IPC Institut für Physikalische Chemie | RWTH AACHEN UNIVERSITY

Bunsen Colloquium

Defects and Diffusion in Solids

Application of new theoretical concepts

November 10-11, 2016
Institute of Physical Chemistry, RWTH Aachen University

Bunsen Colloquium on the occasion of the
75th birthday of Peter C. Schmidt

DBG

Welcome to RWTH Aachen University.

The past years have seen several Bunsen Colloquia devoted to reactivity as well as diffusivity in solids, topics that are of central importance in advanced materials research and engineering. This year's Bunsen Colloquium continues this series. It focuses on defects and diffusion in solids and on the application of new theoretical concepts. Understanding the microscopic properties of solids at the level of defects and diffusion mechanisms is critical for understanding the macroscopic properties of materials. Ever more powerful supercomputers and superior program packages now allow the complex behaviour of atoms and ions to be studied. Approximations that were previously required can now be neglected due to improved algorithms, as will be discussed at this Colloquium. Topics to be covered are, for example, the explicit consideration of phonon-electron coupling in quantum mechanical calculations for electronic conductivity and the application of time-dependent DFT methods to materials' research.

For me personally, this Bunsen Colloquium is of special importance since we host it on the occasion of the 75th birthday of Peter C. Schmidt. In our collaboration, which started more than 30 years ago, Peter Schmidt became a highly valued colleague and friend. It is a privilege to work with him on many different subjects and I hope we can continue our collaboration for a long time.

I hope you enjoy the Bunsen Colloquium and I am looking forward to many exciting discussions.

Manfred Martin

Gratefully acknowledged is financial support by:

FCI
FONDS DER CHEMISCHEN INDUSTRIE

HI MS
HELMHOLTZ-INSTITUTE
IONICS IN ENERGY STORAGE

PROGRAM

Thursday, November 10, 2016

12:00 – 13:00
Registration, Mounting of Posters, Snack

13:00 – 13:15
Opening of the Colloquium

Session 1

13:15 – 13:45
Stefan Blügel (Jülich)
Metastable states of HfO_2 suboxides and resistive switching

13:45 – 14:15
Walter Wolf (Wien)
Defect formation, diffusion, coalescence, precipitation – *ab initio* driven materials simulations for industrial needs

14:15 – 14:45
Volker Eyert (Potsdam)
Defects in solids: Blessing and curse – a view from industrial applications

14:45 – 15:15
Rainer Waser (Aachen)
Some fundamental aspects of redox-based memristive switching in metal oxides

15:15 – 16:00
Coffee Break and Poster Session **RED**

Session 2

16:00 – 16:30
Timo Jacob (Ulm)
Measuring an electrocatalyst's vital signs: the need for in operando studies

16:30 – 17:00
Jörg Neugebauer (Düsseldorf)
Point Defects at Finite Temperatures

17:00 – 17:30
Florian Müller-Plathe (Darmstadt)
Beyond equilibrium: New molecular dynamics approaches to diffusion and permeation

17:30 – 18:30
Poster Session **BLUE** with beer and pretzel

Friday, November 11, 2016

Session 3

9:30 – 10:00
Kurt Stokbro (Kopenhagen)
Comparison of computational approaches for calculating electron-phonon effects on electron transmission

10:00 – 10:30
Tomáš Bučko (Bratislava)
Simulations of activated processes using the DFT simulation package VASP

10:30 – 11:00
Coffee Break and Poster Session **GREEN**

11:00 – 11:30
Eberhard Gross (Halle)
Potential energy surfaces and Berry phases beyond the Born-Oppenheimer approximation: A fresh look at coupled electron-nuclear dynamics

11:30 – 12:00
Jürgen Janek (Gießen)
Lithium Solid Electrolytes – Thermodynamics and Transport Kinetics

12:00 – 12:15
Closing of the Colloquium

12:15
Snack and Departure

INVITED TALKS

Metastable states of HfO_2 suboxides and resistive switching

Konstantin Z. Rushchanskii, Marjana Ležaić, and Stefan Blügel
Peter Grünberg Institut and Institute for Advanced Simulation,
Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Oxides are a versatile class of materials that has garnered much interest because they display such unusual behaviors as flipping between insulating and conducting states, turning magnetism on and off, or even becoming superconducting. Many of these properties are related to oxygen vacancies. Oxides play an important role in resistive random access memories (RRAM), which are considered the next generation of memory devices, which combine the operation speed of volatile DRAM and the nonvolatile ability of flash technology in one device with good scalability. The initial state of the memory cell after electroforming is the filamentary state, about which we know very little if it comes to hard experimental data such as structure and composition on the atomistic scale. The role of oxygen vacancies is unclear. In this presentation we employ concepts and methods of computational crystal structure prediction combining evolutionary algorithms with density functional theory with the aim of translating data to knowledge in order to shine light on the structure and electronic structure of the filamentary state. We apply our investigations to hafnia (HfO_2), a simple binary oxide that is compatible with silicon technology. Thin films of which have valence change memory properties. The main focus is given to suboxides in close vicinity of the HfO_2 ground state, in order to search for possible metastable structures in oxygen deficient conditions. We find metastable crystalline structures, which could occur in the electroforming process and allow for a reversible resistive switching. The obtained structures favor ionic conductivity of oxygen. We characterize electronic and vibrational properties of these phases in order to compare them with experimental data.

We acknowledge financial support by the Helmholtz Young Investigators Group Programme VH-NG-409 and by the DFG through the SFB917 (Nanoswitches). Computations were performed under the auspices of the Jülich Supercomputing Centre of the Forschungszentrum Jülich.

Defect formation, diffusion, coalescence, precipitation – *ab initio* driven materials simulations for industrial needs

Walter Wolf
Materials Design s.a.r.l., 42, avenue Verdier, 92120 Montrouge, France.

Point defects and their mobility play a decisive role for the macroscopic performance of modern materials. Scope and magnitude thereby range from as-designed defect and dopant implantation for tuning electronic devices, to detrimental effects on the mechanical properties of high-strengths alloys due to hydrogen embrittlement and stress-corrosion cracking, up to defect cascades and hydrogen uptake emerging during irradiation of cladding materials under nuclear reactor conditions, resulting in hydrogen induced swelling and breakaway growth. Designing properties as well as addressing materials problems require control and understanding of defect formation, diffusivity and diffusion anisotropy, interaction between defects and the propensity to coalesce thus forming extended defects such as dislocation loops, absorption and dissolution up to the solubility limit, eventually leading to precipitation processes when exceeding the solubility product. Atomistic simulations, and in particular the predictive power of ab initio methods, can have a tremendous impact for the research process, given that each phase of the defect evolution, as paradigmatically sketched above, could be addressed on their appropriate length and time scales. From a methodological point of view multiscale approaches are needed, allowing to extend the predictive power of ab initio methods to much larger time and length scales and millions of configurations. Within the MedeA® modeling environment of Materials Design a seamless integration of such approaches - for instance the Cluster Expansion Technique and Forcefield optimization - offers a high level of automation and interoperability for enhancing the productivity of the overall research process. Computational methods will be briefly outlined and recent applications for research activities addressing industrial materials problems and design will be summarized. Thus, highlights of an extensive study of hydrogen induced irradiation growth of Zircaloy including the impact of alloying elements will be presented, revealing for instance a pronounced retardation effect of self-interstitial Zr diffusion by Nb and Sn alloying additions. In the context of a screening study on candidate phases for precipitation hardening of steels, the accurate computation of solubility products establishing alloy compositions for casting and heat treatment will be outlined, and the monitoring of phase stability and composition-temperature dependent precipitation processes by means of large scale Monte Carlo simulations will be demonstrated for Ni-Cr alloy systems.

Defects in solids: Blessing and curse – a view from industrial applications

Volker Eyert
Materials Design SARL, 42 Avenue Verdier, 92120 Montrouge, France.

While the concepts of crystalline periodicity, reciprocal space, and electronic band structures have proven very powerful for the understanding of solids and for this reason shaped the mindset of generations of chemists, physicists, and materials scientists, imperfections have long been regarded throughout as unwanted but unavoidable perturbations, causing, *e.g.*, materials fatigue due to embrittlement and cracking at the microscopic scale or failure of electronic devices. Only more recently, as with the rapid progress in experimental and theoretical techniques our ability to understand and tune materials properties at the nanoscale has tremendously grown, a more active handling of crystalline imperfections has come into reach, which opened a new research field for materials research. Providing deep insight paired with a high predictive power, atomistic simulations have a large share in this development. Indeed, it would not have become possible without the tremendous increase of capabilities in atomistic simulations, both with respect to methodological developments in multiscale modeling and the explosive increase of computational resources. The MedeA® computational environment of Materials Design has condensed this progress and offers the unique possibility of a comprehensive tool to understand and predict a large variety of properties of all kinds of materials. In my talk I will present some of the capabilities of MedeA and illustrate them with a range of examples. In doing so, I will focus on success stories, where defects and dopants have been used to optimize materials properties or else where the detrimental effect of impurities has been traced back to their roots and overcome as, *e.g.*, at grain boundaries. Examples are taken from battery research and electronics applications.

Some fundamental aspects of redox-based memristive switching in metal oxides

Rainer Waser, Ilia Valov, Regina Dittmann, Stephan Menzel
JARA-FIT & PGI-7/10, Forschungszentrum Jülich, 52425 Jülich, Germany.
IWE2, RWTH Aachen University, 52056 Aachen, Germany.

