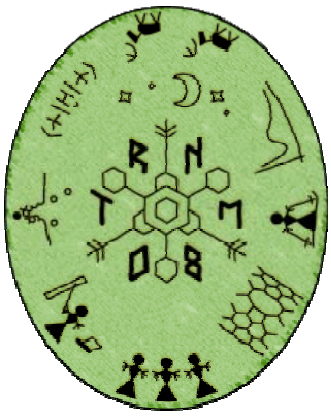
REPORT



On workshop
"Effects of irradiation and defects in nanoscale materials"
("Towards Reality in Nanoscale Materials '08),
December 3rd - 5th 2008, Levi, Finland
http://www.fyslab.hut.fi/~tjh/workshop08.html

The organizers:
Dr. Arkady Krasheninnikov, University of Helsinki
Dr. Adam Foster, Helsinki University of Technology
Prof Kai Nordlund, University of Helsinki
Prof. Risto Nieminen, Helsinki University of Technology

Summary

The workshop "Effects of irradiation and defects in nanoscale materials" ("Towards Reality in Nanoscale Materials'08") took place in Levi, Finland, in December 2008. The workshop was attended by 55 participants (including the organizers) from all over the world. The financial support by the European Science Foundation through the SimBioMa program, the Academy of Finland through the National Graduate School in Materials Physics and the National Graduate School in Nanoscience, and the University of Helsinki made it possible to invite a considerable number of world-renown experts in the computational materials science and nanoscience and, at the same time, minimize the accommodation expenses for students and young researchers.

The main idea behind this workshop was to bring together representatives of solid-state physics and materials science communities who use theoretical computational tools to present and discuss state-of-the-art developments and perspectives of solid-state, computational and molecular physics techniques in modeling of irradiation effects in various nanoscale materials. The lectures given by the experts in simulations of irradiation effects in nanomaterials such as carbon and boron-nitride nanotubes, graphene, small metal clusters etc., were combined with those presented by the developers of the relevant simulation methods (e.g., time-dependent density-functional theory, molecular dynamics algorithms). In addition to the theoretical advances, recent progress in the experiment was covered by several speakers. The latest and most important results in the field were presented by the speakers and 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 In addition to the already published results, a considerable amount of new unpublished data was presented.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 role of defects in the behavior of nanosystems and related issues such as the production of defects under electron and ion irradiation, the characterization of defects by various techniques, and finally the beneficial aspects of defects in engineering the properties of nanosystems and in nano-scale catalysis. 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. Due to a considerable number of students and young postdocs from EU countries who participated in the workshop(about 50% of the attendees), the event was also important in the context of training of young researchers.

Scientific content of the workshop

As mentioned in the workshop proposal, although irradiation of solids with energetic particles such as electrons or ions gives rise to formation of atomic defects in the target and normally spoils the material properties, it may have an overall beneficial effect on the target. This is also true for nanoscale materials: it has been demonstrated that irradiation, especially when combined with heat treatment, can be used for tailoring the atomic morphology, the electronic structure of nanostructured materials [for an overview, see A. V. Krasheninnikov and F. Banhart, Nature Materials, 6 (2007) 723].

At the same time, despite substantial experimental progress, there is still very little understanding of irradiation-induced phenomena in nanoscale materials. Many traditional concepts in ion-solid interaction theory do not work at the nano-scale at all or require substantial modifications. This is due to a small system size in one or more directions, which affects the dissipation of energy brought in by the energetic particle. Finite size of the system also affects the electronic structure and thus the mechanisms of the conversion of electronic excitations to atom kinetic energy.

To accelerate the theoretical research in the field and further the development of the computational tools, in this workshop we tried to bring together the best experts in irradiation effects and defects in nano-scale materials who study these problems by means of atomistic computer simulations. The talks given at the workshop can conventionally divided into five groups according the topics addressed as follow:

1. Simulations of defect production in nano-scale systems under ion and electron irradiation
2. Development of theoretical methods and tools for such simulations
3. Calculations of the properties of nano-systems with defects
4. The role of defects in nano-catalysis
5. Experimental studies of irradiation effects and defects in 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: Simulations of defect production in nano-scale systems under ion and electron irradiation

This issue was addressed in presentations by Dr. Y. Miyamoto and Dr. Sanchez-Portal who used time-dependent density functional theory (TD-DFT) to simulate impact of energetic ions onto carbon nanotubes and LiF nanosystems. This approach, being at the cutting edge of atomistic simulations, makes it possible to go beyond the Born-Oppenheimer approximation, as during impacts of ions with high energies (keV range and up, the actual value depends on the target and ion mass) atom velocities may be comparable to the Fermi velocity in the system. Very recent results published in Physical Review Letters were presented. An overview of the corresponding experimental results on interaction of ions with nanosystems was made by Prof. M. Schleberger .

