NONLINEAR PROCESSES IN SOLIDS

Head of Laboratory *Dr. hab. phys*. Eugene Kotomin

Research Area and Main Problems

Our theoretical research interests are focused on five classes of problems related to:

- kinetics of diffusion-controlled processes, with emphasis on pattern formation and catalytic surface reactions;
- the atomic and electronic structure of numerous advanced materials, with emphasis on calculations of properties of defects, surfaces, metal/insulator interfaces.
- theoretical simulations and experimental studies of nanostructures and nanomaterials;
- stochastization of magnetic field lines in magnetized fusion plasma;
- gyrotron development.

We combine several different techniques, including analytical formalisms and large-scale computer simulations (quantum chemical methods, stochastic simulations as well as Monte Carlo/cellular automata modeling).

Scientific staff:

1. Dr. hab. E. Kotomin
2. Dr. hab. V. Kuzovkov
3. Dr. O. Dumbrajs
4. Dr. Yu. Zhukovskii
5. Dr. A. Popov
6. Dr. R. Eglitis
7. Dr. G. Zvejnieks
8. Dr. S. Piskunov
9. Dr. D. Gryaznov
10. Dr. V. Kashcheyevs

PhD students:

11. Yu. Mastrikov
12. D. Bocharov
13. A. Gopejenko

Scientific visits abroad

1. Dr. hab. E. Kotomin, EC Institute of Transuranium Elements, Karlsruhe, Germany (7 months), Max Planck Institute for Solid State Research, Stuttgart, Germany (3 months).
2. Dr. O. Dumbrajs, Fukui University, Japan (3 months), Max Planck Institut für Plasmaphysik, Garching, Germany (3 months).
3. Dr. Yu. Zhukovskii, Northwestern University, Evanston, USA (4 months), Max Planck Institute for Solid State Research, Stuttgart, Germany (3 weeks), Institute for Materials Research I, Karlsruhe (3 weeks), National Laboratory of Frascati, Italy (2 weeks), St. Petersburg State University, Russia (2 weeks), EC Institute of Transuranium Elements, Karlsruhe, Germany (1 week).
4. Dr. A. Popov, Institute Laue-Langevin, Grenoble, France (7 months), National Laboratory of Frascati, Italy (1 month).
5. Dr. R. Eglitis, Sung Kyun Kwan University, Suwon, Korea (4 months) and Rutgers University, USA (5 months)

6. Dr. S. Piskunov, Forschungszentrum Jülich, Germany (5 months), Northwestern University, Evanston, USA (3 months), University of Duisburg-Essen (2 months), LNF Frascati, Italy (1 week)
7. Dr. D. Gryaznov, EC Institute of Transuranium Elements, Karlsruhe, Germany (10 months), Max Planck Institute for Solid State Physics, Stuttgart, Germany (1 month).
8. V. Kashcheyevs, Ben-Gurion University of the Negev, Beer-Sheva, Israel (8 months), Physikalisch-Technische Bundesanstalt, Braunschweig, Germany (1 month).
9. Yu. Mastrikov, Max Planck Institute for Solid State Rcsearch, Stuttgart, Germany (11 months).
10. A. Gopejenko, Forschungszentrum Karlsruhe, Institut für Materialforschung I, Karlsruhe, Germany (3 months).

