscale.

Topic 2: Effect of defects on the electronic and mechanical properties of nano-structured carbon materials

This topic was addressed in the presentations by Susumu Saito, Tokyo Institute of Technology, Japan. He pointed out that doping of semiconducting nanotubes by boron and nitrogen atoms is an important process to make p-type and n-type semiconductor nanotubes. Experimentally, however, the atomically controlled substitutional doping into nanoscale materials including carbon nanotubes remains to be realized in the future. S. Saito also reported a study of the energetics and geometries of B and N-doped carbon nanotubes in the framework of the density functional theory. The electronic properties of impurity-induced states ("impurity levels") in B and N doped semiconducting carbon nanotubes were also studied in detail. Their spatial distribution is found to correlate well with the depth of the state from the top (bottom) of the valence (conduction) band. Deep states show rather narrow spatial distribution, while shallow states show wider distribution. This topic was also

addressed in the presentations by S. Louie who pointed out that doping of naontubes with B and N atoms may give rise to the new localized states which do not directly contribute to the conductance. S. Louie and D. Tomanek also discussed the effects of defects at the edges of graphene ribbons on the spin-polarized transport in these systems. It was concluded that defects may be beneficial, as edge defects (in practice unavoidable, but different at different edges), may block spin-polarized current with a particular spin value, which may be useful for spintronics.

As for mechanical properties, Laszlo Forro presented experimental results on improvements of the bending modulus of carbon nanotube bundle due to electron irradiation. This happens through irradiation-induced covalent bonds between the nanotubes which prevent sliding, and give rise to an improvement of mechanical properties of nanotube samples: despite a small drop in the Young modulus and tensile strength due to vacancies, irradiation may have an overall positive effect. The theory of irradiation-mediated enhancement of mechanical properties of multi-walled nanotubes, nanotube bundles and nanotube bucky paper were presented by A. Krasheninnikov.

The electronic transport in pristine and defected nanotubes was discussed at length byJ.-C. Charlier, Université Catholique de Louvain, Belgium. He spoke on the modifications induced by various defects in the electronic properties of the carbon nanotubes, as reveled from first-principles calculations. As the defects also play a key role in the chemical reactivity of carbon nanotubes, the study of the modulation of the conductance due to specific molecules adsorbed at the defected nanotube surface was presented.

The effects of defects on the electronic properties of carbon nanomaterials were also discussed by Francesco Mercuri, University of Perugia, Italy, within the framework of a chemical approach. Finally, the influence of defects on the mechanical and electronic properties of carbon nanotubes was discussed by Gotthard Seifert, Dresden University of Technology, Germany, and a comparison to similar phenomena in non-carbon nanotubes was made, corroborated by a presentation focused on experimental studies of inorganic nanotubes by Dmitri Golberg, Japan.

Topic 3: Production of defects in carbon nanotubes and graphene under irradiation

Numerous experiments pointed out that controllable introduction of defects into the carbon network may give rise to new functional devices, e.g., carbon nanotube-based quantum dots. Irradiation is a suitable tool for creation of defects either in the whole sample or in certain parts using focused ion or electron beams. As for the latter, creation of defects by electron beam is particularly hot subject nowadays, as modern electron microscopes with aberration-corrected illumination systems allow the focusing of an electron beam onto a specimen area of 0.1 nm in diameter. Hence, it is not only possible to obtain images by scanning the beam over the specimen but also to irradiate the material in pre-determined areas with atomic-scale precision. As discussed by F. Banhart, atoms in graphitic structures can be displaced by electron beam with electron energies above 80 keV. Thus the transmission electron microscope can be used to create point defects or extended defect structures in graphitic nanomaterials in a controllable manner, so that this technique can be used for engineering the atomic and electronic structure of carbon system. The theoretical aspects of defect production under electron and ion irradiation as well as defect evolution were discussed by O. Yazev, D. Tomanek, A. Krasheninnikov.