The results of more conventional empirical-potential molecular-dynamics simulations of irradiation effects in small metal clusters were presented by Prof. K. Albe (in fact his talk was given by K. Nordlund, as Prof. Albe could not come in time from the USA due to flight cancellations). The experiments in this area were presented by Dr. B. Rellinghaus who reported irradiation-induced structural modifications in binary metal nanoparticles. Not only metal, but also semiconductor clusters were discussed. In particular, Dr. F. Djurabekova presented a talk on amorphization of Ge and Si nanocrystals embedded in amorphous silica under ion irradiation. She showed that semiconductor nanocrystals can be amorphized at a dose which is an order of magnitude lower than that in the bulk phase and that this is related to the outermost part of a structured nanocrystal subjected to an additional stress delivered by the amorphous surroundings. One of the most important conclusions made was that the conventional models based on irradiation of bulk materials cannot be used to estimate the susceptibility of nanoclusters to phase transitions.

The modeling of effects of electron irradiation on carbon and boron-nitride nanotubes were discussed by Dr. A. Zobelli and partly by C. Ewels. New experimental developments were covered by Prof. B. Banhart with a particular stress on graphene. This topic is particularly hot 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. With electron energy above 80 keV, atoms in graphitic structures can be displaced. Thus the transmission electron microscope can be used to create point defects or extended defect structures in graphitic nanomaterials in a controllable manner, that is for engineering the atomic and electronic structure of the system. As the experimental progress is not possible without the complete understanding of defect production, the dialog between the theorists and experimentalist at the workshop was particularly important: the new unpublished experimental results raised questions to the theorists, and the workshop was a very good opportunity to discuss the new simulations challenges.

Topic 2. Development of theoretical methods and tools for simulations of ion impacts onto nanosystems

An overview of DFT–based methods with the focus on simulations of defects in nanosystems was made by Dr. R. van Leeuwen. Such methods are getting more and more popular with the advent of powerful computers with massive parallelization. The recent progress in the conventional empirical potential molecular dynamics simulations of ion and electron impacts which have been widely used for several decades was covered in the presentation by Dr. L. Kantorovich who suggested a new scheme for an efficient connection of the system to the heat bath. With respect to ion impact simulations, this new algorithm should make it possible to simulate more realistically the relaxation of the system to a stable or metastable state after the ion impact. The practical implementation of TD-DFT for ion-irradiation simulations was discussed in the talks by Dr. Y. Miyamoto and Dr. D. Sanchez-Portal.

A self-consistent implementation of the van der Waals density functional in the popular electronic structure code SIESTA code was presented by A. Gulans. The lack of a proper description of long-range dispersion forces in the framework of local and semi-local approximation density-functional theory is a well known issue. A new method was recently developed which relies on the use of a non-local correlation functional, and previous

implementations of the method were very expensive from the viewpoint of the computational cost. A different algorithm embedded in SIESTA, which uses the formalism of linear combination of atomic orbitals was presented. In this approach, the non-local correlation potential at a given point is evaluated as a quadrature on an adaptive mesh. As a result, computational expenses are small enough to become practical for a wide range of applications.

Topic 3. Calculations of the properties of nano-systems with defects

As in the case of bulk solids, defects may completely govern the properties of a nanosystem. Thus, knowing the effects of defects, both irradiation induced and native, is highly important for understanding the behavior of the system.

The role of disorder and defects in general in nanosystems such as carbon nanotubes, functionalized quantum dots and conjugated polymers was addressed in the talk by Dr. S. Tretiak. A combination of DFT and TD-DFT made it possible to interpret the experimentally observed phenomena in the optically active materials. TD-DFT was also used to understand field enhancement inside pristine and defective nanotubes, as reported by Prof. H. Zhang.