Redox-Based Resistive Switching Memories (ReRAM), also called *nanoionic* memories or *memristive* elements, are widely considered to provide a potential leap beyond the limits of Flash (with respect to write speed, write energies) and DRAM (with respect to scalability, retention times) as well as energy-efficient approaches to neuromorphic concepts.

In this talk, some fundamental aspects of the physics and chemistry (lattice disorder, ionic and electronic transport processes, and phase formation) of these elements will be presented. In particular, the ultra-high non-linearity of the switching kinetics of redox-based resistive switching devices will be discussed with an emphasis on the so-called valence change mechanism (VCM) typically encountered as a bipolar switching in metal oxides. The involved electrochemical and physical processes can be either electric field/voltage enhanced or accelerated by a local increase in temperature due to Joule heating. The analysis of the published SET switching kinetics data of VCM-type ReRAM systems showed that their nonlinearity is mainly dominated by temperature-accelerated ion hopping, controlled by the local power during the switching process. The gradual RESET transition can be explained in terms of temperature-accelerated ion movement with counter-acting ion drift and diffusion processes. It will be shown that a designated combination of oxides can significantly improve the long-term kinetics, i.e. the retention time, by tailoring the ion diffusion properties in the oxide layers.

Measuring an electrocatalyst’s vital signs: the need for in operando studies

Timo Jacob
Institute of Electrochemistry, Ulm University, Albert-Einstein-Allee 47, 89081 Ulm, Germany.

Batteries, fuelcells, photocells and many other applications are powered by fundamental electrochemical processes. Compared to surface science under UHV conditions, electrochemical systems combine a wide variety of additional effects. These range from the presence of an electrolyte and a multi-component environment to reaction conditions such as finite temperature, pressure, and electrode potential. Due to this complexity our knowledge of the ongoing processes is mostly limited to the macroscopic regime. However, nowadays interface-sensitive experiments together with theoretical modeling are able to provide deeper insights into structures and processes at the atomic level. This fundamental knowledge makes the development and/or design of improved (electro)catalysts possible.

Following a general overview of electrochemistry, I will compare the concepts of surface science and electrochemistry in detail, addressing both their similarities and differences. Using apparently simple electrocatalytic reactions as model systems, the effects of the reactive surrounding as well as environmental parameters will be successively explored [1,2]. It turns out that pure and perfect catalyst models, which are often used in literature, are in many cases insufficient.

Finally, these concepts will be extended from single crystals to the nanoregime, where nanostructured surfaces and particles are often used for electro-catalytic reactions. Taking transition metal alloys as an example, we will show that nanoparticles are not rigid objects but often change their morphologies and compositions under reaction conditions [3-5]. Thus, understanding the dynamic nature of these catalysts is crucial in our efforts to further extend our ability to rationally design multi-component (electro-)catalysts.

[1] J. A. Keith, T. Jacob, Angew. Chem. Int. Ed. 49 (2010) 9521.

[2] W. Gao, J. A. Keith, J. Anton, T. Jacob, J. Am. Chem. Soc. 132 (2010) 18377.

[3] H. Hoffmannova, M. Okube, V. Petrykin, P. Krtil, J. E. Mueller, T. Jacob, Langmuir 29 (2013) 9046.

[4] M. Okube, V. Petrykin, P. Krtil, J. E. Mueller, D. Fantauzzi, T. Jacob, Chem. Electro. Chem. 1 (2014) 207.

[5] J. E. Mueller, P. Krtil, L. A. Kibler, T. Jacob, Phys. Chem. Chem. Phys. (Perspectives) 16 (2014) 15029.

Point Defects at Finite Temperatures

Jörg Neugebauer, Albert Glensk, Blazej Grabowski, and Tilmann Hickel
Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany.

The key quantity to characterize intrinsic as well as extrinsic point defects with respect to occurrence, concentration and behavior is their temperature dependent Gibbs free formation energy. An accurate determination of defect formation energies over the entire temperature window, i.e. from $T = 0$ K all the way up to the host melting temperature, is challenging both for experiment and theory. Recent methodological advances provide now the opportunity to compute all contributing excitation mechanisms with high precision on a fully ab initio basis, making it possible to derive free energies for bulk systems and defects up to the melting temperature. Applying these approaches to vacancies in fcc metals we were able to derive vacancy formation energies for the entire temperature range. We find that non-Arrhenius effects are unexpectedly large, in a temperature region not accessible to experiment and qualitatively affect our understanding of point defect formation energies and entropies. Particularly, it will be shown that hitherto reported defect energies are off by 10-20% and entropies even by an order of magnitude, calling for a revision of commonly used data sets.

Beyond equilibrium:
New molecular dynamics approaches to diffusion and permeation

Florian Müller-Plathe
Technische Universität Darmstadt, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Alarich-Weiss-Str. 8, 64287 Darmstadt, Germany.

Molecular dynamics offers a direct way of studying transport processes in condensed media. For most transport coefficients, a host of robust procedures and protocols have been established. For the transport of momentum (shear viscosity) and energy (thermal conductivity), so-called reverse non-equilibrium molecular dynamics has become the method of choice. It reverses the usual cause-and-effect relation, as it artificially imposes the relevant fluxes and measures the resulting thermodynamic driving forces, which are usually gradient of some thermodynamic variables. The extension to mass (diffusion) and charge transport (ionic conductivity) is, however, not straightforward. We will describe the first developments in this direction.

Further reading:

[1] H. Yang, J. Zhang, F. Müller-Plathe, and Y. Yang, Chem. Eng. Sci. 130, 1–7 (2015). [DOI: 10.1016/j.ces.2015.03.006]

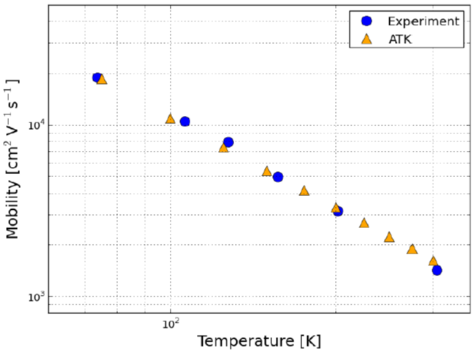
[2] H. Yang, J. Zhang, and F. Müller-Plathe, Mol. Sim. (accepted) [DOI: 10.1080/08927022.2015.1114178].

Comparison of computational approaches for calculating electron-phonon effects on electron transmission

Kurt Stokbro
QuantumWise A/S, Fruebjergvej 3, 2100 Copenhagen, Denmark.

In this presentation I will present and compare 3 different approaches calculating the effect of electron-phonon interaction on the transmission in nanoscale systems. In the first approach we calculate the dynamical matrix and the electron-phonon interaction using finite differences and subsequently calculate the electron mobility by solving the Boltzman equation in the relaxation-time approximation[1]. In the second approach we include the electron-phonon interaction through an additional self-energy in the electron transmission calculation, and solve for the transmission in the first Born approximation[2]. In the third approach we perform MD simulation of the device and average the transmission over the MD trajectory[3].

I will present calculations for the electron transmission and mobility in 1D, 2D and 3D geometries for both semiconductors and metals and the merits of the different approaches will be compared. Future directions for simulating realistic device geometries including the electron-phonon interaction will be discussed.



Theoretical calculation of the phonon-limited mobility of Silicon compared with experimental data.

[1] T. Gunst, T. Markussen, K. Stokbro, M. Brandbyge, First-principles method for electron-phonon coupling and electron mobility: Applications to 2D materials, Phys. Rev. B **93**, 035414 (2016).

[2] Tue Gunst, Troels Markussen, Kurt Stokbro, and Mads Brandbyge, Inelastic vibrational signals in electron transport across graphene nanoconstrictions, Phys. Rev. B **93**, 245415 (2016).

[3] Troels Markussen, Mattias Palsgaard, Daniele Stradi, Tue Gunst, Mads Brandbyge, and Kurt Stokbro, Electron-phonon scattering from Green's function transport combined with Molecular Dynamics: Applications to mobility predictions. In preparation

Simulations of activated processes using the DFT simulation package VASP

Tomáš Bučko
Comenius University in Bratislava, Ilkovičova 6, SK-84215 Bratislava, Slovakia
and Slovak Academy of Sciences, Dúbravská cesta 9, SK-84236 Bratislava, Slovakia.

The simulations of activated processes, which play an important role in chemistry and materials physics, have until recently been limited to “static approach” based on atomic relaxations, sometimes followed by analysis of potential energy surface near the relevant stationary points via harmonic approximation. More accurate schemes, in which the relevant thermodynamic quantities (most prominently the free-energy of activation) are computed by sampling the proper statistical ensembles, have been developed as early as in 1970s but until recently they were used only within the framework of forcefield simulations. Although the computational power commonly available today allows us to combine these approaches with quantum-mechanical calculation of forces, the applications to the “real-world” problems are still relatively scarce and the old-fashioned “static approach” still dominates the realm of computational chemistry and materials physics. Clearly, in order to reverse this situation, the sophisticated methods designed to study activated processes must be available in major simulation packages. In my contribution I will introduce our implementation of advanced molecular dynamics methods into the popular DFT code VASP[1,2] and I will discuss some practical aspects related to their application.

