

NONLINEAR PROCESSES IN SOLIDS

Head of Division *Dr. hab. phys.* Eugene A. Kotomin

Research Area and Main Problems

Our theoretical research interests are focused on two main classes of problems related to the kinetics of diffusion-controlled processes, with emphasis on pattern formation and catalytic surface reactions, as well as on the atomic and electronic structure of advanced materials, with emphasis on calculations of defective properties, surface properties and metal/oxide interfaces. We combine many different techniques, including analytical formalisms and large-scale computer simulations (both quantum chemical methods and Monte Carlo/cellular automata modelling).

Scientific staff:

1. Dr. hab. E. Kotomin
2. Dr. hab. V. Kuzovkov
3. Dr. hab. J.R. Kalnin
4. Dr. Yu. Zhukovskii
5. Dr. A. Popov
6. Dr. R. Eglitis
7. Dr. G. Zvejnieks
8. Dr. S. Piskunov

PhD students:

9. V. Kashcheyevs
10. D. Gryaznov

Students:

11. D. Bocharov

Visitors from abroad

1. Prof. Dr. O. Dumbrajs, Helsinki University of Technology, Espoo, Finland (2 weeks).
2. Prof. Dr. R.A. Evarestov, St. Petersburg University, Russia (3 weeks).

Our scientific visits abroad

1. Dr. hab. E. Kotomin, Max Planck Institute for Solid State Physics, Stuttgart, Germany (9 months), University of Osnabrück, Germany (2 weeks), Northwestern University, USA (1 week), University of Pennsylvania, USA (1 week)
2. Dr. hab. V. Kuzovkov, Braunschweig University of Technology, Germany (3 months)
3. Dr. Yu. Zhukovskii, Max Planck Institute for Solid State Physics, Stuttgart, Germany (1 month), University of Osnabrück, Germany (1 month), St. Petersburg University, Russia (1 month)
4. Dr. A. Popov, European Molecular Biology Laboratory, Grenoble, France (11 months)
5. Dr. R. Eglitis, University of Osnabrück, Germany (11 months)
6. Dr. G. Zvejnieks, JET-EFDA/CSU, Great Britain (1 month)
7. Dr. S. Piskunov, University of Osnabrück, Germany (3 months)
8. V. Kashcheyevs, Tel Aviv University, Israel (11 months)
9. D. Gryaznov, Max Planck Institute, Stuttgart, Germany (11 months)

International Cooperation

Czech Republic

Institute of Physics, Charles University, Prague (Prof. V. Trepakov)

Estonia

Institute of Physics, Tartu University (Prof. A. Lushchik)

Finland

Helsinki University of Technology, Espoo, Finland (Prof. O. Dumbrajs)

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| France | European Molecular Biology Laboratory (EMBL), Grenoble (Dr. D.A.A. Myles) |
| Germany | University of Osnabrück (Prof. G. Borstel) Max Planck Institut (MPI) für Festkörperforschung, Stuttgart (Prof. J. Maier) Max Planck Institut (MPI) für Plasmaphysik, Garching (Prof. H. Zohm) Braunschweig University of Technology (Prof. W. von Niessen) Gesellschaft für Schwerionenforschung, Darmstadt (Prof. K. Schwartz) |
| Israel | School of Physics and Astronomy, Tel Aviv University (Prof. A. Aharony) Ben Gurion University of the Negev (BGU), Beer Sheeva (Prof. D. Fuks) |
| Latvia | Institute of Solid State Physics (ISSP) (Prof. J. Purans) Transport and Telecommunication Institute (TTI) (Prof. Yu.N. Shunin) |
| The Netherlands | Eindhoven University of Tehnology (TUE) (Prof. A.P.J. Jansen) |
| Russia | St. Petersburg University (SpbU) (Prof. R.A. Evarestov) |
| Spain | University of Barcelona (UB) (Prof. F. Illas) |
| Sweden | Uppsala University (Prof. K. Hermansson) |
| UK | King's College London (Prof. L. Kantorovich) University College London (Prof. A.M. Stoneham) |
| USA | California Institute of Technology (CalTech), Pasadena (Dr. E. Heifets) |

Main Results

LARGE-SCALE SIMULATIONS OF SURFACE REACTIONS

V.N. Kuzovkov,

W. von Niessen (*Braunschweig University of Technology, Germany*),

A.P.J. Jansen and R. Salazar (*Eindhoven University of Tehnology, the Netherlands*).