International Cooperation

Finland	1. Helsinki University of Technology (Dr. T.M.J. Ikonen)
France	2. Laue-Langevin Institute, Grenoble (Dr. G.J. McIntyre)
Germany	3. EC Institute of Transuranium Elements, Karlsruhe (Dr. P. van Uffelen). 4. Institut für Hochleistungsimpuls & Mikrowellentechnik, Karlsruhe (Dr. B. Piosczyk) 5. Institut für Materialforschung I Forschungszentrum Karlsruhe (Dr. A. Möslang) 6. Universität Duisburg-Essen (Prof. Dr. E. Spohr) 7. Max Planck Institut (MPI) für Festkörperforschung, Stuttgart (Prof. Dr. J. Maier) 8. Max Planck Institut für Plasmaphysik, Garching (Prof. Dr. H. Zohm) 9. Physikalisch-Technische Bundesanstalt (PTB), Braunschweig (Dr. Bernd Kästner).
Greece	10. School of Electrical and Computer Engineering, National Technical University of Athens, Zographou (Dr. Y. Kominis)
Israel	11. Ben Gurion University of the Negev, Ber Sheeva (Profs. A. Aharony and D. Fuks)
Italy	12. Laboratori Nazionali di Frascati (Dr. S. Bellucci, Dr.M.Cestelli-Guidi)
Japan	13. FIR Center, University of Fukui (Prof. T. Idehara)
Korea	14. Sung Kyun Kwan University, Suwon (Dr. J.C. Lee)
Lithuania	15. Institute of Semiconductor Physics (SPI), Vilnius (Dr. E. Tornau)
Romania	16. University of Craiova (Dr. D. Constantinescu)
Russia	17. St. Petersburg University (SpbU) (Prof. R.A. Evarestov)
Spain	18. University of Barcelona (Prof. F. Illas)
UK	19. Imperial College London (Prof. R.W. Grimes) 20. King's College London (Prof. L. Kantorovich) 21. University College London (Profs. A.M. Stoneham and A. Shluger)
Ukraine	22. National University of Lviv (Prof. I. Bolesta and Prof. V. Savchyn)
USA	23. Northwestern University, Evanston, Illinois (Prof. D.E. Ellis) 24. University of Maryland, College Park (Dr. G.S. Nusinovich) 25. California Institute of Technology, Pasadena (Dr. E. Heifets)

Main Results

KINETIC MONTE-CARLO SIMULATION OF Au/Ni SURFACE ALLOY PHASE SEPARATION

G. Zvejnieks and V. Kuzovkov
E.E. Tornau (*Semiconductor Physics Institute, Vilnius, Lithuania*)

Bimetallic catalysts allow us to fabricate perspective materials with improved properties in activity and selectivity. Recently obtained surface catalysts (bimetallic system that forms alloy just in a surface layer, while the alloy components are immiscible in the bulk) substantially extend the class of available catalysts. However, before the practical application, the stability of the novel alloy has to be analyzed at the industrially relevant high CO pressures, which substantially differ from traditionally studied systems at low vacuum.

In collaboration with the Semiconductor Physics Institute (Vilnius, Lithuania) we proposed a simplified theoretical model for AuNi surface alloy on Ni(111) substrate at high CO pressures. We studied the model using kinetic Monte-Carlo computer simulations and found a parameter interval which correspond to experimentally observed alloy $Au_{0.3}Ni_{0.7}$ phase separation, when Ni atoms are removed due to a carbonyl $Ni(CO)_x$ formation, but remaining Au atoms form clusters. In the simplified model Au diffusion has to be taken into account, while Ni and CO can be immobile. Adsorption and desorption of CO has to be included in the model, but carbonyl formation reaction can be approximated as $Ni + (CO)_2 \rightarrow 0$. Within this model we can describe the experimentally observed step flow rate dependence on CO surface concentration (CO pressure). In turn, an increase of Au mobility increases Au cluster size as well as distance between Au clusters.

ANDERSON LOCALIZATION PROBLEM: AN EXACT SOLUTION FOR 2D ANISOTROPIC SYSTEMS

V. Kuzovkov
W. von Niessen (*TU Braunschweig, Germany*)

Our previous results [*J. Phys.: Condens. Matter* **14** (2002) 13777] dealing with the analytical solution of the two-dimensional (2D) Anderson localization problem due to disorder is generalized for anisotropic systems (two different hopping matrix elements in transverse directions). We discuss the mathematical nature of the metal-insulator phase transition which occurs in the 2D case, in contrast to the 1D case, where such a phase transition does not occur. In anisotropic systems two localization lengths arise instead of one length only.

