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FACULTY OF
MATERIALS- AND GEO-SCIENCES
ANNUAL REPORT
2007

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Preface

The year 2007 of the Department of Materials- and Geo-Sciences was characterized by strong changes in the organisation of the dean’s office. Dr. I. Kinski was acting as scientific coordinator for most of the year before deciding to continue her scientific career at the Fraunhofer Institute in Dresden. Mrs. Ziegler-Krutz joined the dean's office at first mostly taking care of the registrar’s office. Mrs. Hempel is now responsible for the department’s human resources and budget department. After the early retirement of Mrs. Relaford also at the end of 2007 Mrs. Ziegler-Krutz has taken over all administrative duties of the department. Additional support is still given by Dr. Weitzel who serves as senior advisor in part-time. Dr. Brötz is active as coordinator of the characterisation lab supporting education and student advice, Mrs. Bracke is active in public relation issues. Fortunately, some continuity was provided by Mr. Mohren, as acting technical engineer of the department, and Mr. Korzer and his staff. We would like to thank all these people who despite of all organisational turbulences kept the Department of Materials- and Geosciences on track. This was even harder as we had an ongoing internal discussion on the future organisational structure of the department and distribution of money. Any attempt to reach a final discussion on this topic was hindered by the long and complicated search procedure for the new president of the TU Darmstadt. Finally, Prof. Prömel was elected as New President of the TU Darmstadt and visited our department Nov. 23rd 2007 to get direct information on the status-quo and future plans. The development of the number of Materials- and Geo-Science students and graduates are shown in Fig. 1.

Fig. 1a: Number of graduates in Materials Science at Darmstadt University of Technology over the last 7 years
In Materials Science the reoccupation of open academic positions after the retirement of some of the founding professors remains a major challenge during the year 2007. Fortunately, the W2-professorship on “Materials Modelling” could be successfully filled with Prof. Albe. But the search for the succession of the Division of Structural Research Prof. H. Fuess turned out to be very demanding as experienced scientists were sought after with knowledge in the use of large scale facilities but also scientists with a strong materials science background. Unfortunately, we were not able to fill the position in 2007 but in the meantime we are happy to welcome Prof. Donner as successor of Prof. Fuess. For this reason Prof. Fuess has continued to lead this division in 2007. We also were not successful to find a successor for Prof. Eckert in 2007. Fortunately, PD Dr. Müller accepted the duty as an interim head of the division of metal physics. As a consequence all colleagues had the impression that the daily amount of work has considerably increased during the year 2007.

A lot of time was devoted during 2007 to join the national excellence initiative with the final application of an excellence research school “Genesis” on energy science and engineering and on “Matronics” on novel materials beyond silicon. In addition colleagues from materials science were involved in the cluster “Smart Interfaces” and the graduate school “Computational engineering”. Unfortunately, as with the cluster “MECAD”, Genesis and Matronics reached the second round but were finally not granted. As small comfort the cluster smart interfaces and the graduate school computational engineering were granted and some additional funding flows to the department with the sign “excellency” marked on it. The strong efforts of the department were, however, rewarded within the university and the interim president Prof. Buchmann. The senate granted an additional W3-professorship on solid state ionics to the department and also in the cluster smart interface one additional W3-professorship on “Physics of Surfaces” is considered. Afterwards the personnel situation of the department of materials science and the scientific impact will be

![Bar Chart](image.png)

**Fig. 1b: Number of graduates in Applied Geosciences at Darmstadt University of Technology over the last 7 years**
strongly improved. However, these developments can only be implemented, if the needed laboratory and office space is also provided. The planned extension into the chemistry building is not clarified yet. The department of materials science will only be able to contribute to the future profile of the TU Darmstadt if the clear commitments of its members are supported by those of the administration.

Till the end of the year 2007 Prof. Alff as study dean and all involved committee members including very many active students have worked very hard to transform the given Diploma degree program into the Bachelor degree program. In conjunction with the modified reorganisation of the study program improvements of the content and form of the different modules were developed. The Bachelor of Science of Materials Science has been elaborated in time and is now in the accreditation phase. In WS 2008/2009 we will start with our new curriculum. We want to acknowledge the work and the efforts of all people involved and hope for a successful start of our new materials science study program and hope for many new students.

Finally, we also want to announce special honours of members of our department. First of all Prof. Fuess was honoured by the Humboldt Research-Price. The students price of the best MaWi student was given to Dipl. Körber, Pauli und Suffner who presented their Diploma theses during the yearly Summer Party of the Material Science Institute. Mr. Ruben Bischler has obtained the Rotary Student Development Price of the Rotary Club Darmstadt.

The year 2007 in the Materials Science Institute was brought to an end with the traditional Christmas Party to which many people contributed in an more or less active way. Again a number of high level of art, music, and comedy performances has proven that materials scientists have talents beyond their scientific abilities. The party was finished again long time after the early visit of Santa Claus.

Geoscience has to rapidly adjust to the new problems posed by the changing global environment and climate, the expanding economy and their energy needs as well as the land cover changes due to a dramatically growing population. Human activity is understood to stress the Earth System in every of its aspects, far beyond long-term sustainability. Geoscientific disciplines are therefore found in the forefront to provide knowledge about resources, cycles and time aspects of natural developments affected and modified by human impact. Therefore, the Institute of Applied Geosciences has taken several steps to encounter the changing research aims by focussing on research topics in Applied Geoscience, which allows the concentration not only on geological engineering problems but also on environmental and/or material-related problems. In order to meet future requirements, the Institute of Applied Geoscience will offer new BSc and MSc courses focussing on three main topics: (i) Water, (ii) Energy and (iii) Environment. The MSc degree “Geo-Environmental Science and Engineering” will clearly reflect this new concept and, therefore, allow future students to address problems that will affect next generations.

2007 was the second year, where new students enrolled in our international masters course TropHEE (Tropical Hydrogeology, Engineering Geology and Environmental Management). The students come from China, Ethiopia, Guayana, Madagascar, Nigeria, the Philippines, and Zambia.
TropHEE is internationally accredited and certified by ASIIN since March 2005 and supported by grants from DAAD and BMBF. Target groups are professionals from public and private institutions, authorities and enterprises with a geoscientific background as well as students holding a relevant BSc. Special emphasis is put on state of the art methods and applications in hydrogeology, engineering geology and environmental management in tropical, subtropical and semiarid regions. Besides our own lecturers, additional lecturers from other TUD departments, governmental organizations, industrial partners, and private companies contribute to the curriculum. TropHEE is considered an integral part of our efforts to focus our future research as well as teaching activities on applied geoscience questions with particular emphasis on water, energy and environment.

The research focus Geothermal Energy was established by the Engineering Geology Group of Prof. I. Sass. Geothermal energy is one of the few regenerative energy systems, capable of providing a base load with potentially enormous resources. In July 2007, the second Geothermal Summer School with about 60 participants was held in Darmstad, in cooperation with the Institute and Laboratory for Geotechnics. In addition, in cooperation with the “Hessisches Ministerium für Wirtschaft, Verkehr und Landesentwicklung” the second Forum on Deep Geothermal Reservoirs took place at TU-Darmstadt with about 130 participants in September 2007.

As it is the tradition in Geosciences to conclude the year with the ‘Barbara Fest’, all faculty, staff and students got together to discuss the events of the year as well as the future in a very friendly and positive atmosphere.

The outcome and most remarkable results of research in 2007 are summarized in the following pages for the different divisions and working groups of the Department of Materials- and Geo-Science. These results would have been not possible without the strong engagement and outstanding efforts of all people in the department ranging from our excellent workshop headed by J. Korzer to the technical and administrative staff in the research groups, the students, Diploma students, Ph.D. students and last but not least to the PostDocs in the different research groups. We would like to thank all of them for their valuable contributions and hope that it will be possible to carry on the excellent working atmosphere into the upcoming years in an expanding department.

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Institute of Materials Science

Physical Metallurgy

Research and teaching in the Department of Physical Metallurgy are focused on understanding the relationships between processing, microstructure and properties of metallic materials. The major goal of ongoing research is to describe, in quantitative terms, the basic mechanisms governing processing and performance in use, and to predict the influence of process variables on materials’ properties during and after solidification, densification, heat treatment, forming, and shaping. Numerical simulation of recrystallization, sheet drawing and chip formation are covered. Theoretical results are compared to experimental findings obtained by microscopic techniques and all other experimental methods available in the Department.

Current work deals with titanium, aluminium and magnesium based light alloys, steel, superalloys, and other multicomponent alloys. Wear, corrosion and fatigue and their complex interaction are studied. Recent progress includes achievements in the fields of titanium alloys for artificial joints, new alloys for electrical contacts, and functionally graded materials as well as improvements in the wear resistance of metallic alloys by mechanical surface treatments. Ultra-Fine Grained (UFG) microstructures became of special interest in the last years, as they combine extremely high strength with considerable ductility. In several research projects the evolution and the mechanical properties of these microstructures are investigated and new forming processes for the continuous production of UFG-bulk materials are developed in collaboration with the department of mechanical engineering.

Figure 1: UFG microstructure of a HSLA steel

Teaching covers lectures on mechanical properties of engineering materials and fundamentals of deformation and fracture, phase diagrams and phase transformations, solidification and heat treatment mechanisms, and quantitative image analysis for the characterization of microstructures. Extensive laboratory exercises on all levels are offered to facilitate and intensify the technical understanding in these topics and to improve the practical skills for investigating metallic materials.
Cooperation with other groups in the institute and of other Departments of Darmstadt Technical University, particularly with those of Mechanical Engineering, as well as with other universities in Germany and abroad as well as with industry (Opel, Daimler-Benz, Heraeus, Ecoroll, Pfalz-Flugzeugwerke among others) give opportunities for scientific and personal exchange. Department members participate in conferences, seminars and workshops gathering Information which can aid to the actuality of teaching and research, and spreading their ideas in the scientific community.