In collaboration with *Eindhoven University of Technology, the Netherlands* we presented a tool for scaling laws relating the typical space and time scales obtained in microscopic Monte Carlo simulations to both experimental system sizes and relevant diffusion coefficients. One of the most interesting features of surface reactions is that in many cases pattern formation, structures with some well-defined length scale, sometimes with symmetries and temporal behavior, such as oscillations, traveling waves, spirals, Turing patterns, are observed. A usual approach to a study this pattern formation is reaction—diffusion (RD) equations, which simulate the dynamic behavior of chemical reactions on surfaces. However, these partial differential equations give only approximate solutions and gave in several cases completely wrong results, because they are based on the local mean field approximation, meaning well-stirred reactants at the microscopic level, ignoring all local correlations between reactants, as well as fluctuations and lateral interactions among adsorbates. The RD equations operate with the coverages which are macroscopic continuum variables and thus neglect the discrete structure of solids, and do not describe the actual chemical process underlying the pattern formation. An exact method to solve the *master equation* for such systems is the *Monte Carlo* (MC) method. To compare MC simulations with experimental pattern formation, it is necessary to fill the gap between the length scale of the individual particles and the diffusion length. This would be a very large and slow simulation, due to the huge number of particles involved and the fast diffusion rates which means that most of the simulation time is spend for diffusion of particles instead of chemical reactions. Although only the MC simulations provide solutions to the exact master equations for the surface reactions, they are not suitable for efficient parallelization, due to a random selection of lattice sites. However, there is another important approach for simulating the discrete events on the lattices, the Cellular Automata (CA). We have studied, under which conditions the CA could reproduce adequately MC simulations of chemical reactions on surfaces. We found that the main requirement is the use of large diffusion coefficients. We performed large-time and large-size computer simulations for chemical reactions on surfaces. By using large parallel simulations, it is possible to derive scaling laws which allow us to extrapolate results to even larger system sizes and larger diffusion coefficients, thus permitting a direct comparison with real experiments.

In collaboration with *Braunschweig University, Germany* we studied forced oscillations in a self-oscillating surface reaction model. The harmonic resonance, subharmonic and superharmonic entrainment, quasiperiodic and chaotic behavior are well known to occur in nonlinear self-oscillating systems which are subject to a

periodic forcing. Harmonic resonance occurs if the periodic forcing signal has a frequency very similar to that in the undisturbed system and results in an amplification of the oscillations. In this case the so-called *phase locking* occurs, i.e. the system oscillates with the response frequency with a constant phase difference to the external signal. A microscopic lattice gas model for the catalytic CO+O₂ reaction on Pt(110) subject to external periodic forcing is studied by means of cellular automaton simulations. Harmonic resonance, subharmonic and superharmonic entrainment, quasiperiodic as well as chaotic behavior are among the observed phenomena in this model when the gas phase concentration of CO as an external control parameter is periodically varied and interacts with the self-oscillating reaction system.

DISTINGUISHING DETERMINISTIC&NOISE COMPONENTS IN ELM TIME SERIES

V.N. Kuzovkov and G. Zvejnieks,
O. Dumbrajs (*Helsinki University of Technology, Espoo, Finland*),
H. Zohm (*MPI, Garching, Germany*)

In collaboration with *MPI, Garching, Germany*, and *Helsinki University of Technology, Finland* we have developed methodology based on financial engineering principles, which allows us to distinguish deterministic and noise components.