[1] Kresse G and Hafner J 1993 *Phys. Rev. B* **48** 13115

[2] http://cms.mpi.univie.ac.at/vasp/vasp/Advanced_MD_techniques.html

Potential energy surfaces and Berry phases beyond the Born-Oppenheimer approximation: A fresh look at coupled electron-nuclear dynamics

Eberhard K.U. Gross
Max-Planck Institute of Microstructure Physics, Halle (Saale), Germany

The Born-Oppenheimer approximation is among the most fundamental ingredients of modern Theoretical Chemistry and Condensed-Matter Physics. This approximation not only makes calculations feasible, it also provides us with an intuitive picture of chemical reactions. Yet it is an approximation, and some of the most fascinating phenomena, such as photovoltaic dynamics, diffusion in solids, the process of vision, as well as phonon-driven superconductivity occur in the regime where the Born-Oppenheimer approximation breaks down. To tackle such situations one has to face the full Hamiltonian of the complete system of electrons and nuclei. We deduce an exact factorization of the full electron-nuclear wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for these wavefunctions lead to a unique definition of *exact* potential energy surfaces as well as *exact* geometric phases [1], both in the time-dependent and in the static case. We discuss a case where the exact Berry phase vanishes although there is a non-trivial Berry phase for the same system in Born-Oppenheimer approximation, implying that in this particular case the Born-Oppenheimer Berry phase is an artifact [2]. In the time-domain, whenever there is a splitting of the nuclear wavepacket in the vicinity of an avoided crossing, the exact time-dependent surface shows a nearly discontinuous step [3]. This makes the classical force on the nuclei jump from one to another adiabatic surface, reminiscent of Tully surface hopping algorithms. Based on this observation, we propose novel mixed-quantum-classical algorithms [4] which provide a rather accurate, much improved (over surface hopping) description of decoherence. Finally we present a multi-component density functional theory [5] that provides an avenue to make the fully coupled electron-nuclear system tractable in practice.

[1] A. Abedi, N.T. Maitra, E.K.U. Gross, Phys. Rev. Lett. **105**, 123002 (2010).
[2] S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, Phys. Rev. Lett. **113**, 263004 (2014).
[3] A. Abedi, F. Agostini,Y. Suzuki, E.K.U. Gross, Phys. Rev. Lett. **110**, 263001 (2013).
[4] S.K. Min, F. Agostini, E.K.U. Gross, Phys. Rev. Lett. **115**, 073001 (2015).
[5] R. Requist, E.K.U. Gross, Phys. Rev. Lett. (2016, in press)

Lithium Solid Electrolytes – Thermodynamics and Transport Kinetics

Jürgen Janek, Wolfgang Zeier and Dominik Weber
Institute of Physical Chemistry & Laboratory of Materials Science (LaMa),
Justus Liebig University, Gießen, Germany.

Lithium solid electrolytes currently attract strong interest as potential key components of solid state lithium batteries [1]. In the past, the search for superior lithium solid electrolytes relied mainly on chemical intuition and deep knowledge of solid (lattice) structures and their potential transport paths for mobile ionic defects. Meanwhile computational approaches become more important, and recently the simulation of solid electrolytes and their interface stability helps to rationalize solid electrolyte research.

In this lecture we will summarize briefly the state of research on stable lithium solid electrolytes. Lithium solid electrolytes with conductivities higher than of liquid electrolytes are today available [2] and may enter into batteries. However, a critical issue is the stability of superior solid electrolytes in contact with electrodes [3]. Long term operation of solid electrolytes requires stability against reduction at the anode and against oxidation at the cathode. Results from theoretical calculations are reviewed and compared with own experimental studies.

[1] A solid future for battery development, J. Janek and W. Zeier, Nat. Energy 1 (2016) 16141

[2] Structural insights and 3D diffusion pathways within the lithium superionic conductor $Li_{10}GeP_2S_{12}$, D. Weber, A. Senyshyn, K. S. Weldert, S. Wenzel, W. Zhang, R. Kaiser, S. Berendts, J. Janek, and W. G. Zeier, Chem. Mater. 28 (2016) 5905-5915

[3] Interphase formation and degradation of charge transfer kinetics between a lithium metal anode and highly crystalline $Li_7P_3S_{11}$ solid electrolyte, S. Wenzel, D. Weber, T. Leichtweiss, J. Sann, J. Janek, Solid State Ionics 286 (2016) 24-33

POSTER SESSION RED

Bulk and Surface Structure of $Li_4Ti_5O_{12}$

D. Mollenhauer, S. Zahn, K. S. Exner
Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff-Ring 17,
D-35392 Giessen, Germany.
Doreen.Mollenhauer@phys.chemie.uni-giessen.de

First principle calculations can provide a detailed understanding of the lithium diffusion in the solid state or at interfaces, the influence of nano structuring as well as doping effects at the atomistic level of materials relevant for lithium ion batteries (LIB). The start point for such theoretical investigations is the knowledge of the structure. Thus, in a first step of our study we have determined the preferred bulk structure of $Li_4Ti_5O_{12}$ by first principle calculations. [1] $Li_4Ti_5O_{12}$ is an promising alternative to carbon based anode materials in LIB which shows negligible volume change during Li-uptake to $Li_7Ti_5O_{12}$ due to advantageous structural rearrangement from spinel to rock-salt like crystal structure. [2] In a second step, the surface structure of an model $Li_4Ti_5O_{12}$(111) electrode under battery operating conditions has been investigated in order to be able to study lithium diffusion at interfaces. [3] The data also serve to understand size effects of lithium titanate nanoparticles relatet to stability or electrochemical properties. The studies have been extended to alumina doped lithium titanate material as well. The results of the calculations will serve to study and understand lithium ion dynamics in bulk, at interfaces and doped materials.

[1] S. Zahn, J. Janek, D. Mollenhauer, submitted to Journal of the Electrochemical Society.
[2] Zhao, B.; Ran, R.; Liu, M.; Shao, Z. Mater Sci. Eng. R: Rep. 2015, 98, 1–71.
[3] K. S. Exner, J. Anton, T. Jacob, D. Mollenhauer, Manuscript in preparation.

Enhancement of catalytic activity in the neighborhood of surface defects: the HCl oxidation over the chlorinated RuO_2(110) ($RuO_{(2-x)}Cl_x$) surface modeled by DFT-based atomic scale Kinetic Monte Carlo simulations

Franziska Hess and Herbert Over
Physikalisch-Chemisches Institut, Universität Gießen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany.

RuO_2 shows high catalytic activity and stability in the HCl oxidation (Deacon process). Model catalyst studies have pointed out the self-limiting surface chlorination as one of the factors contributing to the exceptional stability under the harsh reaction conditions. Unlike most other oxides, RuO_2 undergoes only superficial chlorination by exchanging some of the oxygen atoms in the terminal oxide layers by Cl when exposed to HCl and Cl_2. These Cl defects passivate the surface by preventing further HCl adsorption as well as deep chlorination. However, the terminal oxygen atoms act as a buffer in the mechanism of HCl oxidation over RuO_2(110) by accepting hydrogen from dissociated HCl. The hydrogen is then transferred in successive reaction steps onto weakly-bound oxygen adsorbed on undercoordinated Ru sites to form the secondary product, H_2O. Because Cl substituting terminal lattice oxygen has no active role in the mechanism of the HCl oxidation, it has been a matter of debate whether the superficial chlorination is exclusively beneficial (by stabilizing the surface), or can be detrimental as well (by reducing the number of catalytically active sites). The HCl oxidation reaction over the $RuO_2(110)$ surface was modeled using Density Functional Theory (DFT)-based Kinetic Monte Carlo (KMC) simulations. The total surface energy was modeled by a Lattice Hamiltonian with lateral interactions up to the third-nearest neighbor and directional hydrogen bonds. We simulated the reaction using the KMC method under industrially relevant conditions and examined the effect of different defect arrangements on the rate of product formation (Cl_2 and H_2O). Despite the fact that the substitution of terminal lattice oxygen by Cl reduces the number of active sites on the catalyst surface, we observe an enhancement of the catalytic activity. The activity enhancement is caused by the formation of especially active centers in the neighborhood of Cl defects, where the local rate of product formation is up to three times as high as the average product formation rate on the unchlorinated surface. This substantial enhancement of catalyst activity is caused by changing the thermodynamics of the rate-determining step of the reaction from thermoneutral to slightly exothermal, thus shifting the equilibrium of this intermediate step toward the product side. This increases the coverage of the weakly-bound hydroxyl groups, which are the precursors for H_2O formation. For low chlorination degrees specific arrangements of Cl defects are identified that form centers with superior activity. Excessive chlorination, however, was found to severely inhibit the catalyst activity, even in the direct neighborhood of the Cl defects, because the ability of the remaining terminal O atoms to accept hydrogen from HCl (i.e., to act as a buffer and transfer agent for hydrogen) is severely diminished when numerous Cl defects are present on the surface.

Simulation and analysis of configurational diffusion of Li ions in occupationally disordered battery materials

Hendrik H. Heenen
Chair for Theoretical Chemistry and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany.