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**Research Projects**

- Corrosion behavior of highly deformed linear split profiles (DFG-SFB 666 2005–2009)
- Wear resistance of surface treated GGG-70L (AiF, jointly with Prof. Groche)
- Influence of a carbon diffusion layer on the hydrogen embrittlement of 1.4301 (Adam Opel GmbH)
- Influence of galvanic Zn-layers, DLC-layers and carbon diffusion layers on the hydrogen embrittlement of steels (Adam Opel GmbH)
- Influence of galvanic and chemical Ni-layers and nitrogen diffusion layers on the hydrogen embrittlement of steels (Adam Opel GmbH)
- Influence of the lamella length on the fatigue properties of TIMETAL 1100
Publications


Materialwissenschaft und Werkstofftechnik
Ceramics Group

The emphasis in the ceramics group is on the correlation between microstructure and mechanical as well as functional properties. A number of processing methods are available in order to accomplish different microstructure classes, to determine their specific properties in an experiment and to rationalize these with straightforward modelling efforts. Thereby a materials optimization is afforded, which allows effective interplay between processing, testing and modelling. The scientific effort can be grouped as follows:

1. Sintering of oxides:
Sintering of ceramics is approached using a continuum mechanical description, which affords inclusion of laminate stresses as arise in sintering of thin films and cosintering of several layers. In order to determine the constitutive equations for the sintering bodies, dilatometry and a new hot forging apparatus are used. This equipment together with a substantial modelling effort allows measurement of sintering stresses and viscosities and thereby predictions of shrinkage and curvature in multilayer structures. From an application points of view, thin optical layers and printed electronics are also investigated.
In collaboration with colleagues from Karlsruhe we also work on melting of nanoparticles and field assisted sintering.
Materials under consideration are ZrO$_2$, Al$_2$O$_3$, TiO$_2$, ZnO as well as LTCC materials.

2. Mechanical properties of ceramics and composites:
Work on mechanical properties is geared towards an improved understanding of fracture strength, fracture toughness, R-curve behaviour and subcritical crack growth.
Together with several European research groups we prepare and characterize metal-ceramic composites and metal-ceramic functionally graded materials
Materials under consideration are ZrO$_2$, Al$_2$O$_3$/Cu and Al$_2$O$_3$/Al as well as various piezoceramics.

3. Ferroelectric materials:
Reliability of piezoceramics for applications as actuator materials is under investigation. An increasing number of electrical cycles leads to a progressive loss of obtainable strain and polarisation in these materials. Therefore electrical fatigue as influenced by the type of electrical loading, uniaxial stress, frequency and temperature are investigated. Recently, we developed a new method for stress-assisted (electromechanical poling), which reduces the required poling field considerably. Different new piezoceramics are being developed, especially new lead-free compositions, but also high-temperature piezoceramics.
Materials under consideration are PZT, lead-free piezoceramics and high-temperature piezoceramics.
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Research Projects

Processing of textured ceramic actuators with high strain (SFB 595, 2003 - 2010)

Mesoscopic and macroscopic fatigue in doped ferroelectric ceramics (SFB 595, 2003 – 2010)

Sintering of TiO$_2$ with additives (Merck, 2004 - 2007)

Knowledge-based multicomponent materials (EU, 6$^{th}$ framework programme, 2004 - 2008)

Melting of ceramic nanoparticles: Application to transient liquid phase sintering (DFG 2006 - 2010)

Electrooptical properties of PLZT (DFG 2006 - 2008)

High-temperature piezoceramics (DFG 2006 - 2008)
Printed Electronics: Thin film ZnO (Merck 2006 - 2009)

Developing a ceramic roadmap (DFG 2005 - 2007)

Synthesis and characterization of nanostructured materials by FAST sintering (DFG 2006 – 2010)

Publications


Rao S.; Rödel J.; Jayaram V.; Crack Growth Resistance (R-Curve) behaviour and thermo-physical properties of Al2O3 particle reinforced AlN/Al matrix composites; Composites: Part A 38, (2007) 1038-1050.


Zhang S.-T.; Kounga A. B.; Aulbach E.; Ehrenberg H.; Rödel J.; Giant strain in lead-free piezoceramics Bi_{0.5}Na_{0.5}TiO_3–BaTiO_3–K_{0.5}Na_{0.5}NbO_3 system; Applied Physics Letters, 91 (2007) 112906.


Electronic Material Properties

The department *Electronic Materials* introduces the aspect of electric functional materials and their properties into the Institute of Materials Science. The associated research concentrates on the characterization of various classes of materials suited for implementation in information storage and organic electronics. Three major research topics are presently addressed:

- Electronic and optoelectronic properties of organic semiconductors.
- Charge transport and polarization in organic dielectrics.
- Photo- and photostimulated luminescence in inorganic phosphors.

A worldwide interest exists in the use of organic semiconductors in electronic and optoelectronic components, such as transistors and organic light-emitting diodes, for novel areas of application. So far, multicolor organic displays have been implemented in commercially available cameras, car-radios, PDAs and mp3-players. Organic devices reaching further into the future might be simple logic circuits, constituting the core of communication electronics such as chip cards for radio-frequency identification (RFID) tags and maybe one day flexible electronic newspapers where the information is continuously renewed via local area networks (LAN). In view of the mandatory technological development, the activities of the group are concerned with the characterization of organic material properties regarding the performance of organic electronic and optoelectronic devices. The major aspect deals with the charge carrier injection and transport taking place in organic field-effect transistors and light-emitting diodes. In particular the impact of electronic properties of the insulator / semiconductor interface on the performance of organic field-effect transistors was subject of recent investigations. This research is of great technological importance, since it opens the field of complementary metal oxide semiconductor (CMOS) technology to organic semiconductors. A further matter of research activities deals with the stability of organic light-emitting diodes. With the intention to enhance the device stability and performance, the influence of the device operation on the device life-time in conjunction with material and device specific properties is in the focus of interest. To conduct these demanding tasks, various experimental techniques for device fabrication and characterization are installed. Beside basic electric measurement setups, a laser spectroscopy setup, used for time-of-flight as well as a life-time measurements, and a Kelvin-probe atomic force microscope (AFM) to visualize the potential distribution of organic devices with nanometer resolution are available.

In the field of polymer electrets present research comprises the characterization of surface charge distribution, charge stability, and charge transport properties of fluoropolymers, as well as their applications in acoustical transducers. Present investigations of charge transport and polarization in organic dielectrics are directed towards the basic understanding of polarization buildup and stabilization in PVDF and novel microporous dielectrics, which are scientifically interesting as model ferroelectric polymers. The available equipment includes poling devices, such as corona and high voltage setups, and a thermally stimulated current setup to investigate the energetic trap structure in dielectrics as well as the thermal charging and discharging under high electric fields.
The field of photo- and photostimulated luminescent (PSL) materials (phosphors) is concerned with the synthesis and characterization of suited inorganic compounds used as wavelength converters in fluorescent lamps and in scintillating and information storing crystals. Present work is focused on x-ray detection materials, which exhibit needle-like growth, needed for improved resolution in medical imaging. In particular cesium halides-based storage phosphors and scintillators are under investigation. Further research is concentrated on the low radiation hardness of CsBr:Eu$^{2+}$. Radiation-induced defects like color centers and precipitations are studied by means of spectroscopic methods, electron microscopy and structural analysis. In the field of storage phosphors also BaFBr:Eu$^{2+}$ used in commercial image plates is investigated. On the one hand the mechanism of PSL-sensitization should be clarified. On the other hand the implementation of BaFBr:Eu$^{2+}$ in foils and glass ceramics is in the focus of the work.

Another topic is the investigation of radiation scintillators, which convert x-ray energy immediately into visible light being detected by a CCD-array. For dynamical imaging in computer tomography (CT) a fast decay of the emitted light is required. Therefore, investigations are focused on the mechanisms which influence the lifetime of the transitions occurring in the light-emitting activator. Furthermore, a general challenge is the sensitization of such phosphors in respect to the radiation energy, which can range from ultraviolet over hard $\gamma$-rays to thermal neutrons.

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Research Projects

Fatigue of organic semiconductor components. (SFB (DFG), 2003-2010)

Phenomenological modelling of bipolar carrier transport in organic semiconducting devices under special consideration of injection, transport and recombination phenomena. (SFB (DFG), 2003-2010)

Polarization and charge in electrically fatigued ferroelectrics (SFB (DFG), 2006-2010)


Self-organisation, orientation and electronic properties of organic thin films based on low molecular weight, oligomeric and polymeric materials at the interface in field-effect transistors. (SPP (DFG) prolonged 2005 – 2007)

Charge carrier injection and transport in doped organic light-emitting diodes. (BMBF-OSRAM OS 2006 - 2009)

Kelvin probe investigation of organic field-effect transistors (MaDriX, BMBF-PolyIC 2007-2010)

Investigation of the OMR effect for the development of OMR sensors (BMBF-Siemens 2007-2010)

Ambipolar light-emitting transistors (TICMO Graduierten Kolleg 1037 2007-2010)

Publications


Surface Science

The surface science division of the institute of materials science uses advanced surface science techniques to investigate surfaces and interfaces of materials and materials combinations of technological use. For this purpose integrated UHV-systems have been built up which combine different surface analytical tools (photoemission, electron diffraction, ion scattering, scanning probe techniques) with the preparation of thin films (thermal evaporation, close-spaced sublimation, magnetron sputtering, MOCVD) and interfaces. The main research interest is directed to devices using polycrystalline compound semiconductors and interfaces between dissimilar materials. The perspectives of energy conversion (e.g. solar cells) or storage (intercalation batteries) devices are of special interest. In addition, the fundamental processes involved in chemical and electrochemical device engineering and oxide thin films for electronic applications are investigated.