It was first observed at ASDEX Tokamak in 1982 that externally heated plasmas can suddenly reach an operating regime of improved confinement. The regimes of low and high confinement are referred to as L-mode and H-mode, respectively. The transition from L-mode to H-mode is normally accompanied by appearance of recurrent magnetohydrodynamic instabilities known as *edge localized modes* (ELMs). These manifest themselves as short bursts of energy and particles as outer layer of plasma is suddenly peeled off and then flows along the magnetic field lines to the divertor plates.

We proposed a new approach to analysis of ELM time-series. This is based on the use of the auto-regressive moving average (ARMA) model. It is demonstrated that the chaos discovered earlier in some ELM time-series by detecting unstable periodic orbits (UPOs) might be fictitious - the result of uncritical processing of experimental data, or of erroneous interpretation of the results of the analysis.

QUANTUM THEORY OF TRANSPORT PHENOMENA IN MESOSCOPIC SYSTEMS

V. Kashcheyevs,
A. Aharony and O. Entin-Wohlman (*Tel Aviv University*)

In collaboration with Tel Aviv University (Profs. A. Aharony and O. Entin-Wohlman), we have performed theoretical analysis of charge transfer by surface acoustic waves (SAWs). Electronic transport generated by SAW is a particular manifestation of adiabatic quantum pumping effect with potential applications in metrology (current and capacitance standards) and quantum computations (solid state implementation of a flying qubit).

A typical experimental setup consists of a few-micrometer long quasi-one-dimensional constriction in a high-mobility two-dimensional electron gas. Surface acoustic waves of several GHz frequency are launched in the longitudinal direction resulting in a finite dc current component along the constriction. We have suggested a simple one-dimensional model that includes the effect of an electrostatic barrier controlled by the external gate and a piezoelectric potential generated by the running SAW. The acoustoelectric current is calculated within the adiabatic approximation. The model qualitatively reproduces all experimentally observed features of the acoustoelectric current: plateau structure in the gate voltage and SAW amplitude dependencies that correspond to the transfer of an integer number of electronic per period; great sensitivity of the accuracy of the plateaus to the phase of a secondary counter-propagating SAW; effects of the longitudinal voltage bias. Application of our recently developed resonance approximation explains the formation of integer steps as a sequential capturing of several electrons in a moving quantum dot formed by the SAW potential.

At low temperatures (milli-kelvin range) correlation effects in closed nanoscale structures get pronounced and the approximation of non-correlated electrons becomes inapplicable. We are working at the extension of our formalism which includes the most important correlation effects (such a formation of the Kondo anomaly at the Fermi level) at a semi-quantitative level. We have recently obtained an exact solution of a non-linear system of truncated equations of motion for a single localized level embedded into an arbitrary external network in the presence of spin-polarizing external field.

DEFECTS AND POLAR SURFACES OF ADVANCED PEROVSKITES

E.A. Kotomin, Yu.F. Zhukovskii, R.I. Eglitis, and S. Piskunov,
G. Borstel (*University of Osnabrück, Germany*),
R.A. Evarestov (*St. Petersburg University, Russia*),
F. Illas, N. Lopez, and J. Carrasco (*University of Barcelona, Spain*)
E. Heifets (*California Institute of Technology, Pasadena, USA*),
D. Fuks (*Ben Gurion University of the Negev, Beer Sheeva, Israel*),
K. Hermansson (*Uppsala University, Sweden*)
and J. Maier (*MPI, Stuttgart, Germany*)

Ab initio quantum chemical calculations have been performed for a number of advanced ABO₃ materials and their solid solutions, widely used in technological applications.