Spinel-type lithium-titanium-oxide ($Li_4Ti_5O_{12}$, LTO) is known as an extraordinarily robust and long-living anode material thanks to its negligible volume change during Li intercalation [1]. In an attempt to provide atomistic insight, first-principles electronic structure calculations have been used before to rationalize this phenomenon in terms of certain underlying elementary ion transport processes [2-4]. Such studies are, however, challenged by a mixed occupancy of octahedral sites by Li and Ti ions in LTO. The resulting occupational disorder in this material is only inadequately represented in the limited periodic supercells of formally correct stoichiometry that are tractable by DFT.

In this study, we overcome this limitation with the use of a reliable, first-principles parametrized interatomic force-field potential [5]. Based on extensive Monte Carlo sampling, the configuration space is explored and the effect of disorder on Li ion diffusion is evaluated via subsequent molecular dynamics (MD) simulations. We show how structural disorder favors localized Li ion mobility and elaborate on the complex details of the underlying diffusion mechanism based on a thorough microscopic analysis. Identifying elementary steps via a discretization procedure we gain access to structural motives piecing together the correlated Li ion motion. This prepares the ground for systematically coarse-graining the MD data yielding a kinetic Monte Carlo model, which enables simulations approaching experimental length and time scales.

[1] S. Scharner, W. Weppner, P.Schmid-Beurmann, J. Electrochem. Soc. 1999, 146, 857
[2] B Ziebarth, M. Klinsmann, T. Eckl, C. Elsässer, Phys. Rev. B 2014, 98, 174301
[3] P.C. Tsai, W.D. Hsu, S.K. Lin, J. Electrochem. Soc. 2014, 161, A439
[4] V. Weber, et al., J. Phys. Chem. C 2015, 119, 9681–9691
[5] M. Vijayakumar et al., J. Power Sources 2011, 196(4), 2211

A site non-stoichiometric lead-free $0.94(Na_yBi_x)TiO_3$-$0.06BaTiO_3$ ceramics

In-Tae Seo, Sebastian Steiner and Till Frömling
Institute of Materials Science, Technische Universität Darmstadt, FB Nichtmetallische-Anorganische Werkstoffe, Alarich-Weiss-Strasse 2, D-64287 Darmstadt, Germany.

The conduction behavior of lead-free ferroelectric $Na_xBi_yTiO_3$ (N_xB_yT) ceramics was well established by Ming Li et. al. Only small changes in the A-site stoichiometry have a significant impact on the conductivity of N_xB_yT ceramics. High values of oxygen ionic conductivity were reached which are in the order to magnitude of excellent oxygen conductors like yttrium stabilized zirconia. Because $0.94(Na_yBi_x)TiO_3$-$0.06BaTiO_3$ (N_yB_xT-BT) ceramics are most promising candidates for lead-free ferroelectric applications, evaluating the impact of changes in A-site stoichiometry on conduction behavior of these ceramics is also major importance. Therefore, effect of A-site non-stoichiometry on the N_yB_xT-BT ceramics was systemically studied in this work. In detail, discussion on the defect chemistry of the N_yB_xT-BT material will be presented which is based on the results obtained from temperature dependent impedance spectroscopy investigations. There is an increase in conductivity due to Bi deficiency but it is by far not as extensive as for pure NBT. While Bi deficiency leads to a dominating ionic contribution for NBT ceramics, electronic conductivity can be still dominant for NBT-BT. However, not only the conductivity, but also the grain growth and piezoelectric constants are influenced by the presence of defects. Hence, the control of the stoichiometry is very important and offers a new way to modify the conduction behavior and piezoelectric response.

Oxygen defects in LTO –
Structural Models and Adapted DFT Treatments

Markus Schuderer, Christoph Scheurer, Karsten Reuter
Chair for Theoretical Chemistry, Technische Universität München, Garching, Germany.

Spinel-structured $Li_4Ti_5O_{12}$ (LTO) is widely studied as a promising anode material for all solid state lithium ion batteries due to its ”zero strain” property during charge/discharge cycles. The limited electronic conductivity of pristine stoichiometric LTO poses a problem in battery applications, which may be overcome e.g. by synthesis under reducing conditions, thereby introducing oxygen vacancies in the material. Experimental results suggest a concomitant reduction of individual titanium ions [1, 2] rendering DFT calculations rather challenging: structural changes in the vicinity of the oxygen vacancies demand the use of large supercells to reduce the artificial interaction of defects with their periodic images while a proper description of electron localization on the transition metal ions can only be achieved using computationally demanding hybrid DFT functionals.

To develop a reliable computational model for the effect of oxygen vacancies on the relevant conduction properties of LTO as a battery electrode material, various structural models are developed and cross validated in combination with different electronic structure methods. To that end we use the CASTEP [3] DFT code, representative for plane-wave basis set and pseudopotential methods, on the one hand and on the other hand the all-electron FHI-aims [4] DFT code with numeric atom-centered orbitals, which allows for computations in periodic boundary conditions as well as finite embedded cluster models. For both codes results from the GGA-functional PBE [5] and the hybrid functional HSE06 [6] are compared and combined with different energy cutoffs and basis sets, respectively, to arrive at a description of the defect with an optimal balance of accuracy vs. computational effort. Large supercells (up to 167 atoms) have been constructed and combined with the HSE06 hybrid functional to achieve a proper localization of the surplus electron density (reduced Ti ions) without computational artifacts. These computations serve as benchmarks for further cluster model calculations based on the QM/MM embedding scheme recently implemented in FHI-aims [7]. This paves the way towards cluster model studies of surface and, more general, interface oxygen defects.

[1] J. Wolfenstine, U. Lee, J. L. Allen, J. Power Sources **2006**, 154, 287.

[2] P. Jakes, J. Granwehr, H. Kungl, R.-A. Eichel, Z. Phys. Chem. **2015**, 229, 1263.

[3] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M.C. Payne, Z. Kristall. **2005**, 220, 567.

[4] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, Comput. Phys. Commun. **2009**, 180, 2175.

[5] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **1996**, 77, 3865.

[6] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, G. E. Scuseria, J. Chem. Phys. **2006**, 125, 224106.

[7] D. Berger, A. J. Logsdail, H. Oberhofer, M. R. Farrow, C. R. A. Catlow, P. Sherwood, A. A. Sokol, V. Blum, and K. Reuter, J. Chem. Phys **2014**, 141, 024105.

Aluminium-26 grain boundary diffusion in polycrystalline α-Al_2O_3: Comparison of experiment and simulation

Peter Fielitz, Günter Borchardt
Technische Universität Clausthal, Institut für Metallurgie, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany, peter.fielitz@tu-clausthal.de

Polycrystalline α-Al_2O_3 is an important refractory material with numerous technical applications. In the polycrystalline microstructures the transport properties of the grain boundaries are of prime importance for the technological performance of α-Al_2O_3. However, to date directly measured grain boundary diffusivities exist only for oxygen using the rare stable oxygen isotope ^{18}O. We present recent directly measured aluminium grain boundary diffusivities in α-Al_2O_3 using the aluminium isotope ^{26}Al as a tracer in combination with Secondary Ion Mass Spectrometry. The measured ^{26}Al tracer diffusivities are compared with calculated diffusivities of aluminium in grain boundaries from the literature.

Defect chemistry and conductivity mechanisms in B-Site doped and A-Site non-stoichiometric $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)

Sebastian Steiner, Dr. In-Tae Seo, Dr. Till Frömling
Technische Universität Darmstadt, Darmstadt, Germany.

As recently reported, the A-site non-stoichiometry as well as the B-site acceptor doping of NBT has a dramatic influence on the oxygen vacancy concentration and ionic conductivity [1, 2]. Mg-doped NBT shows extremely high oxygen ion conductivity comparable with conventionally used solid oxygen ion conductor materials. Considering experience with other lead based or lead free ferroelectric ceramics, this was a rather unexpected result. The origin and defect chemical reason for these results are part of important ongoing research approaches. In this work, we will discuss the formation and effect of oxygen vacancies in A-site non stoichiometric and B-site doped $Na_{0.5}Bi_{0.5}TiO_3$. With the help of temperature and DC-voltage dependent impedance spectroscopy (IS) the defect chemistry and the charge carrier migration process was investigated. From these results we are able to propose how the investigated changes to NBT may affect other NBT related materials.

[1] Li M., Pietrowski M.J., De Souza R.A., Zhang H., Reaney I.M., Cook S.N., et al. Nat. Mater. 2014, 13(1): 31-35.

[2] Li M., Zhang H., Cook S.N., Li L., Kilner J.A., Reaney I.M., et al. Chemistry of Materials 2015, 27(2): 629-634.

Phase formation and stability in extremely non-stoichiometric TiOx and ZrOx thin films

Thomas Leichtweiss[a)], Ralph A. Henning[b)], Daniel Dorow-Gerspach[c)], Rüdiger Schmidt[c)], Niklas Wolff[d)], Ulrich Schürmann[d)], Yannic Decker[b)], Lorenz Kienle[d)], Matthias Wuttig[c)]*, and Jürgen Janek[a), b)]
a) Center for Materials Research, Justus Liebig University Giessen, Heinrich Buff Ring 16, 35392 Giessen, Germany.
b) Institute of Physical Chemistry, Justus Liebig University Giessen, Heinrich Buff Ring 17, 35392 Giessen, Germany.
c) Institute of Physics (IA), RWTH Aachen University, Sommerfeldstraße 14, 52056 Aachen, Germany.
d) Faculty of Engineering, Christian-Albrechts-Universität zu Kiel, Kaiserstrasse 2, 24143 Kiel, Germany.