The main research areas are:

- **Electrochemical Interfaces**
  The aim of this research activity is the better understanding of electrochemical interfaces and contact formation. In addition, empirically derived (electro-)chemical processing steps as the controlled modification and structuring of materials is investigated and further optimized. In the center of our interest are semiconductor/electrolyte contacts.

- **Intercalation Batteries**
  The aim of this research activity is the better understanding of electronic properties of Li-intercalation batteries and of their degradation phenomena. Typically all solid state batteries are prepared and investigated using sputtering and CVD techniques for cathodes and solid electrolytes. In addition, the solid-electrolyte interface and synthetic surface layers are investigated as well as composite systems for increasing the capacity.

- **Thin film solar cells**
  The aim of this research activity is the testing and development of novel materials and materials combinations for photovoltaic applications. In addition, the interfaces in microcrystalline thin film solar cells are to be characterized on a microscopic level to understand and to further improve the empirically based optimisation of solar cells.

- **Organic-inorganic interfaces and composites**
  In this research area we are aiming at the development of composites materials for (opto-)electronic applications. The decisive factors, which govern the electronic properties of interfaces between organic and inorganic materials are studied.

- **Oxide thin films for electronic applications**
  The aim of this research area is to understand electronic surface and interfaces properties of oxides. We are mainly interested in transparent conducting oxide
electrodes for solar cells and organic LEDs but also in dielectric and ferroelectric perovskites.

- **Surface analysis**
  The UHV-surface science equipment and techniques using different and versatile integrated preparation chambers is used for cooperative service investigations.

For the experiments we use integrated UHV-preparation and analysis-systems (UPS, (M)XPS, LEISS, LEED), spectromicroscopy (PEEM) coupled with UHV-STM/AFM. We further apply synchrotron radiation (SXPS, spectromicroscopy), scanning probe methods (STM, AFM), and electrochemical measuring techniques. UHV-preparation chambers dedicated for MBE, CVD, PVD and (electro)chemical treatment are available.

The member of the group are involved in basic courses of the department’s curriculum and offer special courses on the physics, chemistry and engineering of semiconductor devices and solar cells, on surface and interface science, and on thin film and surface technology.

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Research Projects

Dedicated preparation-, transfer and spectrometer system for the analysis of materials modifications and –synthesis at solid-liquid-interfaces with synchrotron radiation (BMBF, 2001-2007)

High performance CdTe thin film solar cells
(BMBF, 2003 – 2007)

Tunable Integrated Components for Microwaves and Optics
Graduiertenkolleg 1037 (07/2004 – 12/2008)

Materials World Network: Interdisciplinary bulk/surface studies of transparent conducting oxides
(DFG, 2006 – 2009)

Hybrid structures of TsLiMPO$_4$ phospho-olivines with C-nanofilaments for Li-ion-batteries: preparation, properties and potential applications
(DFG – SPP1181, 2006 – 2008)

Chemical vapor deposition (PE-MOCVD) of cation-substituted transition metal oxide thin films (Li(Co$_{1-x}$Ni$_x$)$_{1-y}$M$_y$O$_2$ (M=Mg, Al) for intercalation cathodes: structure, electronic structure and electrochemical parameters
(DFG, 2005 – 2007)

Verbundvorhaben – LISA: Insertion compounds and solid state electrolytes for Lithium-Ion-Batteries in Solar Applications
(BMBF, 2007 – 2010)

Advanced Buffer Layers for CdTe Solar Cells
(First Solar, 2007 – 2010)

Publications


Thin films

The Thin Film division works on advanced thin film deposition techniques of novel materials. After having installed a pulsed laser deposition in 2006, we have designed this year another frontier thin film deposition system: a dedicated Advanced Oxide Molecular Beam Epitaxy (ADOMBE) system. This system has been jointly financed by Max-Planck-Institute for Solid State Research in Stuttgart and TU Darmstadt. Both systems will be part of a cluster system allowing for in-situ sample exchange between the different deposition methods and characterization tools.

The class of oxide ceramics, in particular with perovskite and derived structures, comprises a stunning variety of new functional materials. Examples are high-temperature superconductors, magnetic oxides for spintronics, high-$k$ dielectrics, ferroelectrics, and novel thermoelectric materials. As a vision for future, new solid state matter can be created by building hetero- and composite structures combining different oxide materials. While present day electronic devices heavily rely on semiconducting materials, a future way to create novel functional devices could be based on oxide electronics. Oxide electronics and spintronics are part of the research and graduate education program “Matronics” that will be financed by the HMWK.

The characterization tools located in the Thin Film division include x-ray diffraction (XRD), x-ray photoemission spectroscopy (XPS), high-resolution scanning electron microscopy (HREM) with light element sensitive EDX, and SQUID magnetometry. A 16 Tesla magnet cryostat allowing measurements down to liquid helium temperature has been installed. Another magnet cryostat (10 T) lowering the available temperature range to below 300 mK has just been set-up. This cryostat also contains high-frequency feed-throughs (40 GHz). The group is also using external large scale facilities as synchrotron radiation (ESRF, Grenoble) and neutron reactors (ILL, Grenoble / HMI, Berlin) for advanced sample characterization.

Close cooperation exists in particular with the Max-Planck-Institute for Solid State Research in Stuttgart, with the Japanese company NTT in Atsugi near Tokio, with the University of Tokio, and Chalmers University of Technology.

In teaching the group is offering courses and lab exercises in basic materials science. New special courses for advanced students on Magnetism and Magnetic Materials, Spintronics as well as Advanced Materials are being held. The group is also giving a practical introduction in HREM for students and researchers in the field. Throughout 2007 Lambert Alff was working also as a Dean of Studies for Materials Science.

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Yoshiharu Krockenberger  Andreas Winkler
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**Diploma / Master**

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**Research Projects**

Superconductivity in water intercalated Na$_x$CoO$_2$ thin films (TUD, TU Braunschweig, and Max-Planck-Institute for Solid State Research, Stuttgart (DFG, 2006-2010)

Doped SrTiO$_3$ for Microwave Applications and Multiferroics as novel materials for tunable components, within DFG Research Training Group 1037 “Tunable Integrated Components in Microwave Technology and Optics”

Symmetry of the order parameter and pseudogap behavior in electron doped high-temperature superconductors, within Research Unit 538 (DFG, 2004-2007)

Oxide-MBE (MPI-FKF/TUD)

Fabrication of electron-doped high-$T_C$ superconductors (TUD & NTT, Japan, since 1999)

**Publications**


G.A. Ovsyannikov, V.V. Demidov, Y.V. Kislinski, P.V. Komissinski, and D. Winkler, *Conductivity and antiferromagnetism of CaCuO$_2$ thin films doped by Sr, Physica C 460-462, 536 (2007).*
Dispersive Solids

The main research interests of the group are directed towards the development of novel strategies suitable for the synthesis of inorganic, oxidic and non-oxidic materials with properties beyond the state of the art. The materials of interest are advanced oxidic and non-oxidic ceramics with extraordinary properties in terms of thermal stability, hardness and electronic structure. Therefore, synthesis methods such as polymer-pyrolysis, non-oxidic and oxidic sol-gel methods, chemical vapour deposition and novel high pressure methods have been further developed.

Molecular routes to nanoscaled materials
The aim is to develop concepts for the production of novel multifunctional inorganic materials with a tailor-made nanoscaled structure. In accordance with the so-called “bottom-up” approach, specific inorganic molecules are to be assigned to higher molecular networks and solid-state structures in the form of molecular nanotools by means of condensation and polymerisation processes.

Polymer-Derived Ceramics
The thermolytic decomposition of suitable organosilicon polymers provides materials which are denoted as polymer-derived ceramics (PDCs). The main emphasis is on the synthesis and characterization of new ceramic materials in the B-C-N, Si-C-N, Si-O-C, Si-(B,C)-N and Ti-(B-C)-N systems. The structural peculiarities, thermochemical stability, mechanical and electrophysical properties of the PDCs have been investigated in a series of PhD thesis and research projects. Due to their outstanding thermochemical stability as well as excellent oxidation and creep resistance at very high temperatures the PDCs constitute promising materials for high temperature applications. Another advantage of the PDC route is that the materials can be easily shaped in form of fibres, layers or bulk composite materials.

High Pressure Chemistry
Ultra-high pressure techniques like laser heated diamond anvil cell (LH-DAC) or multi anvil devices have been applied to synthesise novel solid state structures which cannot be produced by other methods, for example, inorganic nitrides. This technique was found to be the most promising route in the successful synthesis of carbon nitrides. Most recently, we have succeeded in the synthesis of a novel dense crystalline $\text{C}_2\text{N}_2(\text{NH})$-phase at high pressures and high temperatures using a LH-DAC. The first spinel nitride, $\gamma$-$\text{Si}_3\text{N}_4$, as well as super hard transition metal nitrides were synthesized under high pressure and temperature. In particular, a new family of high-pressure group 4 transition element nitrides, namely c-$\text{Zr}_3\text{N}_4$ and c-$\text{Hf}_3\text{N}_4$, having cubic Th$_3$P$_4$-type structure was discovered in our research-group.