Not only the role of defects, but also impurities in nanosystems was discussed at the workshop. Dr. M. Ferreira presented a talk on the long-range interaction of magnetic impurities (e.g., transition metal atoms) in carbon nanotubes. This work was motivated by the growing interest in magnetic interactions in carbon-based materials. The effect of impurities on the electronic structure of carbon nanotubes was also addressed in the talk by G. Buchs. The experimental aspects of defect detection and identification were also discussed by Dr. Skakalova.

As the juxtaposition of the behavior of defects in nano-sclae materials and their bulk counterparts makes it possible to better understand the properties of defect in nanomaterials, several talks on defects in bulk materials were given at the workshop. Two world renown experts Profs. C. Van de Walle and S. Ervin spoke on defects in various bulk materials such as ZnO, GaN, ZnSe, PbSe, CdSe, followed by several talks by other speakers. The role of the surface and surface defects was also discussed, in particular by Dr. P. Sushko.

Topic 4. The role of defects in nano-catalysis

Clusters with sizes up to a couple tens of atoms reveal chemical and catalytic properties, which are intrinsically different from those of larger nanoparticles or bulk materials. Very recently it has been indeed shown by aberration-corrected scanning transmission electron microscopy that in iron oxide-supported gold catalysts the high catalytic activity for carbon monoxide oxidation is correlated with the presence of bilayer clusters. In fact, upon interaction of the clusters with a support material their properties can drastically be changed. Bearing in mind the importance of this subject, several talks at the workshop were dedicated to the nano-scale catalysis and the role of support. An overview of the most recent experimental results was done by Prof. Heiz and C. Barth. The role of defect in catalysis was discussed by Dr. S. Bromley and I. Lebedeva. As bonding in small clusters and their catalytic properties can sometimes be understood within a simple picture of single-bond and triple-bond covalent radii, some new aspects of chemical bonding in small clusters and big molecules were reported by Prof. P. Pyykko.

Topic 5. Experimental studies of irradiation effects and defects in nanosystems.

Although the main stress of the workshop was on simulations, several talks were given by experimentalists, as an overview of recent relevant experimental results was very important for establishing the links between the simulation and experiments and for finding out new simulations challenges. The description of the scientific content of the experimental talks was given above during the discussion of the previous topics.

All the topics addressed in the talks were further discussed during the poster session. About 30 posters were presented.

Assessment of the results and impact of the event on the future direction of the field

The main idea behind this workshop was to bring together representatives of solid-state physics, chemistry and materials science communities who use theoretical computational tools to present and discuss state-of-the-art developments and perspectives of solid-state, computational and molecular physics techniques in modeling of irradiation effects and defects in various nanoscale materials. The diverse scientific background of the participants ranging from the use of empirical potential molecular dynamics for simulations of irradiation effects in various materials to time dependent density-functional theory methods and from Monte Carlo simulations to experimental work on defects in nanomaterilas resulted in interesting and productive scientific discussions which made it possible to assess the current situation in the filed. The main conclusions are as follow:

1. Recent experiments provided convincing evidence that electron and ion irradiation can be used as a tool to tailor the mechanical, electronic and even magnetic properties of nanosystems. In other words, the controllable production of defects can be useful for achieving the desired functionality of nanomaterials and devices.
2. Lots of insight has been obtained from atomistic computer simulations. Simulations make it possible to not only explain the results of the experiments but also predict the new phenomena, for example, irradiation-mediated increase in the mechanical properties of carbon nanotube paper due to formation of covalent bonds between individual tubes.
3. Due to recent progress in massive parallel computing, accurate but computationally expensive simulation techniques like time-dependent density-functional theory can now be successfully used for modeling irradiation effects (beyond the Born-Oppenheimer approximation) from first principles, as manifested by two papers recently published in Physical Review Letters and presented at the workshop. This may be a break-through in calculations of the electronic stopping power in solids, as all previous simulations were done within a model developed with a considerably larger number of approximations.
4. Nevertheless, the application of these algorithms to electronic stopping power calculations may require modifications and optimization of the existing codes. For example, at high energies the nuclei can be closer to each other than the pseudopotential cut-off radii. As discussed at the workshop, possible solution could be a smooth augmentation of the DFT scheme with a binary empirical potential.
5. Both irradiation-induced and native defects in nanosystems frequently govern their properties, for example, in catalysis. Overall, the existing simulation schemes

successfully work when one wants to simulate defected nanosystems. Nevertheless, many open questions remain: Calculations of Raman spectra of defected carbon materials, interpretation of experimental scanning tunneling microscopy and spectroscopy data of nanosuystems with defects by comparing the results of simulations and experiments, etc.