Most functional materials are thermodynamic equilibrium phases and represent minima in thermodynamic phase space. However, much less is known about metastable non-equilibrium phases, which also may possess highly interesting properties. Here, we report on a systematic approach to prepare thin-films of such phases by sputtering and by Pulsed Laser Deposition (PLD). Our synthetic strategy is to deposit a “precursor phase” which is amorphous or already a crystalline non-equilibrium phase. Subsequent heat treatment leads to the nucleation of crystalline phases which may be again metastable or stable compounds. Here, we focus on the binary systems Ti-O and Zr-O, both systems being widely applied and technologically relevant.

Highly oxygen-deficient titanium oxide ($TiO_{1.6}$) and zirconium oxide (ZrO) films prepared by PLD at room temperature are optically absorbing and show electronic conductivities in the range of 10 S/cm. Both materials are metastable in respect composition and structure. For $TiO_{1.6}$ we find an amorphous matrix with embedded grains of cubic titanium monoxide (γ-TiO) directly after deposition. Upon annealing nanocrystalline grains of metallic Ti are formed in the matrix driven by an internal solid-state disproportionation whereas the electrical conductivity of the films increases and comes close to metal-like conductivity (1000 S/cm) at about 450 °C. Similarly, room temperature deposited ZrO films with an average composition of Zr:O = 1:1 contain small ZrO nanocrystals within an amorphous matrix. Heat treatment again leads to an internal disproportionation reaction and small crystals of Zr_2O and ZrO_2 precipitate at temperatures as low as 75 °C. Increasing the temperature then results in the crystallization of metastable tetragonal ZrO_2 at about 400 °C.

Evaluation of Density Functional Theory for Lithium Ion Migration in 1T-LiTiS2

Vanessa Werth[1,]*, Mohammad M. Islam[2], Kai T. Volgmann[1], Paul Heitjans[1], Thomas Bredow[2]
[1]Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstr. 3-3a, 30167 Hannover, Germany.
[2]Mulliken Center for Theoretical Chemistry, Universität Bonn, Beringstr. 4-6, 53115 Bonn, Germany.
*vanessa.werth@pci.uni-hannover.de

Weak interactions and properties of solids containing transition metals are often problematic to describe with standard generalized gradient approximations (GGA). One challenge for GGA is the experimentally well studied host material 1T-TiS_2, where lithium is the most prominent intercalation material. The addition of dispersion corrections[1,2,3] and an on-site Coulomb repulsion term[4] to the Perdew-Burke-Enzernhof (PBE) functional is studied[5] using the plane-wave program package VASP. An overall improvement to experimental data can be observed in comparison to the PBE functional. The most significant improvement is the structural description, in particular the *c* lattice parameter, of TiS_2 and the calculated band gap of TiS_2. Also quadrupole coupling constants and chemical shifts are closer to experimental data, if both correction terms are included. The calculated activation energy in 1T-Li_xTiS_2 for $x \approx 1$ for a Li ion migration to a tetrahedral interstitial position is 0.4 eV and close to experimental values.

[1] Grimme, S. and Antony, J. and Ehrlich, S. and Krieg, H. A consistent and accurate ab intio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. The Journal of Chemical Physics **2010**, 132, 154104.

[2] Grimme, S. and Ehrlich, S. and Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. Journal of Computational Chemistry **2011**, 32, 1456–1465.

[3] Tkatchenko, A. and Scheffler, M. Accurate Molecular Van der Waals Interactions from Ground-State Electrin Density and Free-Atom Reference Data. Physical Review Letters **2009**, 102, 073005.

[4] Dudarev, S. L. and Botton, G. A. and Savrasov, S. Y. and Humphreys, C. J. and Sutton, A. P. Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study. Physical Review B **1998**, 57, 1505–1509.

[5] Werth, V. and Islam, M. M. and Volgmann, K. T. and Heitjans, P. and Bredow, T. Evaluation of Density Functional Theory for Lithium Ion Migration in 1T-$LiTiS_2$ **2016** (*in preparation*).

POSTER SESSION BLUE

Field-enhanced Ion Transport Revisited

A. R. Genreith-Schriever[1] and R. A. De Souza[1, 2]
[1]Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen, Germany.
[2]JARA-FIT, 52056 Aachen, Germany.

Classical molecular-dynamics simulations were used to examine the effect of an electric field on the mobility of oxygen ions in the model crystalline oxide CeO_2. Simulation cells containing oxygen vacancies were subjected at temperatures $1000 \leq T/K \leq 1600$ to electric field strengths $0.1 \leq E/\text{MV cm}^{-1} \leq 40$ to obtain the oxygen-ion mobility $u_\text{i}(E,T)$. Simulations were performed up to field strengths that are difficult to apply in transport experiments but that maybe reached in space-charge layers at interfaces or in resistive switching devices. In addition, static Nudged-Elastic-Band calculations were performed to obtain directly the forward/reverse barriers for oxygen-ion migration, $\Delta H_\text{mig}^\text{f/r}$. Qualitatively, u_i behaves as expected: independent of E at low values of E and exponentially dependent on E at high values. We find that neither the standard Mott–Gurney expression nor the alternative Fromhold–Cook expression is able to describe the observed behavior [$\Delta H_\text{mig}^\text{f/r}(E)$ and $u_\text{i}(E)$]. On this basis we derived a new expression. Our approach predicts a critical field strength at which the crystal becomes unstable (E_cr). Furthermore, it describes exactly $\Delta H_\text{mig}^\text{f/r}(E)$ up to E_cr and $u_\text{i}(E)$ up to ca. 0.5 E_cr.

Origin and Influence of the Electronic Current in thin Oxide Resistive Switching Layers

C. Funck[1], P. C. Schmidt[4]; M. Martin[3], R. Waser[1,2] and S. Menzel[2]
[1]Institut für Werkstoffe der Elektrotechnik II, RWTH Aachen University, 52074 Aachen, Germany.
[2]Peter Grünberg Institut, Research Center Jülich, 52428 Jülich, Germany.
[3]Institut für Physikalische Chemie, RWTH Aachen University, 52074 Aachen, Germany.
[4]Physikalische Chemie, TU Darmstadt, 64287 Darmstadt, Germany.

The upcoming class of redox based resistive switching devices is a promising technology for new memories. The key to understanding those ReRAM cells is obtained by the defect chemistry. In this study, we will show how the defect chemistry and physics modulates the electronic transport by means of density functional theory in combination with the non-equilibrium Greens function method. Especially, we will show a Schottky contact between $SrTiO_3$ and Pt, which is modified by the presence of an oxygen vacancy in front of this contact. This allows us to determine the dominating conduction mechanism and to investigate the temperature dependence of the electrical current. From this point of view, we will present a continuum resistive switching model based on the movement of oxygen vacancies, which act as mobile donors. Here, the special dependence of the switching behaviour on the electronic mobility is highlighted.

Influence of Texture and Misorientation on the O^{2-} Conduction in YSZ / Rare Earth Sesquioxides Multilayers – Interface Strain in Competition with Blocking Grain Boundaries

C. Korte*[,a], J. Keppner[a,b], A. Peters[b], N. Schichtel[b], H. Aydin[b] and J. Janek[b]
[a] Institut für Energie- und Klimaforschung (IEK-3), Forschungszentrum Jülich
[b] Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen

Ionic conduction in micro- and nanoscaled thin films differs significantly compared to bulk phase transport which can be attributed to the special transport properties in interfaces and surfaces. Boundaries transport between ionic materials is still less understood. In the case of extrinsic ionic conductors with a high concentration of mobile point defects (solid electrolytes) theoretical models based on the formation of space charge regions close to the interfaces are only limited applicable. Structural parameters like misfit dislocations and less dense packed interface regions, get in the focus of interest. Interface strain as an origin of an increased (or decreased) ionic transport along interfaces is intensely discussed. By reviewing the literature data, one observes that the reported magnitudes of the strain/interface effects differs unfortunately several orders of magnitude [1].

In this study the O^{2-} ion transport in multilayers parallel to the phase boundaries and the interfacial strain states are measured vs. the layer thickness. The samples were prepared by pulsed laser deposition and consist of alternating layers of YSZ (extrinsic O^{2-} ion conductor) and an insulating rare earth metal sesquioxide RE_2O_3. The misfit induced strain is varied by changing the rare earth metal (Y_2O_3, Sc_2O_3, Dy_2O_3 and Er_2O_3). The O^{2-} ion transport of the YSZ layers is measured by impedance spectroscopy and ^{18}O tracer diffusion experiments; texture and interface strain is determined by XRD. The extent of the strained interface regions in the YSZ layers can be estimated to ~10 nm [2]. The results principally backup a model considering exponential decaying interface strain fields and a positive activation volume for the ionic transport. Tensile strain enhances and compressive strain decreases the interfacial transport compared to the bulk.

The preparation conditions and thus the texture of the layers have a strong influence on the measurable (thickness dependent) strain fields and the interface transport. Only in case of samples with two azimuthal orientation variants (or fibre texture), the interface strain induced effects on ionic transport can be detected as described by the model. In the case of highly textured samples with only one azimuthal orientation variant the anisotropic ionic transport completely superposes the strain induced effects. The influence of texture, grain boundaries and crystallite size is in the same order of magnitude as the influence of interface strain on the total transport in thin films.