In collaboration with *Osnabrück University, Germany*, and *California Institute of Technology, Pasadena, USA*, we performed first principles calculations, using both Hartree-Fock method (with electron correlation corrections, HF-CC), Density Functional Theory (DFT) and their hybrids (B3PW, B3LYP). We have studied the atomic and electronic structure of polar surfaces of ABO₃ perovskites, e.g. SrTiO₃ (110) surfaces, which serve as substrates for growth of technologically important high T_c materials. We have optimized the atomic coordinates in four planes near the surface, considered surface rumpling and compression, and estimated their effective charges and surface polarization. Results are compared with LEED and RHEED experiments. We studied also the atomic and electronic nature of the polarons and excitons in perovskites and suggested an interpretation of widely observed "green" luminescence (2.2-2.3 eV) as a radiative recombination of nearest electron and hole polarons localized on Ti(Nb) ion and neighboring O²⁻ ion. This theoretical study permits to make choice between many hypothetical models of the green luminescence. We studied also the atomic structure of the KNb_xTa_{1-x}O₃ perovskite solid solution and demonstrated that Nb impurities even at very low concentrations reveal a cooperative self-ordering effect, which drives the phase transition in incipient KTaO₃ ferroelectric.

In collaboration with *St. Petersburg University, Russia*, *University of Barcelona, Spain*, and *Uppsala University, Sweden* we have studied F centers (O vacancies) in SrTiO₃ perovskite and demonstrated that their properties are much closer to defects in partly covalent SiO₂ rather traditional F -centers in ionic oxides (MgO and Al₂O₃). For first principles calculations on the defective structures of cubic SrTiO₃ we have used both CRYSTAL and VASP codes. Due to existence of different kinds of bonds in SrTiO₃ one can observe a competition between the tendency to trap the electrons associated with the missing oxygen in vacancy (F center) or to localize them on the Ti $3d$ orbitals. The creation of a neutral O vacancy results in the new electronic state below the conduction band, which is consistent with experimental estimate indicated small ionization energy for the oxygen vacancy. The formation energy of the F center with respect to oxygen atoms depends on the size of supercell and was found to vary from 8.94 eV to 7.65 eV for supercell sizes containing from 40 to 240 atoms. The formation of oxygen vacancies is accompanied by a large relaxation of the first and second nearest neighbours. The localization of the electrons on titanium ions is consistent with photoemission studies on the surface of SrTiO₃, which indicate the formation of Ti³⁺ ions when surface defects are created by Ar⁺-ion bombardment.

Progress in solid oxide fuel cells needs new materials for cathodes. One of promising materials is LaMnO₃ perovskite doped with Sr. Of principal interest is O₂ molecule adsorption on its surface, dissociation, O atom diffusion and penetration through the electrolyte to anode, where O meets with H atoms. In collaboration with *Max Planck Institute for Solid State Researches, Stuttgart, Germany*, *St. Petersburg University, Russia*, and *California Institute of Technology, Pasadena, USA* we performed detailed *ab initio* and shell model

calculations of the (100) and (110) LaMnO_3 surfaces, with emphasis on the surface energies and polarization. We have demonstrated that the stabilization of the (110) surface needs a reconstruction through incorporation of large concentration of O vacancies. This removes an infinite dipole moment and stabilizes the surface. On the other hand, the polar (100) surface could be stabilized by the charge redistribution near the surface. Both surfaces, the (100) and (110), reveal a strong increase of the Mn-O bond covalency in the first three planes nearest to the vacuum, which should affect the defect structure and oxygen adsorption properties which is now in progress

FIRST PRINCIPLES MODELING AND THERMODYNAMIC STUDY OF THIN METAL FILM GROWTH, METAL OXIDATION AND CORROSION

Yu.F. Zhukovskii and E.A. Kotomin,
A.M. Stoneham (*University College London, UK*),
D. Fuks (*Ben Gurion University of the Negev, Beer Sheeva, Israel*),
G. Borstel (*University of Osnabrück, Germany*), J. Maier (*MPI, Stuttgart, Germany*),

Ab initio DFT calculations using CRYSTAL'98 and CRYSTAL'03 codes are performed, in order to describe both bulk and surface properties of Al, Ag and Cu metals as well as their reactivity towards molecular oxygen and $\text{MgO}(001)$ surface, respectively. Optimization procedure realized in both CRYSTAL and VASP codes is used also to understand better the nature of conductivity in the $\text{AgCl}(111)/\alpha\text{-Al}_2\text{O}_3(0001)$ interface.