Functional Materials
Further research topics are related to the development of materials suitable for applications in the fields of microelectromechanical Systems (MEMS), optoelectronics (LEDs), pressure, temperature and gas sensors as well as thermoresistant ceramic membranes for hight temperature gas separation. Another main topic of the scientific activities deals with the correlation of material properties with the molecular structure of the preceramic polymer used. The integration of state-of-the art spectroscopic methods is applied to understand the mechanisms responsible for sensing and catalytic properties.
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Research Projects

Novel functional ceramics with substitution of anions in oxidic systems, (DFG, SFB 595, project A4, since Jan. 2003)

New oxidation stable and creep resistant Si(Al,B)CO gradient fibres from modified polysiloxanes (DFG, since June 2004)

Synthesis and functional materials properties of 2-D arranged SiC and SiCN materials (DFG, since Dec. 2004)

Coordination of SPP 1181 Nanoscale inorganic materials with by molecular design: novel materials for advanced technologies (DFG, since Dec. 2005)

Unusual stability of amorphous polymer derived ceramics at high temperatures (DFG, since July 2005 - June 2008)

Ceramic temperature and pressure sensors based on molecularly derived SiOC ceramic by injection molding process (DFG, within SPP1181, Jan. 2006 - Dec. 2007)


High-pressure syntheses of novel binary and ternary superhard phases in the Si-C-N system (DFG, within SPP 1236, since June 2006)

High-pressure / high-temperature syntheses of novel oxonitrides in the system MN-M₂O₃ with M = Ga, In (DFG, within SPP 1236, since June 2006)

Integration and application of nano-wires by micro-nano-fabrication and micro-assembling - INANOMIK (BMBF, June 2007 - April 2008)


Polymer derived SiCO/HfO₂ and SiCN/HfO₂ ceramic nanocomposites for ultrahigh-temperature applications (DFG, within SPP 1181, Oct. 2007 - Sep. 2009)

Publications


Dzivenko, D.; Zerr, A.; Schweitzer, E.; Göken, M.; Boehler, R.; Riedel, R.; Elastic Moduli and Hardness of c-Zr$_{2.86}$(N$_{0.88}$$^{0.12}$)$_4$ having Th$_3$P$_4$-Type Structure, Appl. Phys. Lett. 90 (2007) 191910.


Structure Research

The scientific activities during the year 2007 concerned the field of magnetic oxides, materials for heterogeneous catalysis, batteries and piezoceramics. Eight young researchers finished their work as PhD-students and were promoted to Dr.-Ing. degrees. The neutron powder diffractometer SPODI at the research reactor FRM II is very popular among neutron users. The funding of the beam-line is assured until 2010 through the BMBF-program „Joint Research at Large Scale Facilities“ (Verbundforschung kondensierter Materie an Großgeräten). The successful operation of the Synchrotron powder diffractometer beam-line B2 at HASYLAB under the responsibility of Professor Fuess ended in February 2008. The instrument will be operated by Hasylab after the refurbishment of the Doris-ring.

Ingrid Svoboda retired at the end of 2007 but will continue to solve single crystal structures in the group of structure research. All members of the group are extremely grateful to her. Her unofficial responsibility for the well-being of people over the years was greatly appreciated and we are all very thankful to her.

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Prof. Dr. Roman Boca, Technical Univ. Bratislava, Slovakia
Prof. Dr. Abdelwahab Cheikhrouhou, Univ. of Sfax, Tunisia
Research Projects


Design, realisation and operation of the new neutron structure powder diffractometer SPODI at the FRM-II, TU München in Garching (BMBF, 1998-2010).

Investigation of superionic conducting properties in the copper silver selenium system (BMBF, 2004-2007).

Conception and development of solid high performance electrodes for fuel cells (BMBF, 2007-2009), jointly with Prof. Roth


Controlled deposition and structural investigations of metallic nanowires for field emission applications (cooperation with GSI, Darmstadt, 2004-2007).


Preparation of new orthomolybdates of alkaline and 3d-transition metals and characterization of magnetic, ion conducting and catalytic properties (DFG, 2004-2007).

High pressure synthesis and magnetism of orthorhenates (DFG, 2005-2007).

Electron and magnetization density in the transition metal oxide Co$_3$V$_2$O$_8$ (DFG, 2005-2008).


Heterogeneously catalyzed partial oxidation of acrolein to acrylic acid structure, function and dynamics of the V-Mo-W mixed oxides (DFG 2006-2008)

Heterogeneously catalyzed partial oxidation of acrolein to acrylic-acid structure, influence of water of the V-Mo-W mixed oxides (DFG 2007-2010)

DAAD exchange program with Slovakia (2006-2009).

Structural investigations into the electric fatigue in PZT (DFG-SFB, 2003-2010)

In-situ investigations of the degradation of intercalation batteries und their modelling (DFG-SFB, 2003-2010)

Spinel cathode materials LiM$_2$Mn$_{2-x}$O$_4$, M=Cr, Fe, Co, Ni, optimized for high-power Li-ion batteries with high cell voltages (DFG, 2007-2010)

**Publications**

Aleska, V.; Barkauskas, V.; Pogorelov, V.; Fuess, H.; Balevicius, R.;


Dincer, I.; Elerman, Y.; Elmali, A.; Ehrenberg, H.; Andrè, G.; Neutron diffraction study of the La$_{1-x}$Pr$_x$Mn$_2$Si$_2$ ($x = 0.4$, 0.7 and 1) compounds and the general description of the magnetic behavior of Mn in RMn$_2$Ge$_2$ and RMn$_2$Si$_2$, J. Magn. Magn. Mater. 313 (2007) 342-353.

Dincer, I.; Elerman, Y.; Duman, E.; Elmali, A.; Ehrenberg, H.; Fuess, H.; The influence of substitution of Co for Mn on magnetism of the HoMn$_{6-x}$Co$_x$Sn$_6$ compounds ($0 \leq x \leq 0.25$), J. Magn. Magn. Mater. 313 (2007) 204-209.


Nikolowski, K.; Bramnik, K.G.; Bächt, C.; Ehrenberg, H.; Fuess, H.; Behaviour of LiNi0.8Co0.2O2-cathodes at high cycle numbers, J. Power Sources 174 (2007) 818-822.


Pavlyuk, V. V.; Dmytriv, G. S.; Tarasiuk, I.; Senyshyn, A.; Pauly, H.; Ehrenberg, H.; The ternary indides Li278(In,Ag)154: a new n=6 variant of cubic n × n × n W-type superstructures, Intermetallics 15 (2007) 1409-1415.

Peters, L.; Knorr, K.; Evans, J.S.O.; Senyshyn, A.; Rahmoun, S.-N.; Depmeier, W.; Proton positions and thermal behaviour of the phase 4 CaO . 3 Al2O3. 3 H2O and its thermal decomposition to [(OCa4)2 [ Al12O24]-SOD, determined by neutron/X-ray powder diffraction and IR spectroscopic investigations, Z. Kristallogr. 222 (2007) 365-375.


Walha, I.; Ehrenberg, H.; Fuess, H.; Cheikhrouhou, A.; Structure and magnetic properties of lanthanum and calcium-deficient La$_{0.5}$Ca$_{0.5}$MnO$_3$ manganites, J. Alloys Compd. 433 (2007) 63-67.


Zhang, S.-T.; A. B. Kounga, A. B.; Aulbach, E.; Ehrenberg, H.; Rödel, J.; Giant strain in lead-free piezoceramics Bi$_{0.5}$Na$_{0.5}$TiO$_3$-BaTiO$_3$-K$_{0.5}$Na$_{0.5}$NbO$_3$, Appl. Phys. Lett. 91 (2007) 112906.


About 100 additional publications of single crystal structures published in Acta Cryst E and Z. Kristallogr.
Chemical Analytics

The scientific program of the chemical analytics division combines the synthesis, the modification and the characterization of advanced material, including qualitative, semiquantitative and quantitative analytics of elemental composition and characterisation of chemical binding in solid and liquid samples.

For solids, measurements with high spatial resolution are carried out by Electron Probe Micro Analysis (EPMA), Rutherford Backscattering Spectrometry (RBS), and Secondary Ion Mass Spectrometry (SIMS). The latter is also used for thin film analysis with high depth resolution.

Average compositions of solids are analyzed by X-ray Fluorescence Analysis (XRF), solutions of materials are measured by Atomic Absorption Spectrometry (AAS), ICP Optical Emission Spectrometry (ICP-OES) and Gas Chromatography, coupled with high resolution Mass Spectrometry (GC-MS).

The materials investigated include metals, amorphous and crystalline alloys, semiconductors, oxide, nitride and carbide ceramics in the form of clusters, thin films, multilayers and bulk materials.

Present research topics are:

Thin film speciation

In thin film technology, the identification of chemical compounds, phases and binding conditions is of basic importance. In a collaboration with Physikalisch-Technische Bundesanstalt in Berlin and institutes in Novosibirsk/Russia, thin films of boron carbonitride and silicon carbonitride are prepared and characterized. The preparation techniques are plasma enhanced chemical vapour deposition and sputtering (physical vapour deposition). The chemical composition of the films is measured by SIMS. The atomic binding states are investigated by Near Edge X-ray Absorption Fine Structure (NEXAFS) measurements, partially in Total reflection and Glancing Incidence X-ray Fluorescence (TXRF, GIXRF) geometry, by X-ray Photoelectron Spectrometry (XPS – collaboration with Dr. A. Klein, Surface Science), and by Transmission Electron Microscopy with Electron Energy Loss Spectrometry (TEM-EELS). The TXRF-NEXAFS experiments are carried out at BESSY II.