SAWTOOTH CRASH IN ASDEX UPGRADE TOKAMAK

O. Dumbrajs
V. Igochine, and H. Zohm (*MPI für Plasmaphysik, Garching, Germany*),

In magnetically confined fusion plasmas, a variety of magnetohydrodynamic (MHD) instabilities can occur, driven by gradients of kinetic pressure or current density. The

sawtooth oscillation is one of the fundamental instabilities in tokamaks. This phenomenon is characterized by a repetitive and rapid crash of the central electron temperature. We demonstrate on the basis of the soft X-ray and electron cyclotron emission measurements that during the pre-crash phase the quasiperiodic transition to chaos occurs. Magnetohydrodynamic oscillations with two frequencies develop before the crash. Consistent with the most energetically favorable transition from quasi-periodicity to chaos, their frequency ratio is close to the golden mean ratio $G = f_2 / f_1 = \left(\sqrt{5}-1\right)/2 \approx 0.618..$

We use a hysteresis model to describe experimental data on sawtooth crash in ASDEX Upgrade tokamak. The model is based on hysteresis which arises due to the fact that the value of the current density gradient (approximated, for the H-mode discharges studied here, by the temperature gradient) at the q=1 surface required to turn on the instability is greater than the gradient required to maintain the instability once it is turned on. The value of the hysteresis parameter can be chosen such that the model reproduces correctly the two time scales of the sawtooth crash in ASDEX Upgrade tokamak: the slow rise time (~7 ms) and the rapid crash time (~50 micros).

GYROTRON DEVELOPMENT FOR ITER AND GENERAL GYROTRON THEORY

O. Dumbrajs,
G. Gantenbein, S. Kern, and B. Piosczyk (*Forschungszentrum Karlsruhe, Germany*),
Y. Kominis and K.A. Avramides (*National Technical University of Athens, Greece*),
Z. C. Ioannidis and I. G. Tigelis (*Dept. Electronics, Computing, Telecommunications and Control, Faculty of Physics, National and Kapodistrian University of Athens*),
G.S. Nusinovich (*University of Maryland, College Park, USA*)
T. Idehara (*Fukui University, Fukui, Japan*)

The development of high-power high-frequency gyrotrons is strongly driven by the needs of fusion technology. Gyrotrons are superior to other rf sources in the frequency range relevant for electron cyclotron resonance heating (ECRH), or about 170 GHz for ITER. To make an ECRH system cost-effective, the output power of a single gyrotron should be around continuous 2 MW power. Coaxial cavity gyrotrons have the potential to fulfill this requirement as has been experimentally demonstrated within the development program performed as an *ITER task at Forschungszentrum Karlsruhe (FZK*). In proof of principle experiments carried out at FZK Karlsruhe on a 165 GHz coaxial cavity gyrotron during the last years, the feasibility of manufacturing a 2 MW, CW coaxial gyrotron at 170 GHz has been demonstrated and information necessary for a technical design has been obtained. Our laboratory actively participates in this development mainly by investigating mode competition scenarios.

In addition several cotributions to general gyrotron theory have been made. In particular, linear and non-linear inserts for genuinely wideband continuous frequency tunable coaxial gyrotron cavities have been proposed, the mathematical formulation and numerical results for the resonance characteristics of the TM_{mp} modes in a coaxial cavity with longitudinally corrugated insert has been developed, and single mode hysteresis calculations have been generalized to the multimode case with emphasis on mode competition in 170 GHz gyrotrons for ITER.

SINGLE-PARAMETER NON-ADIABATIC QUANTIZED CHARGE PUMPING

V. Kashcheyevs,
B. Kästner (*Physikalisch-Technische Bundesanstalt, Braunschweig, Germany*)

An important application of quantum dot devices is the development of a current standard based on a controlled dc current generation in response to external ac driving. The goal of the so-called quantized charge pumping is to insure that the average number of electrons passing in the circuit during one cycle is as close as possible to an integer as possible. In *collaboration with the experimental group at Physikalisch-Technische Bundesanstalt (Braunschweig, Germany)* we have proposed a new mechanism of non-adiabatic blockade of tunnelling which makes quantized charge pumping possible with a single driving gate. Such possibility may have decisive implications for achieving metrological accuracy in a battery of electron pumps. The first experiment, performed on a single wet-etched AlGaAs/GaAs nanowire, has demonstrated single-parameter quantized pumping with up to four current quantization plateaus.