In collaboration with *Osnabrück University, Germany, University College London, UK, and Ben Gurion University Beer Sheeva, Israel* we continue large-scale *ab initio* calculations and thermodynamic study of copper and silver adhesion onto magnesia substrate. We carefully re-optimized basis sets of Ag and Cu for reliable CRYSTAL calculations and then checked both bulk and surface properties of copper and silver. Due to a 15% mismatch between the lattice constants of Cu and MgO the probability of the aggregation of adsorbed Cu atoms into clusters is noticeably higher than in the case of the $\text{Ag}/\text{MgO}(001)$ interface where this mismatch is markedly smaller ($\sim 3\%$). We also continue to study various adhesive and electronic properties of both regular and defective $\text{Ag}/\text{MgO}(001)$ and $\text{Cu}/\text{MgO}(001)$ interfaces, which allow us to make comparative analysis of the nature of various metals adhesion on ceramic substrate depending on the electronic structure of adsorbate and structural morphology of adsorbent.

In collaboration with *Osnabrück University, Germany*, we have performed *ab initio* calculations for copper adsorption on a regular, defect-free TiO_2 - and BaO - terminated (001) surfaces of a cubic BaTiO_3 , using *a posteriori* HF-CC method as implemented into the *CRYSTAL-03* computer code. To clarify the nature of the interfacial bonding, we use slab models of the $\text{Cu}/\text{BaTiO}_3(001)$ interfaces with different one-side substrate coverages, varied from 1/8 monolayer (ML) up to 1/2 ML, over both TiO_2 - and BaO -terminated surfaces. TiO_2 termination has been found to be energetically more favorable for the adsorption of copper atoms. In agreement with previous experimental and theoretical data, our calculations indicate essential contribution of atomic polarization into the interaction between Cu atoms and surface O^{2-} ions. An increase of substrate coverage by copper simultaneously reduces the (*per adatom*) binding energy and enhances the interatomic interactions inside growing metallic film.

In collaboration with *Max Planck Institute for Solid State Research, Stuttgart, Germany*, we continue first principles calculations on the $\text{AgCl}(111)$ slabs of various thickness as well as the $\text{AgCl}(111)/\alpha\text{-Al}_2\text{O}_3(0001)$ interface using procedure of geometry optimization realized in both CRYSTAL'03 and VASP codes. For optimal adsorption configuration of silver chloride film on the corundum substrate we have shown enhanced probability of diffusion of Ag^+ ions, which may cause ionic conductivity, which is predicted from experimental studies of this interface.

STORAGE PHOSPHOR AND IMAGE PLATE DEVELOPMENT FOR NEUTRON IMAGING

A.I. Popov,

D.A.A. Myles and F. Dauvergne (*EMBL, Grenoble, France*),

C. Wilkinson (*King's College London, UK*)

Storage phosphor imaging plate (IP) are widely used as two-dimensional integrating position-sensitive detector based on the effect of photo-stimulated luminescence (PSL). By admixture of Gd_2O_3 the storage phosphor can be sensitized to thermal neutrons utilizing the extremely high absorption cross section of gadolinium in this energy range. In collaboration with *European Molecular Biology Laboratory, Grenoble, France*, and *King's College London, UK*, we have studied neutron sensitive image plates in combination with a suitable scanning system, which exhibit excellent characteristics. We have performed comparative measurements PSL recorded using a Molecular Dynamics 'Storm' scanner (635 nm) after neutron irradiation of a number of new combinations of converter/storage phosphors. Measurements have been made for a number of advanced materials, in order to characterize the intrinsic fading of the PSL signal with time after neutron irradiation. The X-ray sensitivity and fading of several of these compounds have also been measured.

We have prepared image plates by layering Eu^{2+} doped BaSrFBr phosphor alternately with Gd_2O_3 converter. Prototype image plates have been constructed and tested using a spraying technique for the phosphor/converter. The method has the potential to produce large image plates with good uniformity. Use of optical spectroscopy for the characterization of radiation defect aggregation in oxide materials.