6. In many cases the behavior of a nanosystem with defects can be qualitatively understood from that of its bulk counterpart. However, the size quantization and other effects related to the nanosize of the system may result in considerable quantitative changes in the system properties. Moreover, sometimes the model developed for bulk defected systems do not work at all, so that they should be applied very cautiously.

The workshop gave a unique opportunity to discuss the latest advances in the filed. A combination of complementary topics addressed at the workshop (theory/experiment, theoretical method development/applications etc.) and participation of the researchers with different backgrounds facilitated the exchange of ideas at the workshop and could eventually give rise to new collaborations. Thus one can expect that the workshop should have a strong impact on the development of the field. Due to a considerable number of PhD students and young postdocs from EU countries (about 50% of the participants) who participated in the workshop, the event was also important in the context of training of young researchers.

The topics discussed at the workshop were very close to those listed in the proposal, except one area: simulations of irradiation effects in biosystems by atomistic methods. Although this idea has been up in the air for several years, very little has been actually done. The reason is that despite the apparent simplicity of using atomistic computer simulations for modeling of impacts of energetic particles such as ions and electrons on bio-objects, the force field models normally used in simulations of biological systems are not reactive, while irradiation breaks and creates chemical bonds. On the other hand, the conventional methods which can describe bond breaking in system composed of light chemical elements, may be computationally too expensive due to a high number of atoms involved. The organizers found only one speaker in this area who eventually was not able to come, so that this topic will be addressed in the future workshops.

Workshop program (see the workshop webpage for detail)

Wednesday 03.12.2008

K. Albe: Atomic Scale Computer Simulations of L1o Nanoparticles: Thermodynamics, Kinetics
and Irradiation
B. Rellinghaus: Irradiation-induced Structural Modi cations of Binary Metal Nanoparticles
P. V. Sushko: Exciting corners: Ultra-fast dynamics of excitons at oxide surfaces
F. Djurabekova: Amorphization of Ge and Si nanocrystals embedded in amorphous silica under ion irradiation
C. Ewels: Tuning the properties of carbon nanomaterials
F. Banhart: Creating and imaging defects in graphene and graphitic structures by focused electron beams
A. Zobelli: Defects in BN structures: from single vacancies to dislocation lines
R. van Leeuwen: Developments in many-body and time-dependent density functional theory
S. Tretiak: Functionalized Quantum Dots and Conjugated Polymers for Light Harvesting
H. Zhang: Field Enhancement inside Carbon Nanotubes

Thursday 04.12.2008

D. Sanchez-Portal: Electronic stopping power in LiF from first-principles real-time TDDFT simulations
Y. Miyamoto: Collision of charged ion to nano-graphite simulated by the time-dependent density functional theory
M. S. Ferreira: Long range interaction in magnetically-doped carbon nanotubes
G. Buchs: Local Modification and Characterization of the Electronic Structure of Carbon Nanotubes
L. Kantorovich: Generalized Langevin Equation for Solids: rigorous derivation and stochastic boundary conditions
A. Gulans: Self-consistent implementation of the van der Waals density functional in SIESTA
S. Erwin: Theory of Doping in Semiconductor Nanocrystals
M. Ganchenkova: Vacancies, Interstitials and Gas Atoms in Beryllium: Ab Initio Study
C. Barth: Kelvin probe force microscopy on MgO(001) surfaces and supported Pd nanoclusters
V. Skákalová: Ion-irradiated carbon nanotube networks: correlated changes in conduction and other properties .