We have developed a quantum-mechanical model for the double-barrier structure employed in the experiment, and calculated the pumped current as a function of experimentally controllable parameters. Our time-dependent rate equation calculations demonstrate the quantization mechanism and show the formation of the first quantization plateaux.

AB INITIO CALCULATIONS OF DEFECTS IN ADVANCED NUCLEAR FUELS

E. Kotomin, Yu. Zhukovskii, Yu. Mastrikov, D. Gryaznov, D. Bocharov,
P. Van Uffelen and V. Rondinella (*EC Joint Research Center, Institute of Transuranium Elements, Karlsruhe, Germany*), R. Grimes (*Imperial College, London*)

The actinide nitrides belong to the family of non-oxide ceramic nuclear fuels which are considered as promising candidates for so-called Generation-IV nuclear reactors. Prediction of their behavior under normal and extremal conditions needs knowledge of the physico-chemical properties including effect of defects produced as a result of self-irradiation. In a close collaboration with the *Institute for Transuranium Elements, Karlsruhe*, we continued first-principles calculations of UN fuels using the plane wave computer codes combined with large supercells containing up to 250 atoms.

Our study has demonstrated that atomic scale DFT-GGA-plane wave calculations with scalar relativistic pseudopotentials as implemented in the VASP and CASTEP codes (collaboration with *Imperial College, London*) could be used successfully to model a series of uranium nitride perfect lattice structures and also point defects in uranium mononitride. The only difference between the two sets of calculations were the pseudopotentials employed PAW (VASP) *vs.* ultrasoft pseudopotentials (CASTEP). Small differences in results that arose are attributed to this.

In particular, we have shown that V_N defects have hardly any affect on the UN lattice constant, even for concentrations as high as 25%. For this defect the lattice response is confined to small inward displacements of the nearest neighbour uranium ions and a very local defect induced electronic density redistribution. (This response to the formation of a vacancy is more reminiscent of a metal rather than an ionic or semiconducting material, *e.g.*, UO_2). Conversely, V_U defects induce somewhat larger (but still small) defect volumes

which increase in magnitude as a function of defect concentration. In this case the nearest neighbour nitrogen atoms are displaced outwards and the hole is distributed over first and to a lesser extent second neighbour atoms. Lastly, we find that, once complete lattice relaxation has been performed, the Frenkel and Schottky pair formation energies are very similar. Consequently, intrinsic vacancy and interstitial defects will exist in comparable concentrations so that both are available to mediate defect transport. Analysis of the electron density redistribution shows that the effective charge of N atoms depends critically on their position and environment, which limits the applicability of MD simulations based on formal invariant charged species to defect studies in nitrides.

As a continuation of this study, we modelled UN surfaces. The main findings are as follows: (i) at low temperatures the FM magnetic state of the thin films of UN(001) become energetically more preferable, although experimental observation at room temperature indicate higher stability of the AFM magnetic state, (ii) The formation energy of surface U vacancy at UN(001) substrate is found to be noticeably lower than that for N vacancy, which contradicts the results obtained for defects in the UN bulk. It can be explained by a higher flexibility of neighboring N atoms at surface, which results in their substantial outward displacement from regular lattice sites. (iii) Atomic adsorption upon the UN(001) substrate clearly demonstrate metallic behavior of UN chemical bonding due to high values of adsorption energy per O atom (8.1 vs. 7.1 eV atop surface U or N atoms, respectively). (iv) Spontaneous O_2 molecule dissociation is energetically favorable on the UN(001) surface. This can occur when a molecule is oriented parallel to the substrate and its bond directed towards the nearest surface U atoms (the center of molecule is located atop either a hollow position or surface N atom). Neither a vertical adsorption of O_2 molecule nor horizontal one with the oxygen ends oriented towards the nearest surface N atoms lead to its dissociation; (v) The calculated projected DOS can be used for the interpretation of the UPS experimental data for oxidised UN obtained recently at ITU.