In another project, thin films (nanofilms) of carbides of boron, silicon, titanium, and tantalum are formed by hydrocarbon plasma immersion ion implantation, in collaboration with Industrial Technology Center of Nagasaki. The chemical film composition is analyzed by SIMS, the phase composition by X-ray diffraction. Film morphology and microstructure are investigated by scanning electron microscopy and by atomic force microscopy.

Corrosion

Phenomena of aqueous corrosion of metals, depending on their chemical composition, phase and structure, are investigated by electrochemical and trace analytical methods. The methods include potential-time and current-potential
(polarization, cyclic voltammetry) measurements, Electrochemical Noise Analysis (ENA) and Electrochemical Impedance Spectroscopy (EIS). Immersion tests with chemical analysis of the dissolved material are carried out by e.g. Atomic Absorption Spectrometry and ICP Optical Emission Spectrometry. The materials investigated are the metals aluminium, magnesium, and iron, and alloys.

A special topic is the corrosion of thin films, formed by plasma and ion beam methods, such as diamond-like amorphous carbon, or by sol-gel synthesis in combination with spin coating, such as zirconium oxide. These films (on the nanometer scale, i.e. nanofilms) suffer from microporosity which greatly influences the film/substrate corrosion performance. The underlying corrosion mechanisms and the correlation between film deposition parameters and corrosion protection ability are investigated.

Nanopores and nanowires

In collaboration with Gesellschaft für Schwerionenforschung (GSI), membranes or microfilters are formed by irradiation of polymer foils (polycarbonate, polyimide) and chemical etching the latent ion tracks to pores. These ion track filters (ITNF: ion track nanofilters, when the pores have diameters < 100 nm) can be used for filtering liquids from particles, collecting aerosols, for gas separation, and for analyzing small molecules and molecular fragments by translocation.

In a further process step, the nanopores are galvanically filled with metals, such as copper or gold, forming nanowires. The nanowires can be gained by dissolution of the polymer template. Dimensions, surface topography, microstructure, and crystallinity are investigated. Further, properties such as electrical conductivity and thermal stability are studied. The wires decay upon heating to a chain of spheres (Rayleigh instability). This effect is investigated.

Materials in Radiation Fields

In a number of applications, such as in nuclear facilities, particle accelerators and in space, materials are exposed to energetic ionizing radiation. The irradiation may lead to a degradation of the materials properties. Polymers are particularly sensitive towards ionizing radiation. In a collaboration with GSI, polyimide and polyepoxide, which are components of superconducting beam guiding magnets, were irradiated with relativistic heavy ions and characterized for their properties, such as network degradation and electrical conductivity. Another material is polycrystalline graphite, which is being used as the target wheel and as the beam dump.

Ion Beam Analysis

In frame of our close (internal and external) cooperations with other research groups and research institutes (GSI, Darmstadt, Institut für Kernphysik J.W. Goethe Universität, Frankfurt, Institut für Technische Physik, TU Graz, etc.) we apply regularly ion beam methods for modification and analysis of advanced materials. Ion beams (containing light and heavy ions) will be used in different energy ranges (from 100 keV up to several GeV) for irradiation and tailoring of material properties. Using the wide energy range it is possible to study and compare effects induced by nuclear
and/or electronic energy loss. Composition, film thickness and diffusion properties will be studied by ion beam analysis methods like Rutherford Backscattering Spectrometry (RBS), Secondary Ion Mass Spectroscopy (SIMS) and Nuclear Reaction Analysis (NRA). Crystalline quality and epitaxial growth can be verified by channelling experiments. The defect structure will be investigated using Positron Annihilation Spectroscopy (PAS).

**Collaborations**

The above mentioned and a number of further topics, e.g., from semiconductor research and from nuclear research, are investigated in collaboration with national institutes and with research centers and institutes abroad, such as

- Physikalisches-Technische Bundesanstalt, Berlin;
- Gesellschaft für Schwerionenforschung, Darmstadt;
- Deutsches Kunststoff-Institut, Darmstadt;
- Institut für Kernphysik, University of Frankfurt
- National Inst. of Advanced Industrial Science and Technology, Osaka, Japan;
- Industrial Technology Center of Nagasaki, Japan
- Rutherford Appleton Laboratory, Didcot, England
- Centre Interdisciplinaire de Recherche Ions Lasers, Caen, France
- Institut für Technische Physik, University of Graz
- Joint Institute for Nuclear Research, Dubna, Russia;
- Institute of Inorganic Chemistry, Novosibirsk, Russia;
- Institute for Water and Environmental Problems, Barnaul, Russia;
- Institute of Earth Crust, Irkutsk, Russia;

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Research Projects

Chemical and physical characterization of nanofilm systems (nanofilm speciation) (jointly with PTB, Berlin; DFG 2005-2008)

Deposition and implantation of carbon from hydrocarbons by plasma immersion ion implantation (DFG, 2005-2007)

Internal target experiments with highly energetic stored and cooled secondary beams at the International Acceleration Facility, Darmstadt Ion Research and Antiproton Center (EU, 2005-2007)


Radiation stability of graphite as production target and ion beam dump of the Super- FRS (GSI, 2007-2009)

Fabrication and characterization of gold nanowires (GSI, 2004-2007)

Separation of lithium and caesium isotopes from the primary coolant system of a pressurized water reactor (EnBW AG Kernkraftwerk Philippsburg, 2005-2007)

Study of defect structure and diffusion in ferroelectric materials, Project B2, Collaborative Research Center (SFB 595 2003-2010)

Atomic transport and transient processes in nanostructured metal/ceramic and ceramic/ceramic systems (BMBF, UKR 05/003 2006-2008)

Interface properties and atomic transport in nanoscaled heterostructures (BMBF, MOE 07/R61 2007-2008)

Study of defect structure in semiconductors and intermetallic phases, Scientific cooperation between TU Darmstadt & TU Graz, since 1996

Publications


W. Ensinger, Formation of nanopore membranes and nanowires by high energy ion irradiation of polymer foils, Surface and Coatings Technology, 201 (2007) 8442


Teaching by this division addresses the atomistic foundations of materials science, including the concepts underlying their representation, from the theoretical physics point of view. Research focuses on materials modelling, being a powerful tool for materials development. Experimental results will be understood, and predictions of further observations given, in the light of theoretical evidence, both to aid the optimization of the properties or the performance of materials already in use and to guide the design of novel materials with properties, or behaviour, required in future engineering applications.

Current investigations centre on the following classes of materials:

**Transition metals and related alloys**
For this class of materials, represented by Ta and Fe or, respectively, steels, the goal is examining their suitability for structural components of high-power spallation neutron sources that are exposed to intense proton beams. Irradiation-induced hydrogen production under the operating conditions of the envisaged European spallation source is predicted to generate high internal concentrations of atomic hydrogen which, further enhanced by stress-driven hydrogen accumulation near microstructural cracks, may lead to a severe degradation of the mechanical properties of steel, whereas no noticeable deterioration is to be expected in the case of tantalum.

**High-temperature superconductors**
For this class of materials, typified by YBa$_2$Cu$_3$O$_7$ and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ in thin-film or bulk form, great interest is directed towards investigating extended defects (e.g. low-angle grain and twin boundaries) which are considered as weak-links between superconducting grains. There are two principal aims: (i) exploring the connection between the electromagnetic response (e.g. the current-voltage relation) and the characteristic defect morphology so as to obtain insight into constitutive parameters of superconducting films; (ii) searching for possibilities to improve the current-carrying capability of superconducting materials, which is limited by the above-mentioned types of defect. Preliminary studies of novel heterostructures involving superconductor strips with a single grain boundary defect, placed in open magnetic cavities, show that magnetic shielding here is a promising way forward. Another field of research addresses the interaction between electromagnetic radiation and multilayered heterostructures made up of highly anisotropic superconductors as well as a range of different classes of materials with a view to examining their suitability for novel photonic crystals. Of special interest are materials whose properties can be controlled by external parameters and fields.

**Organic semiconductors**
For this class of materials, represented by Alq$_3$ and PPV, emphasis is placed on modelling of bipolar charge carrier injection, transfer and recombination as well as on a theoretical analysis of thermally stimulated luminescence phenomena with the aim of extracting, in conjunction with experiments, information about the electronic structure of inherent traps so as to assist technological exploitation and further materials development. Some of the most important features to be taken into account...
hereby are the field dependence of the injection barriers present, apart from allowing for the variation of the distribution of traps in space and depth.

**Ferroelectrics**

For this class of materials, typified by BaTiO$_3$ and PZT, attention is focussed on the process of ageing, i.e. the gradual change of materials properties with time, isothermal conditions and absence of external mechanical loads implied. This process manifests itself in alterations of static and, respectively, kinetic characteristics such as the clamping pressure exerted on the walls of ferroelectric domains, the electric permittivity and the asymmetry of the electrical conductivity regarding current flow parallel or antiparallel to the direction of the spontaneous polarization; phenomena, which may be explained in terms of migration of charged point defects under the influence of internal or external electric fields. Preliminary results obtained with a drift-diffusion approach suggest that the experimentally observed drastic rise of the clamping pressure and the decrease of the electric permittivity with time may indeed be controlled by a mechanism of this kind.