Friday 05.12.2008

U. Heiz: Cluster Catalysis: The role of the support
P. Pyykkö: Simple understanding of chemical bonding
M. Schleberger: Creation of defects in graphene with swift heavy ions
S. Bromley: Understanding the low reactivity of non-bridging oxygen defects on stoichiometric silica surfaces
C. Cheng: Magnetism by nonmagnetic defects in a 2D BN sheet: ab initio studies
I. Lebedeva: Modelling of nucleation of carbon nanostructures on catalyst surface
C. Van de Walle: Defect Creation and Annihilation in GaN and ZnO

List of participants

1	Albe	Karsten	male	Germany		inv. speaker
2	Backman	Marie	female	Finland	PhD student	
3	Banhart	Florian	male	France		speaker
4	Barth	Clemens	male	France		
5	Borschel	Christian	male	Germany	PhD student	speaker
6	Bromley	Stefan	male	Spain		speaker
7	Buchs	Gilles	male	Netherlands	young postdoc	speaker
8	Cheng	Ching	female	Taiwan		speaker
9	Djurabekova	Flyura	female	Finland		speaker
10	Erwin	Steven	male	USA		inv. speaker
11	Esch	Friedrich	male	Italy		speaker
12	Ewels	Chris	male	France		inv. speaker
13	Ferreira	Mauro	male	Ireland		speaker
14	Foster	Adam	male	Finland		
15	Ganchenkova	Maria	female	Finland	young postdoc	speaker
16	Gloos	Kurt	male	Finland		
17	Gulans	Andris	male	Finland	PhD student	speaker
18	Heiz	Ulrich	male	Germany		inv. speaker
19	Hashemi	Javad	male	Finland	PhD student	
20	Hynninen	Teemu	male	Finland	PhD student	
21	Järvi	Tommi	male	Finland	PhD student	
22	Kantorovich	Lev	male	UK		speaker
23	Kashcheyevs	Vyacheslavs	male	Latvia	young postdoc	
24	Kaukonen	Markus	male	Finland		
25	Kelkkanen	André	male	Denmark	PhD student	
26	Kohlbach	Iris	female	Germany	PhD student	
27	Korff	Björn	male	Germany	PhD student	
28	Krasheninnikov	Arkady	male	Finland		
29	Laaksonen	Katri	female	Finland	PhD student	
30	Lebedeva	Irina	female	Russia	PhD student	speaker
31	Lievonen	Jarkko	male	Finland	PhD student	
32	Miyamoto	Yoshiyuki	male	Japan		inv. speaker
33	Nieminen	Risto	male	Finland		
34	Nordlund	Kai	male	Finland		
35	Oikkonen	Laura	female	Finland	PhD student	
36	Rellinghaus	Bernd	male	Germany		inv. speaker
37	Riikonen	Sampsa	male	Finland	young postdoc	
38	Pyykkö	Pekka	male	Finland		inv. speaker
39	Sanchez-Portal	Daniel	male	Spain		inv. speaker
40	Schleberger	Marika	female	Germany		inv. speaker
41	Senda	Yasuhir	male	Finland	young postdoc	
42	Sushko	Peter	male	UK		speaker
43	Skakalova	Viera	female	Germany		speaker
44	Tolvanen	Antti	male	Finland	PhD student	
45	Tretiak	Sergei	male	USA		inv. speaker
46	Van de Walle	Chris	male	USA		inv. speaker
47	Van Leeuwen	Robert	male	Finland		inv. speaker
48	Vehviläinen	Timo	male	Finland	PhD student	
49	Zhang	Hong	female	China		speaker
50	Zobelli	Alberto	male	France	young postdoc	speaker
51	Lanzani	Georgio	male	Finland	young postdoc	
52	Ritter	Yvonne	female	Germany	PhD student	
53	Schaefer	Jonathan	male	Germany	PhD student	
54	Borodin	Vladimir	male	Russia		
55	Agoston	Peter	male	Germany	PhD student	

Budget

(The figures may still slightly change, as one of the bills from the hotel has not yet arrived).

Outgoing

Travel expenses of the speakers:	4260
Renting conference facilities (incl. lunches, breakfasts, coffee etc)	5100
Accommodation	13520
Dinner	3900
TOTAL	26780

Incoming

ESF SimBioMa	6000
National graduate school in Materials Science	7700
National graduate school in Nano Science	7000
Accommodation/dinner fee paid by the participants directly to the hotel (190 Euros per person x 32)	6080
TOTAL	26780