Topic 4: Defect-mediated magnetism in nanostructured carbon materials

Observations of magnetism in various metal-free carbon systems such as polymerized fullerenes and graphite have stimulated much experimental and theoretical research work on the magnetic properties of all-carbon systems. The driving force behind these studies was not only to create technologically-important, light, non-metallic magnets with a Curie point well above room temperature, but also to understand a fundamental problem: the origin of magnetism in a system which traditionally has been thought to show diamagnetic behavior only. The observed magnetism may originate from defects. Indeed, irradiation of graphite with protons resulted in a significant magnetic signal, which was explained in terms of vacancy-hydrogen interstitial atom complexes. The overview of this problem, along with DFT simulations of magnetic carbon systems with defects, was given by O. Yayzev.

A theoretical study of substitutional Ni, Co and Fe impurities in graphene was presented by Daniel Sanchez Portal, Centro de Fisica de Materiales, San Sebastian, Spain. It was shown that only Co atoms are magnetic with a magnetic moment of ~1μB for the isolated impurity, and that the magnetic moment depends on the number of Co substitutions in A and B graphene sublattices. In contrast to Co impurities, Ni substitutional defects show a zero magnetic moment in flat graphene. However, Ni impurities develop a non-zero magnetic moment in metallic carbon nanotubes. This surprising behavior stems from the peculiar curvature dependence of the electronic structure of Ni impurities. It was concluded that magnetic/nonmagnetic transitions in systems with Ni impurities can be expected by applying anisotropic strain to a flat graphene layer.

Topic 5: Experimental studies of native and irradiation-induced defects in carbon nanosystems

The new developments in experiments were presented by F. Banhart, D. Golberg, O. Groening and non-invited participants of the workshop, as discussed above. The dialog between the theorists and experimentalist at the workshop was particularly important: the new unpublished experimental results posed new questions to the theorists, and the workshop was a very good opportunity to discuss new simulations challenges.

Unfortunately, due to three cancellations (Y. Miyamoto, M. Endo from Japan had to cancel their trips due restrictions introduced by their organizations in the light of swine flu; A. Rubio could not come due to personal matters), several important aspect of defects in nanostrucutred carbon materials (annihilation of defects during the growth of carbon nanotubes, spectroscopic characterization of defects) were not fully addressed. Nevertheless, based on presentations and discussion during the workshop, one can draw the following conclusions:

Main scientific conclusions:

- The level of theoretical understanding of defects in single-layer carbon nanomaterials such as graphene and single-walled carbon nanotubes is quite high, as evident from a good agreement between theoretical and experimental results. Less is known about defects in multi-walled carbon nanotubes or multi-layer graphene. The problem here is the rigorous account for van der Waals interaction between the graphitic sheets.

- sp^2-bonded carbon nanomaterials have a unique ability to heal defects such as vacancy clusters by forming new bonds and mending the "holes" trough non-hexagonal rings.

- Due to high energetic barriers separating different atomic configurations in carbon nanomaterials the concentration of defects may be nonequilibrium under certain conditions.

- Defects in carbon nanomaterials can have an overall positive effect on the mechanical and electronic properties in carbon nanomaterials.

- Defect may give rise to magnetism in graphene and graphite, and the experimental results on the appearance of magnetic signal in carbon systems after irradiation can naturally be explained in terms of irradiation-induced defects.

- Controllable introduction of defects by electron and ion irradiation is a promising tool for tailoring the properties of nanostructured carbon materials.

Workshop program and the list of participant are given in the workshop booklet.

Budget*

Outgoing

Travel expenses of the speakers:	4500
Accommodation	4000
Dinner	1600
Per diem	1300
TOTAL	11400**

Incoming

CECAM	7500
Psi-K	4000
Springer	500
TOTAL	12000

*Round-off numbers are given. The exact figures can be obtained from Emilie Bernard, CECAM secretary, who took care of all the payments and travel documents).

** Some money was not spent due to last-minute cancellations, see above.