The theories underlying these investigations range from microscopic to macroscopic; their realizations employ analytical as well as computational techniques.

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Prof. Dr. Igor L. Lyubchanskii, D.Sc.

---

**Research Project**

Kinetic Modelling of the Charge Transfer in Organic Semiconductors and Ionic Conductors (Collaborative Research Centre (SFB) "Electric Fatigue in Functional Materials", 2007-2010, with Prof. Dr. H. v. Seggern, Darmstadt University of Technology)
Publications


Materials Modelling

The research of the Materials Modelling Division is focused on multi-physics modelling of defect structures in materials across various time and length scales. Materials of interest include functional nanoparticles, ferroelectrics, transparent and organic semiconductors as well as nanostructured metals and high-pressure phases. We are combining discrete models and continuum descriptions depending on the corresponding problem.

Quantum mechanical calculations based on density functional theory are used for electronic structure calculations. Large-scale molecular dynamics with analytical interatomic potentials are the method of choice for studying kinetic processes and plastic deformation. Kinetic lattice Monte-Carlo simulations are extensively used for simulations of diffusional and transport processes on extended time scales. The group is operating several HPC-computers and has access to the Hessian High Performance Computers in Frankfurt and Darmstadt.

The current research areas are:

- Structure and mobility of point defects in transparent conducting oxides and ferroelectric materials
- Lead-free piezoelectric materials
- Mechanical properties of nanocrystalline metals and alloys
- Metallic nanoglasses
- Thermodynamic and kinetic properties of functional nanoparticles
- Reactive interatomic potentials for compound systems

Besides the mandatory teaching of undergraduate courses the Materials Modelling Division is currently offering a 2-semester course on atomic scale methods for materials simulations. In 2007 Dr. Michael Müller received a PhD-degree for his research on magnetic FePt nanoparticles and joined the research division of Schott Solar. Dr. Paul Erhart received an award of the alumni association "Freunde der TU Darmstadt" for his PhD-thesis. Dr. Jani Kotakoski joined the group as research associate in January 2007. Alexander Stukowski, Peter Agoston, Daniel Sopu, Yvonne Ritter and Silke Hayn started to work on their PhD projects, while Prof. Dr. K. Albe was appointed as full professor for materials modelling in August 2007.

Staff Members

**Head**
Prof. Dr. Karsten Albe

**Research Associates**
Dr. Jani Kotakoski
Dr. Michael Müller (until Juli 2007)

**PhD Students**
Dipl.-Ing. Peter Agoston
Dipl.-Phys. Alexander Stukowski
M. Sc. Daniel Sopu
Dipl.-Ing. Yvonne Ritter
Dipl.-Ing. Silke Hayn

**Diploma Students**
Johann Pohl (until May 2007)
Mathias Nalepa
Technical Personnel
Andreas Hönl (Trainee) Susanne Müller (apprentice)
Kathleen Feustel (apprentice)

Secretary
Renate Hernichel

Guest Scientist
Tommi Järvi, MSc; University of Helsinki, Finland
Darius Pohl, IFW Dresden
Dr. Xu Ye, Fudan University Shanghai

Research Projects
Quantum mechanical computer simulations on the electronic and defect structure of oxide materials (DFG-SFB 595, Project C1, 2007-2010)
Atomistic computer simulations of defects and their mobility in metal-oxides (DFG-SFB 595, Project C2, 2007-2010)
Polymeric nitrogen (DFG, Al 578-3, 2005-2008)
Metallic nanoglasses (DFG Al 578-6, 2007 – 2008)
Atomic level simulations of structure and growth of nanoalloys (DAAD, PPP-Finland, 2007-2009)

Publications


**Awards**

Paul Erhart, “2007 Award for Excellent Academic Achievements” awarded by the Alumni Association “Freunde der TU Darmstadt”
Materials for Renewable Energies

The Renewable Energies team has been established at the Institute for Materials Science in December 2004. The group’s research focuses on low-temperature fuel cells and related electrocatalysis using advanced ex situ, and in particular, operando techniques for the detailed structural and electrochemical characterization of nanoscale catalysts. Techniques applied on the structural side include X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM), whereas electrocatalytic activities are measured using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and single cell fuel cell tests.

Recent projects concern the systematic investigation of the membrane-electrode assembly in polymer electrolyte fuel cells (PEMFC) before and after use, and its optimization according to the requirements for efficient operation. In this project, a new methodology for TEM sample preparation and characterization has been developed providing fascinating insights into the MEA structure. In another approach, a special in-situ fuel cell has been designed and successfully applied at beamlines X1, Hasylab, Hamburg, and at BM29, ESRF, Grenoble. Detailed operando experiments have been performed at both the anode and the cathode side shedding light on fundamental mechanisms taking place during real fuel cell operation.

The group has established various national and international collaborations in the fuel cell community. A novel data analysis procedure developed by Prof. David Ramaker and his group at George Washington University has been applied to our operando fuel cell data allowing us to monitor changes in catalyst structure and adsorbate coverage during real cell operation. But also several projects were carried out in cooperation with industry in order to get further insight into degradation mechanisms taking place during long-term operation and to explain the observed performance losses. These projects are largely covered by funds from the German Science foundation (DFG) and the BMBF.

Teaching activities in 2007 included the regular curricula lecture “Methods in Materials Science I: Structural analysis” and the linked practical course. The group’s research interests are covered by a lecture on “Fuel Cells – from fundamentals to application” and a practical course “X-ray absorption spectroscopy – fundamentals and data analysis”. Furthermore, a workshop on “Scientific work and presentation skills” is offered on request.
Staff Members

Head
Dr. Christina Roth

Secretary
Maria Holzmann (joint with Prof. Fuess)

Post-Docs
Dr. Marc Michel

PHD students
Dipl.-Ing. Virginie Croze
Dipl.-Ing. Frank Ettingshausen
Dipl.-Ing. Susanne Zils

PHD students (extern, ISE)
Dipl.-Ing. Julia Melke (joint with Prof. Fuess)
Dipl.-Ing. Frieder Scheiba

Diploma students
Stefan Hirsch
Christian Proff

Guest Scientists
Prof. Dr. David Ramaker

Research Projects

In-situ X-ray diffraction and X-ray absorption spectroscopy for investigation of the cathode catalyst in a working fuel cell (DFG project 2005-2008)

Structural investigation of membrane-electrode assemblies in fuel cells using ESEM (DFG project 2006-2009)

Synchrotron- and neutron-based investigation of PEM fuel cells (RunPEM) (BMBF project 2007-2010)

Publications


Joint Research Laboratory Nanomaterials

The Joint Research Laboratory Nanomaterials was established in 2004 to enhance the cooperation between the Institute for Nanotechnology at the Forschungszentrum Karlsruhe and the Institute of Materials Science at the Technische Universität Darmstadt. The start-up to establish the laboratory was provided by both institutions. Scientific personell is financed by the Forschungszentrum Karlsruhe and by external grants of funding agencies in Germany and of the EU as well as by industrial cooperations. The laboratory interacts in several areas with research groups in Materials Science and Chemistry. The research activities are concentrated in the area of nanoparticulate systems, their synthesis and processing, microstructural characterization and their properties. The focus is currently on developing nanoporous structures as bulk materials and thin films on a variety of substrates for developing catalyst support materials and catalysts, gas sensors and templates for the growth of light-harvesting molecular structures (porphyrines) and the development of alternative solar cells for low light conditions. An additional engineering focus of the research is on the stability of nanostructured materials under operation conditions, such as high temperatures and gas environments, as well as the study of mechanical performance of nanoporous structures. The nanomaterials are prepared using Chemical Vapor Synthesis and Nebulized Spray Pyrolysis starting from metal-organic precursors and metal salts. Using these methods a wide range of nanostructures can be synthesized. In addition to several synthesis systems, characterization equipment is available including X-ray diffraction, nitrogen adsorption, light scattering and Zeta potential and gas chromatography.

Staff Members

Head
Prof. Dr.-Ing. Horst Hahn (Director Institute for Nanotechnology)

Research Associates
Dr. Mohammad Ghafari
Dr. Jens Ellrich
Dr. Hermann Sieger (until May 2007)

Secretary
Renate Hernichel

PhD Students
Dipl.-Ing. Thorsten Enz
Dipl.-Ing. Sebastian Gottschalk
Dipl.-Ing. Peter Marek
Dipl.-Ing. Mohsen Pouryazdan
Dipl.-Ing. Philipp Leufke
Dipl.-Ing. Jens Suffner
Dipl.-Ing. Azad Jaberidarbandi
Dipl. Phys. Anna Castrup
Dipl.-Ing. Simon Bubel
Dipl.-Ing. Subho Dasqupta

Diploma Students
Clemens Wall
Ravimohan Prasad
Guest Scientists
Mohammad Imteyaz Ahmad, IIT Madras
Saptha Gireesh Subbarayan, IIT Madras
Mani Mahesh Kumar, IIT Kharagpur
Durga Madhad Mishra, IIT Dehli
Prof. Subhu Battacharya, IIT Madras

Research Projects

Defect structure and diffusion in ferroelectric materials (SFB 595 2003 – 2006)
Processing of Nanostructured Materials through Metastable Transformations Namamet (EU 2004 – 2008)

DIRAC secondary-Beams (EU/GSI 2005 – 2008)


Metallische Nanogläser (DFG 2006 – 2008)

Publications


Collaborative Research Center (SFB)

„Electric Fatigue in Functional Materials“

Phase II: Jan. 2007 – Dec. 2010
www.sfb595.tu-darmstadt.de

The center for collaborative studies (Sonderforschungsbereich) has been awarded by the Deutsche Forschungsgemeinschaft in 2002 to TU Darmstadt and is centered in the Department of Materials and Earth Sciences with important contributions from the Department of Chemistry and the Departments of Civil Engineering, Mechanical Engineering as well as the Mechanical Engineering Department of the University of Karlsruhe. The center was renewed in 2006 and has recently started its second four-year funding period.