ABO_3 PEROVSKITE SOLID SOLUTIONS AND DEFECTS

E. Kotomin, Yu. Zhukovskii, S. Piskunov, A. Gopeyenko, Yu. Mastrikov,
R.A. Evarestov (*St. Petersburg University, Russia*)
D.E. Ellis (*Northwestern University, Evanston, USA*)
E. Spohr (*Universität Duisburg-Essen, Germany*)
T. Jacob (*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*)
R. Merkle and J. Maier (*Max Planck Institute for Solid State Research, Stuttgart, Germany*)

Understanding and control of properties for a wide class of functional materials - mixed electronic and ionic conductors such as $(Sr,La)MnO_3$ or $Sr(Fe,Ti)O_3$ solid solutions – important for their numerous applications in fuel cells, electrochemical sensors, permeation membranes, spintronics, and catalysis. In collaboration with the *Research Center in Juelich*, we have performed hybrid DFT-HF calculations with the B3LYP exchange-correlation functional of the magnetic and electronic structure of $La_{0.875}Sr_{0.125}MnO_3$ and pure $LaMnO_3$. The calculations show that, in agreement with previous calculations, LMO has an antiferromagnetically ordered ground state. The metallic LSM, on the other hand, has at low temperature a strong prevalence for a ferromagnetically ordered state. This prevalence for the ferromagnetic state is more pronounced as the one for the antiferromagnetic state in LMO and increases further in the

high-temperature pseudo-cubic phase. Furthermore, we see, at least for the system sizes studied here, no indication of significant charge ordering around the Sr defect. Thus, we concluded from our calculations that LSM at high temperature is pseudo-cubic and prefers ferromagnetically ordered domains. Contrary to LMO, the LSM DOS shows half-metallic spin states in the band gap, which could be responsible for the electronic conductivity of LSM SOFC cathodes.

In collaboration with the *laboratory of EXAFS spectroscopy at ISSP and Max Planck Institute in Stuttgart*, we performed structural studies for a whole series of solid solutions $Sr(Fe_xTi_{1-x})O_3$−perovskites as a function of composition, $0<x<1$ and iron oxidation state. The XRD, Fe and Ti *K*-edge XAS, and vibrational Raman and infrared spectroscopy were used with the emphasis on the possible Jahn-Teller distortion around Fe^{4+} ions predicted by us theoretically. The local electronic structure probed by XANES, as well as the long range order probed by XRD and the short range order reflected in EXAFS, showed a dependence on composition as well as on iron oxidation state. The variation of the pre-edge peak intensity in the XANES signals is attributed to the modification of the Fe-Ti-O bond lengths and *B*–O–*B* bonding angles, resulting in a change of localization of 3*d*-metal states and their occupation numbers n_d. Although none of the individual observations alone gives a final proof of a JT distortion around Fe^{4+} ions, the combination of results obtained by XAS, especially the iron concentration dependence of the Fe^{4+}-O^{2-} MSRD and vibrational spectroscopies, strongly supports its presence, most pronounced for $x<0.03$ and decreasing for higher iron concentrations. The decrease of the JT effect with increasing x can be understood qualitatively by the change in the electronic structure of the materials from insulator to metal. A quantitative modeling of the variation of the Fe^{4+}-O^{2-} MSRD and the intensities of the Raman lines remains a challenging theoretical problem.

The atomic and electronic structure of a main defect in oxides, in general, and ABO_3-type perovskites in particular -- oxygen vacancy—is important for understanding their properties. *In collaboration with St. Petersburg University and Northwestern University*, we wrote a review article summarizing recent first principles simulations of the neutral oxygen vacancies (*F* centers) existing as native or radiation-induced point defects in various crystalline metal oxides in different forms (bulk, bare substrate surface, and on the interface with metal adsorbates). We considered periodic models in calculations of point defects using the metal oxide supercell or cyclic clusters. We compared different formalisms of first principles calculations, mostly the Density Functional Theory (DFT) as implemented in the framework of either localized basis set of atomic orbitals or delocalized basis sets of plane waves. We analyzed in detail the structural and electronic properties of the *F* centers in binary oxides of light metals (MgO and Al_2O_3) and ternary metal oxides ($SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $KNbO_3$, and $PbZrO_3$ perovskites). When available, we compared results of *ab initio* periodic defect calculations with experimental data, results of *ab ibitio* cluster calculations (both embedded and molecular) as well as semi-empirical calculations.