[1] C Korte, J. Keppner, A. Peters, N. Schichtel, H. Aydin and J. Janek,
Phys. Chem. Chem. Phys. 16, 24575-24591 (2014)

[2] J. Keppner, C. Korte, J. Schubert, W. Zander, M. Ziegner and D. Stolten,
Solid State Ionics 273, 2-7 (2015)

Decomposition of $SrTiO_3$ induced by electrochemical stress

Christian Rodenbücher, Gustav Bihlmayer, Paul Meuffels, Rainer Waser, Kristof Szot
Peter-Grünberg-Institut and JARA-FIT, Forschungszentrum Jülich, 52425 Jülich, Germany.

Transition metal oxides are the key materials for future energy-efficient electronics in particular for logic and memory devices based on the resistive switching effect. Since the switching effect is related to a local reaction of the oxide to an external gradient of the electrical and chemical potential, we investigate the influence of electrochemical stress on the prototype perovskite $SrTiO_3$. We demonstrate that upon application of a DC voltage under UHV conditions, the surface region of alkaline earth titanates transforms into lower binary oxides with nanoporous structure. By means of IRT, XPS, EDX, HR-TEM, and LC-AFM we present that this transformation takes place at relatively low temperatures and is related to a fundamental macroscopic decomposition of the oxide changing the physical properties of the surface region up to depths of several tens of micrometers. Our results demonstrate that in ternary oxides phase transformations can be induced by gradients of the electrochemical potential. The presented method not only opens up a new way for tailoring micro layers of functional transition metal oxides with bespoke properties for optical, electronic and chemical applications but also demonstrates the mutability of metal oxides under electrical stress being relevant for the understanding of the electroforming and switching process in novel memristive devices.

Orientation dependent conductivity relaxation in titanium dioxide

K. Skaja[1], F. Gunkel[2], S. Hoffmann-Eifert[1], R. Dittmann[1], R. Waser[1,2]
[1]Peter Grünberg Institut, Forschungszentrum Jülich, 52425 Jülich, Germany.
[2]Institute of Electronic Materials (IWE II), RWTH Aachen University, 52056 Aachen, Germany.

The relaxation processes in rutile single crystals in (001) and (110) orientation as well as in polycrystalline TiO_{2-x} thin films deposited on r-plane sapphire single crystals were investigated by electronic conductivity relaxation measurements. The equilibration kinetics were studied for a temperature range of 1000 K – 1100 K under reducing oxygen partial pressure conditions. We show that a surface exchange process mainly controlled the relaxation in the studied single crystalline rutile. The surface exchange coefficient strongly depends on the surface orientation. The surface exchange process of the (001) orientation is orders of magnitude faster in comparison to the (110) orientation, which can be correlated to a lower formation energy of oxygen vacancies at the surface. A heterogeneous relaxation process controls the equilibration kinetics of the thin film. Two surface exchange coefficients for a slow and a fast process can be determined, which can be caused by different orientations of the grains or some inhomogeneities in the thin film by preparation. In contrast to the values for the single crystals, the surface exchange coefficients are one to two orders of magnitude lower. This may be induced by a retarding field due to an additional energy barrier at the grain boundaries. Furthermore, an oxygen partial pressure induced space charge potential at the surface might also influence the surface exchange process.

Surface Reconstructions and Related Local Properties of a $BiFeO_3$ Thin Film

L. Jin[1,2], P.X. Xu[3], Y. Zeng[1,4], L. Lu[4], J. Barthel[2,5], T. Schulthess[3], R. E. Dunin-Borkowski[1,2], H. Wang[4,6], C.L. Jia[1,2,4,6]
[1]Peter Grünberg Institute (PGI-5), Research Centre Jülich, D-52425 Jülich, Germany.
[2]Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C), Research Centre Jülich, D-52425 Jülich, Germany.
[3]Institute for Theoretical Physics, ETH Zürich, 8093 Zürich, Switzerland.
[4]The School of Electronic and Information Engineering, Xi’an Jiaotong University, Xi’an 710049, China.
[5]Central Facility for Electron Microscopy (GFE), RWTH Aachen University, D-52074 Aachen, Germany.
[6]State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, China.

Coupling between lattice and order parameters, such as polarization in ferroelectrics and/or polarity in polar structures, has a strong impact on surface relaxation and reconstruction. However, up to now, surface structures that involve the termination of both matrix polarization and polar atomic planes have received little attention, particularly on the atomic scale. Here, we study surface structures on multiferroic $BiFeO_3$ thin film using atomic-resolution scanning transmission electron microscopy and spectroscopy. Two types of surface structure are found, depending on the polarization of the underlying ferroelectric

domain. On domains that have an upward polarization component, a layer with an Aurivillius-Bi_2O_2-like structural unit is observed. Dramatic increase in local ferroelectricity is measured directly below the surface layer. On domains that have a downward polarization component, no reconstructions are visible. Calculations based on ab initio density functional theory reproduce the results and are used to interpret the formation of the surface structures.

Ionic transport in amorphous HfO_x

Marcel Schie
IWE 2, RWTH Aachen, Sommerfeldstraße 24, 52074 Aachen, Germany.

The migration of anions and cations in amorphous HfO_x was investigated by means of large-scale, classical molecular-dynamics simulations over the temperature range $1000 < T/\mathrm{K} < 2000$ and the timescale of a nanosecond. Both stoichiometric and oxygen-deficient forms (with $x = 2$ and $x = 1.9875$) of am-HfO_x were studied. The mean square displacement of oxygen and hafnium ions was found to not evolve linearly as a function of time, instead the behavior was sub-diffusive. That oxygen-ion migration was observed for the stoichiometric phase argues strongly against applying the traditional model of vacancy-mediated migration in crystals to amorphous HfO_2. In addition, cation migration, whilst not observed for the crystalline phases as no cation defects were present, was observed for both amorphous phases. In order to still obtain activation enthalpies of migration the residence times of the migrating ions were analyzed. All results are joined to propose a picture of diffusion in am-HfO_x, including short length and timescales, and are supported by simple KMC simulations.

Investigation of oxygen vacancies formation and migration in HfO_2 from density functional theory

Marta Gibertini, Daniel Wortmann, Gustav Bihlmayer, Shigeru Tsukamoto and Stefan Blügel
Peter Grünberg Institute and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany.

Among the investigated storage devices, resistive random access memory (ReRAMs) are currently considered relevant because of the high-speed/high-density properties and the low energy required for the writing/rewriting circles. A study of point defects and dopants in the materials used is important for understanding the role that they play in those devices.

We present a density functional theory (DFT) study aimed at the investigation of the formation energies and the migration energy barriers of oxygen vacancies in the monoclinic HfO_2. Furthermore, the influence of yttrium substitutional defects and the effect on the diffusion are analyzed. The nudged elastic band method is applied and the DFT calculations are performed with the electronic structure code jüRS, a real-space finite-difference implementation of the projector augmented wave (PAW) method. The real-space formalism is chosen because it allows a flexible treatment of the boundary conditions and therefore it is also favorable at the implementation of an external electric field or chemical gradients.

Probing the space charge layer of donor doped $SrTiO_3$ by in-situ spectroscopy

M. Andrä[1], S. Nemsak[1], F. Dvořák[2], M. Vorokhta[2], N. Raab[1], V. Matolin[2], C. M. Schneider[1], R. Dittmann[1], F. Gunkel[1,3], D. N. Müller[1], and R. Waser[1,3]
[1] Peter Grünberg Institut, Forschungszentrum Jülich GmbH, Jülich, 52425, Germany.
[2] Department of Surface and Plasma Science, MFF UK, Charles University in Prague, Prague 18000, Czech Republic.
[3] Institute of Electronic Materials (IWE2), RWTH Aachen University, Aachen, 52074, Germany.

Resistive gas sensors utilizing the formation of a space charge layer at the solid/gas interface of metal oxides have been known and used for a long time.[1] Recent research on donor doped $SrTiO_3$ showed the existence of a similar space charge layer[2][3]; the underlying mechanism of formation, however, is yet to be understood. A recent work attributed the formation of the space charge layer to intrinsic ionic defects[4] – namely strontium vacancies – incorporated upon oxidation, as predicted from the defect chemistry model of donor doped $SrTiO_3$.[5] It is proposed that this defect formation at the surface modifies the surface space charge layer in donor doped $SrTiO_3$ resulting in a change of the electric conductivity.[6] While bulk incorporation of strontium vacancies is a comparably slow process at reasonable temperatures, the surface reaction is considered to be fast enough to be suitable for an application as a sensor.

In this study the surface space charge layer of donor doped $SrTiO_3$ thin films was investigated by near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). Donor doped $SrTiO_3$ single crystals and homoepitaxial thin films with a thickness of 16 nm and 32 nm were analyzed by Impedance Spectroscopy and NAP-XPS at a temperature of 770 K as a function of pO_2. We observed the vanishing of all carbon and oxygen related adsorbates and contaminations at high temperatures and comparably low pO_2. Therefore, any effects of adsorbates or contaminants at the surface are unlikely under experimental conditions.

In addition, we detected a rigid shift of the binding energies of all characteristic $SrTiO_3$ core level peaks and the valence band maximum. This rigid shift is attributed to a relative shift of the Fermi level towards the valence band, which is consistent with a recently proposed surface oxidation model[4] and the rigid band model.[7] The results clearly indicate a spectroscopic as well as an electronic response of the surface of donor doped $SrTiO_3$ to the pO_2 at a temperature of 770 K.