It is comprised of a total of 19 projects and financial resources for four years of about 8 Mio. €. The center has an active guest program with guests visiting from 2 days to 3 months. For specific information, please contact either the secretary of the center, Mrs. Gila Voelzke, or the director of the center, Prof. Jürgen Rödel.

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SFB 595: Electrical Fatigue in Functional Materials
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Electrical fatigue in functional materials encompasses a set of phenomena, which lead to the degradation of materials with an increasing number of electrical cycles. Electrical cycling leads to both reversible and irreversible currents and polarisations. Ionic and electronic charge carriers interact with each other and with microstructural elements in the bulk as well as at interfaces (grain boundaries and domain walls) and interphases (electrode/electrolyte). This in turn causes local changes in the distribution of electric currents and electric potentials. As a consequence local overloads and material degradation ensues and leads to irreversible loss of material properties. This material degradation can lead finally to mechanical damage as well as to dissociation reactions. The basic phenomena of electrical fatigue are not yet understood on a microscopic level.

The goal of this center of excellence in the second phase is the understanding of the mechanisms leading to electrical fatigue. An understanding of the experimental results is supported by concurrent materials modelling which is geared to encompass different time and length scales from the material to the component.
A key feature of the center is therefore the steady comparison between theory and experiment. This is utilized to find the physico-chemical origins of electrical fatigue as well as to develop strategies for new materials and improved material combinations. The materials of interest are ferroelectrics, electrical conductors (cathode materials for lithium batteries and transparent conducting oxides) and semiconducting polymers.

Projects:

**Division A: Synthesis**

**A1**  
P.I.: Prof. J. Rödel  
Topic: Manufacturing of textured ceramics actuators with high strain

**A2**  
P.I.: Prof. M. J. Hoffmann  
Topic: Manufacturing and characterization of PZT-ceramics under dc loading

**A3**  
P.I.: Prof. W. Jaegermann  
Topic: Boundary layers and thin films of ionic conductors: Electronic structure, electrochemical potentials, defect formation and degradation mechanisms

**A4**  
P.I.: Prof. R. Riedel  
Topic: Novel functional ceramics using anionic substitution in oxic systems

**A5**  
P.I.: Prof. M. Rehahn  
Topic: Synthesis of semiconducting model polymers and their characterization before and after cyclic electric fatigue

**Division B: Characterization**

**B1**  
P.I.: Dr. R.-A. Eichel / Prof. K.-P. Dinse  
Topic: EPR-Investigations of defects in ferroelectric ceramic material

**B2**  
P.I.: Dr. A. G. Balogh  
Topic: Investigations of the defect structure and diffusion in ferroelectric materials

**B3**  
P.I.: Prof. H.-J. Kleebe / Prof. H. Fueß  
Topic: Structural investigations into the electrical fatigue in PZT
B4
P.I.: Dr. H. Ehrenberg
Topic: In-situ investigations of the degradation of intercalation batteries und their modelling

B7
P.I.: Prof. H. v. Seggern / Dr. A. Klein
Topic: Dynamics of electrical properties in fatigued PZT

**Division C: Modelling**

C1
P.I.: Prof. K. Albe
Topic: Quantum mechanical computer simulations for electron and defect structure of oxides

C2
P.I.: Prof. K. Albe
Topic: Atomistic computer simulations of defects and their mobility in metal oxides

C3
P.I.: Prof. R. Müller / Prof. W. Becker
Topic: Microscopic investigations into defect agglomeration and its effect on the mobility of domain walls

C5
P.I.: Dr. Y. Genenko / Prof. H. v. Seggern
Topic: Phenomenological modelling of bipolar carrier transport in organic semiconducting devices under special consideration of injection, transport and recombination phenomena

**Division D: Component properties**

D1
P.I.: Prof. J. Rödel / Dr. T. Granzow
Topic: Mesoscopic and macroscopic fatigue in doped ferroelectric ceramics

D3
P.I.: Dr. A. Klein
Topic: Function and fatigue of conducting electrodes in organic LEDs and piezoceramic actuators

D4
P.I.: Dr. Ch. Melzer / Prof. H. v. Seggern
Topic: Fatigue of organic semiconductor components

D5
P.I.: Prof. W. Jaegermann
Topic: Processing and characterization of Li-ion thin film batteries
Developing alternative piezoelectric ceramic materials which are free of toxic elements esp. lead (Pb) is one of the world-wide hot issues these days. Both intensive and extensive research activities during the last decade have proposed many of potentially promising materials. They can be categorized mainly into three groups, i.e. Ba-based, Bi-based, and KNN-based. However, each one has a critical drawback for real time applications, e.g. a low Curie temperature for Ba-based systems, the undesirable presence of the depolarization temperature a way below the Curie temperature in Bi-based systems, and poor reproducibility due to a high volatility of metallic elements in KNN-based systems. To overcome the inherent weaknesses of these systems, most research works these days are directed either to utilize the dopant effect on them or to locate and test the morphotropic phase boundaries (MPB) in solid solutions of them. Since the intrinsic piezoelectric properties of a material establish a basis for further tuning of the properties by the addition of dopants, the direction of our investigation was oriented to find compositions with desirable strain level in a ternary system (1-x-y)(Bi\(_{0.5}\)Na\(_{0.5}\))TiO\(_3\) – xBaTiO\(_3\) – y(K\(_{0.5}\)Na\(_{0.5}\))NbO\(_3\) (BNT–xBT–yKNN), especially near the MPB of the binary system, 0.94(Bi\(_{0.5}\)Na\(_{0.5}\))TiO\(_3\) – 0.06BaTiO\(_3\).

Some of the piezoelectric responses of importance of the line which connects the MPB between rhombohedral BNT and tetragonal BT and that between orthorhombic KNN and tetragonal BT are presented in Fig. 1. It is noted that BNT-6BT-2KNN.
shows an exceptionally high $\frac{S_{\text{max}}}{E_{\text{max}}}$ value of about 560pm/V was observed. This value corresponds to 0.45% strain level at 8kV/mm, which has never been achieved in lead-free piezoceramics yet. Interestingly, this large strain value comes not from the intrinsic piezoelectric effect, as is evident from the comparison of large and small signal $d_{33}$ values in Fig. 1. From the shape of bipolar, unipolar strain as well as polarization curves, this large level of strain is mostly due to an electric field induced antiferroelectric (AFE) to ferroelectric (FE) phase transition. To confirm and understand the mechanism involved in this exceptionally large electric field induced strain, a further detailed investigation on the nearby compositions of xy(6,2) was performed.

Figure 2 shows the bipolar strain responses of nearby 8 compositions with xy(6,2). The 9 compositions investigated can be classified into two groups with respect to the presence of 'negative strain,' which refer to the difference between the minimum and zero-field strain. Note that the absence of negative strain indicates the AFE order is dominant in the system. It is quite evident that xy(6,2) with the best unipolar strain that is one of the most important parameters during the actuator application resides on the boundary between FE and AFE dominant compositions. In regards, we believe that the extremely high strain level achieved in xy(6,2) is the consequence of a competitive free energy of FE and AFE order for the composition. We further believe that the invention of this new type of lead-free piezoceramics will bring a new concept to the community working on the lead-free piezoceramics for the actuator applications.
The organic light-emitting field-effect transistor
Martin Schidleja, Christian Melzer, Heinz von Seggern

In ambipolar organic field-effect transistors (OFETs) electron and hole conduction is possible in the same device depending on the applied voltages. Assuming strong recombination, the transistor channel of an ambipolar OFET driven in the electron accumulation can be divided into a unipolar n-type region near the source and a unipolar p-type region near the drain electrode separated by the recombination zone [1]. By using organic semiconductors with appropriate bandgaps the recombination of charge carriers in ambipolar OFETs can lead to visible light emission from the region where electrons and holes meet. OFETs with spatially adjustable emission zones have only been achieved recently [2], even though light emission from OFETs was reported already in 2003 [3]. These new devices provide deeper insight into the function of ambipolar OFETs and open new fields of research and new possibilities for applications.

For the realization of a light-emitting OFET a setup presented by Zaumseil et al. [4] was used. As shown schematically in figure 1, the transistor was built in a top-gate bottom-contact configuration. The gold source, drain and gate electrodes were deposited by physical vapour deposition. The dielectric PMMA (poly(methyl methacrylate)) and the organic semiconductor F8BT (poly(9,9-di-n-octyl-fluorene-alt-benzothiadiazole)) were deposited by spin-coating from solution in butyl acetate and toluene, respectively.

Figure 2 shows the transfer characteristic of an OFET at \( V_D = 100 \) V and the position of the recombination zone during the gate voltage sweep. The position of the recombination zone was extracted from optical micrographs of the channel taken during the measurement. At low gate voltages the potential between the hole injecting drain electrode and the gate is maximal and decreases with increasing gate voltage. The channel and thus the drain current are dominated by holes. With increasing gate voltage electrons are additionally injected from the source resulting in recombination with the already present holes. Light emission from the transistor channel close to the source is observed. Since the recombination zone is located at that position of the channel, where the potential equals the gate potential, the increase of the gate voltage leads to a movement of the recombination zone towards the drain electrode. At high gate voltages the p-channel region becomes shorter and finally the light emission breaks down once the p-
channel region disappears. Now, the current is dominated by electrons.