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FIRST-PRINCIPLES CALCULATIONS OF $BaZrO_3$ (001) AND (011) SURFACES

R. Eglitis
J.C. Lee (*Sung Kyun Kwan University, Suwon, Korea*)

Atomistic study of perovkite surfaces is important for ferroelectric and many other applications. The atomic/electronic structure of $BaZrO_3$ (001) and (011) surfaces was

modeled using the B3PW hybrid functionals. According to the results of these calculations, all upper layer atoms for ZrO_2- and BaO terminated surfaces relax inwards. The surface rumpling for the BaO-terminated surface is much larger than for the ZrO_2- terminated. Both BaO-terminated and ZrO_2- terminated surfaces are stable and energetically equally favourable. Unlike the $BaZrO_3$(001) surface, different terminations of the (011) surface lead to great differences in the surface energies. The A-type O-terminated surface has the lowest energy (2.32 eV);. the Ba-terminated surface has much higher surface energy of 2.90 eV, while the ZrO-terminated (011) surface has the highest energy (3.09 eV). We predict a considerable increase of the Zr–O chemical bond covalency near the (011) surface, as compared to both the bulk and the (001) surface.

FIRST-PRINCIPLES CALCULATIONS ON SURFACE REACTIVITY OF LIGHT METAL OXIDES AND FLUORIDES

Yu. Zhukovskii, E. Kotomin,
D. Fuks (*Ben Gurion University of the Negev, Beer Sheeva, Israel*),
D.E. Ellis (*Northwestern University, Evanston, Illinois, USA*)
P. Balaya and J. Maier (*MPI for Solid State Research, Stuttgart, Germany*)

Prediction and control of the metal adhesion and growth mode of thin metallic films is important for micro- and nanoelectronics. In collaboration with *Northwestern University, Evanston and Ben Gurion University, Beer Sheva,* we performed first principles calculations based on the hybrid B3LYP method combined with the thermodynamic study of Ag and Cu adhesion onto defective MgO(001) substrate.

We observe a strong change of the bonding between the metal adatoms and substrate in the vicinity of the surface F_s centers (neutral O vacancies), which affects the thermodynamic conditions and the morphology of the growing metallic layer. For a perfect MgO surface we confirm the experimentally observed submonolayer growth of *metallic islands*. However, the surface F_s centers weaken the trend toward metal atom aggregation and above some critical surface concentration lead to formation of *disordered* 2D metallic films; *i.e.*, introduction of surface defects could change the island formation mode for the layer-by-layer growth mode. For silver films, the effect of the F_s centers is less pronounced than for copper: substantially higher atomic fraction of defects (at least 35-40 per cent) is needed for the growth of uniform Ag film, which is substantially larger than that for Cu (<10 *per cent*).

To clarify the mechanism of lithium storage anomaly in LiF nanocomposites in the context of lithium batteries, we have performed comparative DFT hybrid calculations on the atomic and electronic structure of the non-polar Cu/LiF(001) and model Li/LiF(001) interfaces, *in collaboration with Max Planck Institute for Solid State Research, Stuttgart*. For this aim, we have modeled the extra Li atoms incorporated at several possible sites of the Me/LiF interface, including the free surface of the substrate slab and interstitial sites inside a slab. Increase of Li concentration at the substrate side of interfaces is accompanied by an increased electron charge transfer from the extra Li atoms towards the transition metal adlayers, in agreement with a proposed mechanism of interfacial charge storage. Interfacial stability and charge transfer depends on the number of extra Li atoms and Me adatoms *per* LiF(001) surface unit cell. The Li diffusion on the interface is found to be energetically much easier than Li penetration into the bulk.