[1] T. Seiyama, A. Kato, K. Fujiishi, M. Nagatani. A New Detector for Gaseous Components Using Semiconductive Thin Films. Anal. Chem. Volume 34(11), 1962

[2] A. Ohtomo and H. Y. Hwang. Surface depletion in doped $SrTiO_3$ thin films, Appl. Phys. Lett. Volume 84, 1716, 2004

[3] A. Marchewka, D. Cooper, C. Lenser, S. Menzel, H. Du, R. Dittmann, R. E. Dunin-Borkowski, and R. Waser. Determination of the electrostatic potential distribution in Pt/Fe:$SrTiO_3$/Nb:$SrTiO_3$ thin-film structures by electron holography. Scie. Rep.,

Volume 4,6975, 2014

[4] R. Meyer, A. Zurhelle, R. A. De Souza, R. Waser, and F. Gunkel. Dynamics of the metal-insulator transition of donor doped $SrTiO_3$. Phys. Rev. B, Volume 94, 115408, 2016

Quantitative Electron Paramagnetic Resonance (EPR) Spectroscopy Analyzing Li_2MnO_3 Mass-fraction in Synthesized Lithium Manganese Spinel and Its Consequence for Li-Mn Stoichiometry

R. Sun, P. Jakes, S. Eurich, H. Kungl, J. Granwehr, R. A. Eichel
Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-9: Fundamental Electrochemistry), Leo-Brandt-Str., D-52425 Juelich, Germany.

Li_2MnO_3 may be formed as a by-product in small quantities during synthesis of $LiMn_2O_4$. Particular synthesis routes based on reactant compositions with lithium-excess favor the formation of Li_2MnO_3 as a secondary phase. One consequence of the Li_2MnO_3 formation is the impact on the exact stoichiometry of the lithium manganese spinel. When present in trace amounts, Li_2MnO_3 is not detectable by XRD. However, the trace amounts of Li_2MnO_3 in synthesized lithium manganese spinel materials can be detected by Electron Paramagnetic Resonance (EPR) spectroscopy due to its high sensitivity on Mn^{4+} ions.

In this work, an X-band (9.4 GHz) continuous-wave (c.w.) EPR spectroscopic technique is applied on synthesized lithium manganese spinel materials at room temperature. The studied samples are synthesized via solid-state route with Li-excess, Li-stoichiometric and Li-deficit. In the samples with Li-excess, the existence of Li_2MnO_3 is confirmed in their EPR spectra. The EPR spectrum of Li_2MnO_3 is successfully simulated and extracted from the total spectra of Li-excess samples. Combining the simulation of Li_2MnO_3 partial spectrum and a calibration experiment from pure phased Li_2MnO_3 reference samples, the mass-fraction of Li_2MnO_3 is quantified. Accordingly, based on the defect model of Li substitution on *16d* sites, the exact Li-Mn stoichiometry of $Li_{1+x}Mn_{2-x}O_{4\pm\delta}$ in synthesized material is determined. The results show that even when the mass-fraction of Li_2MnO_3 is less than 1%, its impact on the Li/Mn stoichiometry cannot be neglected. In addition, the residual EPR spectra of $Li_{1+x}Mn_{2-x}O_{4\pm\delta}$ represent a correlation between Li substitution and the magnetism of lithium manganese spinels.

Defect interaction in non-stoichiometric doped ceria from first principles

Steffen Grieshammer[1], Manfred Martin[2]
[1]Helmholtz-Institut Münster (IEK-12), Forschungszentrum Jülich GmbH, Corrensstr. 46, 48149 Münster, Germany.
[2]Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany.

Cerium oxide, in pure and doped form, is an important material in various industrial applications such as chemical catalysis, automotive exhaust purification, and energy conversion devices, e.g. solid oxide fuel cells and rechargeable oxygen batteries. These applications harness either the high reducibility and oxygen storage capacity of ceria or the fast ion conduction which is enabled by doping with aliovalent ions. Reduction of doped ceria leads to the formation of a concentrated solution of defects, namely oxygen vacancies, dopant ions and small polarons with mutual interactions.

In this study we investigate the interaction and distribution of defects in non-stoichiometric ceria doped with rare-earth oxide $Ce_{1-x}\,RE_xO_{2-x/2-\delta}$ by means of DFT+U calculations and Monte Carlo simulations. We describe this system by the pair interaction energies of the prevalent defects and examine the influence of defect interaction on the energy of reduction.

The simulations reveal that the ordering of defects in thermodynamic equilibrium decreases the total energy of the solid solution with increasing non-stoichiometry as well as increasing dopant fraction due to the interaction of oxygen vacancies with dopant ions and small polarons. This effect can explain the decrease of the enthalpy of reduction as observed in experiments.

From the simulations we extract the free energy difference between an interacting and non-interacting system and investigate the influence on the non-stoichiometry for varying oxygen partial pressure. The results clearly reveal the relevance of defect interactions for the non-stoichiometry of ceria.

Computational Study of Oxygen Diffusion along a[100] Dislocations in the Perovskite Oxide $SrTiO_3$

Stephan P. Waldow, Roger A. De Souza
Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany.

Classical molecular-dynamics simulations, using empirical pair potentials were employed to study the atomistic structure of a periodic array of edge dislocations comprising a symmetrical 6:0◦ [100] tilt grain boundary in $SrTiO_3$. Furthermore the diffusion of oxygen ions in oxygen-deficient bulk STO and along the array of edge dislocations were simulated, yielding oxygen tracer diffusion coefficients. The simulations were conducted at temperatures in the range of $1000 < T$ / K < 2300. The calculated tracer diffusion coefficients for bulk STO agree extremely well with experimental data. Both types of dislocation cores (TiO_2 - type and SrO - type) are stable at elevated temperatures and even the oxygen-deficient cores maintain their characteristic, dissociated structures. Oxygen vacancies resided preferably at the cores and in their close proximity. Oxygen migration in the grain boundary cell seemed to be hindered in comparison to the bulk cell, as the obtained tracer diffusion coefficients for the grain boundary cell are lower than for the bulk while the corresponding migration enthalpy for the grain boundary is higher than for the bulk structure.[1]

[1] S. P. Waldow and R. A. De Souza, ACS Appl. Mater. Interfaces, 2016, 8 (19), 12246

Tunable Charging of Neutral Domain Walls as Conductive Channels in Oxide Ferroelectrics

Xian-Kui Wei[1,2], Tomas Sluka[1], Barbara Fraygola[1], Ludwig Feigl[1], Hong-Chu Du[2,3], Lei Jin[2], Chun-Lin Jia[2,4] and Nava Setter[1]
[1] Ceramics laboratory, EPFL-Swiss Federal Institute of Technology, Lausanne 1015, Switzerland.
[2] Peter Grünberg Institute and Ernst Ruska Center for Microscopy and Spectroscopy with Electrons, Research Center Jülich, 52425 Jülich, Germany.
[3] Gemeinschaftslabor für Elektronenmikroskopie (GFE) RWTH Aachen, Ahornstraße 55, 52074 Aachen, Germany.
[4] International Centre of Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China.

Metallic-type conductivity of charged domain walls (DWs) in ferroelectric oxides promises potential application in future logic circuits and sensors. However, creation of strongly charged DWs is sophisticated due to their high formation energy and low stability. Therefore, searching for substitutions of the charged DWs with stable and robust conduction performance becomes the urgent priority taken into account of their potential usage. Through a systematic study using probe-corrected scanning transmission electron microscopy, we find that the DW charging in ferroelectric $Pb(Zr_{0.1}Ti_{0.9})O_3$ thin films can be controlled to a large extent including change of polarity. The experimental and phase-field modeling data reveal that the charging of DWs is controlled by strain-release regulated DW bending, type of doping, polarization orientation and work-function of adjacent electrodes. Our findings provide a practical strategy towards fabrication of stable conductive channels in oxide ferroelectrics, thus paving the way for utilization of DW-based nanoelectronic devices in the future.

An investigation of deformation microstructure evolution of a high-Mn austenitic TRIP/TWIP steel by *in-situ* synchrotron X-ray diffraction

Yan Ma, Wenwen Song, Wolfgang Bleck
Steel Institute, RWTH Aachen University, Germany.

The quantitative characterization of the deformation microstructure evolution in high-Mn austenitic TRIP/TWIP steel is of great importance for the understanding of its strain hardening behavior. Stacking fault energy (SFE) exhibits the decisive role to control the strain hardening behavior in high-Mn austenitic steels. In the present work, the *in-situ* tensile test tracked by high-energy synchrotron X-ray diffraction was carried out at beamline P02.1 in DESY to investigate the TRIP and TWIP effect during the deformation of Fe-17Mn-1.5Al-0.3C steel. By Rietveld refinement method, the microstructure evolution was analyzed, in term of ε-martensite and α´-martensite phase fraction, stacking faults and twin faults probability, and dislocation density. The strain hardening behavior in different deformation stages was further discussed. In addition, the stacking fault energy was calculated based on the synchrotron measurement and further compared with the thermodynamic calculation using subregular model.

POSTER SESSION GREEN

Degree of activation for diffusion in solids

Adetona Morakinyo Oladele
Postgraduate School, University of Ibadan, Nigeria.

Activation degrees for the following simple models of lattice defects are calculated: (a) simple vacancy in a monatomic lattice, (b) simple vacancy with elastic theory of relaxation, (c) Schottky defect in an ionic crystal with dielectric theory of relaxation, (d) surface tension model of a vacancy in a metal, (e) elastic sphere model of an interstitial atom, and (f) strain energy theory of defect motion. The calculations are compared with experimental measurements. The comparison is satisfactory in many cases. In particular, it is observed that most of the data can be represented by the equation $\Delta V=4\beta\cdot\Delta H$ (β=compressibility, ΔH=activation energy), and that an equation of this type can be derived from several of the models. This equation can be used with a result of Lawson's to derive Zener's expression for the activation entropy of diffusion.

Investigation of point defects in Heusler alloys: an *ab initio* study

Biswanath Dutta, Tilmann Hickel, Jörg Neugebauer
Max-Planck-Institut für Eisenforschung GmbH, D-40237 Düsseldorf, Germany.

Functional properties of magnetic Heusler alloys such as magnetic shape memory and magnetocaloric effect can be tailored by understanding and modifying their magnetic properties. To this end, vacancies can play a decisive role. Recent experiments have indicated that vacancies can strongly influence the ordering kinetics and hence the subsequent magnetic properties of these alloys. Within this study, we employ density functional theory along with Monte Carlo (MC) simulations to understand the impact of vacancies on the phase stability and transformation behavior in Ni-Mn-based Heusler alloys. We discuss the results in terms of chemical potentials, which are constrained by the formation of various secondary phases. Our calculations reveal high vacancy concentrations for Ni and Mn with the vacancy formation energy for Ni being the lowest. The nudged elastic band method is employed to compute the vacancy migration barrier, which indicates that the most likely diffusion path involves both Ni and Mn atoms. The computed results for the self-diffusion activation energy of vacancies also show good agreement with experimental values. Our calculations on vacancies provide useful insights into the ordering process of these alloys.

Statistical thermodynamics of defects in ceria and perovskite based oxides

Brendan Bulfin, Josua Vieten, Matthias Lange, Martin Roeb and Christian Sattler
Institute of Solar Research, German Aerospace Center (DLR), Cologne, Germany.

The formation of oxygen vacancy defects in ceria and ceria zirconia solid solutions are analysed with a new methodology for modelling such systems based on the statistical mechanics of lattice configurations. Experimental thermogravimetric equilibrium data obtained for small non-stoichiometry measurements are combined with literature data to cover a large range of non-stoichiometry (CeO_{2-d}, $d = 0.001 - 0.32$), temperature (1073 –

1773 K) and oxygen partial pressure ($1 – 10^{-13}$ bar). A dilute species model of defect clusters ($\mathrm{Ce}'\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}\mathrm{Ce}'$), obeying the law of mass action, was sufficient to describe the system over the whole range of conditions, leading to a simple analytical equation of state for the system. This offers new physical insight into the redox properties of ceria based materials, and the theoretical methods developed have also been successfully applied to model non-stoichiometry in perovskite based oxides.

Insertion and Diffusion of H-3 and Cl-36 in UNGG Graphite: Insights from a Multi-Scale Approach

Christoph Lechner[1], Philippe Baranek[1], Holger Vach[2]
[1]EDF R&D - Department Materials and Mechanics of Components (MMC) EDF Lab Les Renardières, Avenue des Renardières, F-77818 Moret-sur-Loing Cedex, France.
[2]LPICM, CNRS, Ecole Polytechnique, Université Paris-Saclay, F-91128 Palaiseau, France.

In order to optimize the waste management of nuclear graphite used in power plants, it is important to understand the properties of the activated impurities it contains, such as tritium and chlorine 36. First, we studied the interaction of tritium and chlorine 36 with defects in graphite with density functional theory (DFT). While the bonding of hydrogen is mostly covalent for chemisorption and van der Waals for physisorption, the behavior of chlorine is much more complex. Depending on the defect site, both, dominantly covalent and dominantly charge transfer bonding, is observed. Then, the ab initio data were used to determine the basic parameters of a molecular dynamics approach to study the insertion and diffusion of both radionuclides in graphite. In order to model the interaction of chlorine and the graphite matrix, a bond order potential, which attributes for both, short and long range interactions was developed. For the tritium-graphite interactions, the bond order potential AIREBO was used. Molecular dynamics simulations of the behaviors of both radionuclides were then carried out in order to evaluate the temperature dependence of their properties.

Electronic and electrical conductivity characteristics of (AB) and (AA) stacked bilayers graphene sheet

Mohamedou Mohamed lemine
University of Mohammed V, 4 Avenue Ibn Battouta B.P, 1014 Agdal, Rabat, Morocco.

This humble work attempts to study the electronic and electrical conductivity characteristics of (AB) and (AA) stacked bilayers graphene sheet (BLG), by using ab-initio calculation. The Electronic transport Coefficient was calculated by using Boltzmann transport equations implanted in Boltztrap package at various temperatures from 80 K to 380 K. Firstably, this study will begin to experiment interlayer spacing from 3.55 Å and 3.35 Å respectively for AA and AB-BLG. If the distance between the layers is more than 5.00 Å, the energy increasing or decreasing does depend on the interlayers spacing so band gap equal zero. The electrical conductivity of AA and AB-BLG is compared to the experimental electrical conductivity of graphene monolayer under increasing spacing between layers to 4.00 Å. Band gap decreases with the space increasing while conductivity increases with space increasing. AA-BLG electrical conductivity shows a value near to experimental electrical conductivity of graphene

Ribbon for 4.00 Å at 380 K. Nevertheless, the distance variation doesn't much affect the electronic and electrical characteristics of AB-BLG. In addition, the increasing between the interlayers distance does not influence so much the electrical conductivity. Therefore, increasing the distance between interlayers decreases the electrical conductivity due to the increasing of band gap.

Controlling Diffusivity in Titanium Aluminum Nitride by point defect engineering

Moritz to Baben[a,b,*], Marcus Hans[a], Daniel Primetzhofer[c], Simon Evertz[a], Holger Ruess[a], Klaus Hack[b], Jochen M. Schneider[a]
[a]Materials Chemistry, RWTH Aachen University, 52074 Aachen, Germany.
[b]GTT-Technologies, 52134 Herzogenrath, Germany.
[c]Department of Physics and Astronomy, Uppsala University, 75120 Uppsala, Sweden.
[*]mtb@gtt-technologies.de

Extreme cooling rates during physical vapor deposition (PVD) allow for growth of metastable phases. One example is metastable (Ti,Al)N, the industrial benchmark coating for wear protection, that decomposes spinodally above 800°C into TiN and AlN.

Using ab initio calculations as input for CalPhaD calculations, we developed a thermodynamic model including vacancies on both the metal and the non-metal sublattice: (Ti,Al,Va)(N,Va). This allowed us to describe metal- and nitrogen-vacancy concentrations as function of composition and temperature. We show that avoiding previously unidentified nitrogen overstoichiometry in $(Ti,Al)N_x$ allows for decreasing metal vacancy concentration and hence diffusivity by several orders of magnitude. This theoretical prediction is supported by atom probe tomography measurements indicating no significant spinodal decomposition in $(Ti,Al)N_x$ for $x \approx 1$ after annealing up to 1200°C.

The thermodynamic approach formulated here opens a pathway for thermal stability engineering by point defects in reactively deposited thin films.

[to Baben et al., "Unprecedented thermal stability of inherently metastable Titanium Aluminum Nitride by point defect engineering" Materials Research Letters, accepted. Article will be available under: http://dx.doi.org/10.1080/21663831.2016.1233914]

Molecular structure, vibrational spectroscopy and HOMO-LUMO study of N, N-Diethyl-4 - [(E) - (pyridin-3-yl) diazenyl] aniline using DFT theoretical calculations

Nawel Khelloul
Laboratory of Technology and Solid’s Properties, Faculty of Sciences and Technology, University Abdelhamid Ibn Badis of Mostaganem, 27000 Mostaganem, Algeria.

In this work, we are interested in the theoretical and experimental study of a compound of optically nonlinear properties. This compound crystallizes in a orthorhombic system with a space group (P21, P21, P21) and the lattice parameters a = 7.4332 (7) Å, b = 9.1093 (8) Å, c = 20.1946 (19) Å V = 1367.4 (2) Å, Z = 4. the determination of the structure of the test compound was conducted using the method of functional theory of density using two hybrid functional B3LYP and B3PW91 with the base calculation 6-31G (d, p). All calculations were performed by the program GAUSSIAN 09. To highlight the charge transfer phenomenon and its management within the molecule, we determined the dipole moment and the electrostatic potential. Thus the setting: the polarizability α and β, the hyperpolarisability are calculated in the same method. The molecular orbital calculations boundaries clearly show the inverse relationship of the HOMO-LUMO gap with hyper total static polarizability. Vibration frequencies were calculated using the method (DFT) B3PW91 and B3LYP / 6-31G (d, p).

Lehrstuhl für Physikalische Chemie I
Institute of Physical Chemistry
RWTH Aachen University
Landoltweg 2
52074 Aachen
Phone: +49 241 80 94712
Fax: +49 241 80 92128
E-Mail: martin@rwth-aachen.de

Scientific Committee
Manfred Martin
Roger A. De Souza

Local Organizers
Fabian Draber
Philipp Hein
Julius Köttgen