THEORETICAL SIMULATIONS OF OXIDE DISPERSED STRENGTHENED STEELS AS STRUCTURE MATERIALS FOR FUSION REACTORS

Yu. Zhukovskii, E. Kotomin, A. Gopeyenko,
A. Möslang and P.V. Vladimirov (*Institute for Materials Research I, Karlsruhe Research Center, Germany*)

Reduced activation steels strengthened by Y_2O_3 precipitates are considered as candidate structure materials for future fusion reactors. Both size and spatial distributions of oxides significantly affect mechanical properties and irradiation resistance of oxide dispersion strengthened (ODS) steels synthesized by hot isostatic pressing at temperature around 1000-1200°C and pressure ~100 MPa. It was proposed that the morphology and structure of oxide particles are determined besides powder composition primarily by the *milling* process and the *hipping* temperature. However, the recent experimental findings indicate that the picture of oxide particle formation is still not clear. There is evidence that their formation occurs at the *hipping* stage as a result of yttrium-oxygen co-precipitation. Comprehensive experimental studies on ODS steels with atomic resolution performed at the *Institute for Materials Research I, Karlsruhe Research Center, Germany*, show *stability* of pure Y_2O_3-ODS and yttria nanoparticles.

The first step of multi-scale modeling of ODS particle formation in steel performed together with *IMR-I, Karlsruhe,* has included large-scale VASP calculations on *fcc* lattice of γ-Fe with further inclusion of O and Y impurities and formation of Fe vacancies. Together with calculated pair-wise interactions (Fe-O, Fe-vacancy, Fe-Y, O-O vacancy-O, O-Y vacancy-vacancy, vacancy-Y and Y-Y) as well as energy barriers for diffusion of impurities and vacancies supply us with the necessary parameters for further kinetic simulations. VASP calculations have been performed for large Fe supercells (at least for 4×4×4 extension using full geometry optimization). We have developed the methodology for these calculations, choosing proper sets of computational parameters as well as electronic and magnetic states of systems. Perdew-Wang-91 GGA (Generalized Gradient Approximation) non-local exchange-correlation functional and the scalar relativistic PAW (Projected Augmented Wave) pseudopotentials have been used. The Monkhorst-Pack scheme for 12×12×12 k-point mesh in the Brillouin zone was used.

We have calculated key parameters of the atomic and electronic structure for all configurations described above: lattice parameter and bulk modulus, densities of states (DOS) and band structure, equilibrium geometry of defective structures around vacancies and impurities re-distributions of electronic and spin densities in *fcc*-Fe under influence of vacancies and impurities. Presence of Fe vacancy noticeably re-distributes the electronic density in iron matrix. The vacancy formation energy for has been found to be 2.95 eV with 0.75% inward relaxation. Energy gain due to insertion of O atom at the center of octahedron formed by the nearest six Fe atoms has been found to be 3.21 eV whereas relaxation energy is 2.67 eV necessary for expansion of the first coordination sphere around impurity atom by ~9 percent. It was found that O impurities possess excessive electronic charge -1.3-1.4 *e* whereas Y can only substitute Fe atom in its vacancy (in the center of cuboctahedron formed by the nearest twelve Fe atoms) serving as a donor of electronic density (~1 *e*). The energy gain due to insertion of Y atom into γ-Fe lattice can be considered as 0.71 eV (substantially smaller than after insertion of oxygen impurity) with relaxation energy 1.40 eV and 7% expansion of the first coordination sphere. The next

step of atomistic simulation on ODS is the kinetic MC modelling based on our *ab initio* calculations.

AB INITIO SIMULATIONS ON THE ATOMIC AND ELECTRONIC STRUCTURE OF REGULAR AND DEFECTIVE AlN NANOTUBES

Yu. Zhukovskii,
S. Bellucci and C. Balasubramanian (*Laboratori Nazionali di Frascati, National Institute of Nuclear Physics, Italy*)

Due to numerous technological applications, AlN nanostructures attract enhanced attention of both experimentalists and theorists. Different AlN nanotubes (NTs) of a wide range of diameters (up to 80 nm) were recently synthesized using either a method of highly non-equilibrium direct current (DC) arc-plasma-induced melting of aluminium in N-Ar ambient or simply nitriding impregnated Al powder in a tubular furnace. In both cases, nanotubes identified using high-resolution transmission electron microscopy (HRTEM) were accompanied by nanoclusters and nanowires. AlN nanosystems containing both nanotubes and nanoparticles have been recently studied experimentally using spectroscopic methods of XANES (X-Ray absorption near edge spectroscopy), FTIR (Fourier transform infra-red spectroscopy), XAS (X-ray absorption spectroscopy) as well as by neutron scattering and luminescence.

For theoretical simulation on AlN nanotubes (NTs) of different chiralities (armchairand zigzag-type) and uniform diameters, we have considered their single-walled (SW) 1D periodic models. For this aim, we have performed *ab initio* DFT calculations on AlN SW NTs using formalism of the localized Gaussian-type atomic functions as implemented in *CRYSTAL-03* computer code. We have shown that the smaller the diameter of AlN single-walled nanotube is, the closer its electronic and structural properties to AlN bulk. We have analysed an influence of N vacancies (neutral *F* centres) created by either soft irradiation of nanotubes or under experimental conditions of their growth, on the atomic and electronic structure of AlN SW NTs. We have found the small inward relaxation of the Al nearest neighbours and the N next-nearest neighbours around each point defect formed on 1 nm AlN NTs of both chiralities. Presence of N vacancy in both types of nanotubes has resulted in appearance of the two defect energy levels in their band gaps consisting of mainly 3*s* and 3*p* states of the nearest Al atoms.

OPTICAL PROPERTIES OF CADMIUM CLUSTERS IN CdI_2 LAYERED CRYSTALS.

A. Popov
I. Bolesta, I. Karbovnyk, V. Lesivciv and S. Velgosh (*Ivan Franko National University of Lviv, Ukraine*)
M. Cestelli Guidi and S. Bellucci (*Laboratori Nazionali di Frascati, National Institute of Nuclear Physics, Italy*)

Cadmium iodide single crystals, CdI_2, belong to the class of compounds having layered structure. These crystals can be considered as two-dimensional systems and their investigations are important for the physics of low-dimensional structures. Besides that,

CdI_2 also has relevance from the industrial point of view as a prospective scintillator with subnanosecond luminescence decay time for use in electromagnetic calorimeters
In collaboration with National University of Lviv and LNF INFN, Frascati we have investigated the influence of overstoichiometric Cd*i* atoms on the optical properties of cadmium iodide crystals. The results of optical absorption, luminescence, and luminescence excitation studies of CdI_2 crystals with controlled deviation from stoichiometric composition allow observing correlations between the Cd*i* concentration and features in absorption and emission spectra up to concentrations of 10^{18} cm^{-3}. At higher concentrations the overstoichiometric cadmium atoms form clusters, which were observed using scanning electron microscopy. The extinction spectra of $(CdI_i)_n$ clusters are calculated in the frame of Mie theory and are found to correlate with the optical studies.

CHARGE TRANSPORT IN ELECTRICALLY RESPONSIVE POLYMER LAYERS

A. Popov
O. Aksimentyeva, O. Konopelnyk, I. Bolesta, I. Karbovnyk, and D. Poliovyi (Ivan Franko National University of Lviv, Ukraine)

A great interest to nano-opto-electronic devices based on the conducting polymers (polythiophenes, polyaniline, polyphenylenevinylene) such as "smart windows", optical memory devices, IR-switching, electrochromic displays and sensors caused a study of electrochromic materials in wide spectral range – from near UV to visible and near IR-region

In collaboration with *National University of Lviv, Ukraine,* we have studied the processes of charge transport in the conducting polymer electrochromic films by means of spectral-electrochemical method, impedance spectroscopy and cyclic voltametry measurements. The polymer films on ITO surface were obtained by means of the electrochemical polymerization.

It was shown that charge transport during the coloration-bleaching processes is not a symmetric phenomenon. Using impedance spectroscopy the effective diffusion coefficients for anode and cathode charge transport have been measured. The higher rate of charge transport in the bleaching process as compared to coloration is considered in the frame of conformation rebuilding of conducting polymer chains. The obtained results show that the rate of color switching is defined by the both the polymer structure and electrolyte nature.

Scientific papers published in 2007

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