An analytical description of the charge transport in ambipolar OFETs without contact resistors was given by Schmechel et al. [1]. The comparison of the experimental results (see figure 2) and the analytical model shows that a qualitative behaviour of the drain current and the position of the recombination zone during the gate voltage sweep can be obtained. A fit to the experimentally determined position of the recombination zone is shown in figure 2 yielding rather balanced mobilities ($\mu_h/\mu_e = 1.9$) and high threshold voltages ($V_{th,e} = 32$ V, $V_{th,h} = -26$ V). Using the same set of parameters, the drain current does only fit qualitatively as illustrated in figure 2. One explanation for this misfit is the neglect of contact resistances, which should be substantial since injection barriers of about 1 eV are expected for both charge carrier types [4].

The simplest way to include contact resistances is to assume constant resistors at source $R_S$ and drain $R_D$, as shown in figure 3, and already suggested by Schmechel et al. [1] for unipolar OFETs. In figure 3, calculations for ambipolar OFETs without threshold voltages are presented. The results of the calculation show that with increasing contact resistance the ambipolar regime, indicated by the part of the transfer characteristic, where the recombination zone is within the channel, narrows from a gate voltage range of 100 V without contact resistances to 20 V with resistances of $1\times10^8$ $\Omega$. This narrowing of the ambipolar region agrees with the experimentally observed results presented in figure 2. With increasing resistance a narrowing of the quadratic part of the current/voltage characteristic is observed, which indicates the actual ambipolar regime. Furthermore, a voltage dependent lowering of the drain current at high and low gate voltages is observed due to an increasing voltage drop at the contact resistors for high drain currents. The latter could explain the deviation of the data calculated with the model of Schmechel et al. and the experimental data at high gate voltages presented in figure 2. The asymmetry of the experimentally determined current/voltage characteristic could be due to asymmetric contact resistances.

References:

Fig. 3: Shown is the position of the recombination zone during a gate voltage sweep at a constant drain voltage of 100 V. The inset shows the transfer characteristics of the device.
Formation of PSL-active luminescent centers in water treated CsBr:Eu$^{2+}$

G. A. Appleby, J. Zimmermann, R. Eichel, H. von Seggern

Storage phosphors used in imaging plates for x-ray radiography can store information with a process of radiation induced generation of electron/hole pairs and the subsequent trapping of these charges. In this state a latent image is stored which can be read out by a laser scanner using the mechanism of photostimulated luminescence (PSL). Thereby the electrons, trapped as F-centers, are excited to a state near the conduction band from where it is easily activated thermally into the conduction band. The electron can migrate to a nearby hole and recombine with it. The recombination energy is transferred to a luminescent activator doped in the phosphor matrix. But this is only possible if the hole is trapped close to the activator.

The storage phosphor CsBr:Eu is a promising material concerning spatial resolution and PSL-intensity. It can grow in columnar needles acting as light guides and therefore minimizing the scattering of the read out light. This makes this storage phosphor better suitable than the commercially utilized powdered BaFBr:Eu concerning the spatial resolution.

Another general aim in the field of storage phosphors is the improvement of the PSL-intensity which is important in medical applications to minimize the required x-ray dose. For CsBr:Eu the PSL-intensity is dramatically dependent on the treatment, i.e. atmosphere and temperature. It can be shown that even keeping a powdered sample at room temperature in a humid atmosphere changes the PSL-intensity. Furthermore thermally stimulated luminescence (TSL) measurements of CsBr:Eu, which indicates the number of different traps and their depth, reveal considerable difference between differently treated samples is shown (Fig. 1).

Fig. 3: TSL spectra for CsBr:Eu (a) fresh, (b) stored in a humid environment for 10min, and (c) for 60min. samples were irradiated at 10K.
It is clear that water treatment leads to the formation of very shallow traps. Moreover these shallow traps are somehow correlated with non-europium like luminescence centers. In the literature the luminescence at around 500 nm is related to oxygen whereas the centers with luminescence at 360 nm are assumed to be due to hydroxide. Since these centers are only observed at low temperatures, it is assumed, that they are due to shallow traps formed near the surface of the powder particles. This could also explain the correlation of traps with hydroxide and oxygen which is most probably adsorbed at the surface. However, keeping a fresh sample in 100% relative humidity for 30 min also leads to an increase of the PSL-intensity by a factor of about 20 (Fig. 2b). One could assume that the increase of the PSL is only due to adsorbed water. But subsequent annealing up to 400°C under inert atmosphere does not influence this state seriously. Further increase of the annealing temperature leads to a decrease of the PSL-intensity. Since the PSL-sensitivity is stable up to this high temperature, where adsorbed water is definitely boiled out, there must be another explanation. On the one hand the TSL spectra at low temperatures show the formation of oxygen and hydroxide centers increasing with increasing exposure time to humid atmosphere (see Fig. 1a – 1c). This leads to the assumption that water is decomposed and the fragments are incorporated in the CsBr-lattice. On the other hand it can be shown by electron paramagnetic resonance (EPR) that the crystal field in the vicinity of Eu-center is modified by an exposure of CsBr:Eu to humidity, indicating the formation of a dipole with the introduced fragments, most likely oxygen, with europium. The dipole field is assumed to be the reason for efficient hole trapping in the vicinity of Eu²⁺ and therewith the enhancement of the PSL-intensity.

In a recent EPR-measurement on a sample annealed in dry oxygen it is found that the spectrum is halfway between Figures 3a and 3b (not shown here). Hence it can be suggested that oxygen is responsible for the spectral change even in humid treated samples. However, oxygen treatment is not so efficient concerning the enhancement of the PSL-intensity like the treatment in water containing atmosphere. It can be concluded that the exposure of CsBr:Eu to humid atmosphere leads to the formation of shallow traps correlated with oxygen and hydroxide, and – much more important – to the enhancement of the PSL-intensity, probably due to the formation of dipoles of oxygen and europium.

![Figure 2: PSL intensity of samples hydrated in a humid atmosphere for the shown times following annealing for 30 min. The data is normalized so that the PSL from the samples before hydration is one, and the values at 0°C represent the PSL intensity before and after hydration.](image)

Figure 2: PSL intensity of samples hydrated in a humid atmosphere for the shown times following annealing for 30 min. The data is normalized so that the PSL from the samples before hydration is one, and the values at 0°C represent the PSL intensity before and after hydration.

![Figure 3: EPR spectra of (a) a fresh sample and (b) a sample exposed to humid atmosphere.](image)

Figure 3: EPR spectra of (a) a fresh sample and (b) a sample exposed to humid atmosphere.
Josephson Effect in Hybrid Oxide Heterostructures with an Antiferromagnetic Layer

Philipp Komissinskiy, Sandra Heinz, and Lambert Alff

In spite of recently renewed interest to superconducting structures with magnetically active materials, there is still a lack of experimental results on Josephson junctions with antiferromagnetic weak links, in particular, comprised of oxide HTS and AFM materials. Here we report on Josephson junctions between s- (Nb) and $\sigma$-wave ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) superconductors through a 50nm thick $\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$ antiferromagnetic layer (AFM) [1]. The Josephson effect in the Nb/Au/Ca$_{1-x}$Sr$_x$CuO$_2$/$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ heterostructures was investigated at various temperatures, magnetic fields, and applied millimeter-wave electromagnetic radiation. The magnetic field dependence of the supercurrent $I_c(H)$ exhibits anomalously rapid oscillations, which is the first experimental evidence of the theoretically predicted giant magneto-oscillations in Josephson junctions with antiferromagnetic interlayers.

Coexistence of superconducting and magnetic ordering in solids is of great interest for fundamental studies and electronic applications. In bulk compounds the exchange mechanism of ferromagnetic order tends to align spins of superconducting Cooper pairs in the same direction preventing singlet superconducting pairing. At the interfaces between superconducting and magnetic materials, however, superconducting and magnetic order parameters may interact due to the proximity effect resulting in interplay between superconducting and magnetic ordering and novel physical phenomena. For instance, superconductivity in Ferromagnetic/Superconducting/Ferromagnetic (FM/S/FM) spin-valve junctions can be controlled by spin orientations in the FM-electrodes. Another effect is the damped oscillatory behavior of the superconducting order parameter induced in the ferromagnetic layer across S/FM interfaces that may lead to a $\pi$ phase shift in the supercurrent of S/FM/S Josephson junctions.

We would expect interesting mesoscopic physical effects also at interfaces between superconductors and antiferromagnets. Monotonous suppression of the superconducting order parameter at the S/AFM interface with band type AFM and novel low-energy Andreev bound states originating from spin dependent quasiparticle reflections at S/AFM interfaces have been theoretically predicted.

We study dc and rf current transport in hybrid thin film S-N-AFM-D Antiferromagnetic Junctions (AFM-junctions) fabricated in the form of Nb/Au/Ca$_{1-x}$Sr$_x$CuO$_2$/$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ mesa heterostructures with areas from 10×10 up to 50×50 $\mu$m$^2$ (see Fig. 1a).

Fig. 1. (a) A sketch of the Nb/Au/Ca$_{1-x}$Sr$_x$CuO$_2$/$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ AFM-junction geometry and used electric measurement scheme. (b) A sketch of the ČSCO antiferromagnetic structure.
Here Nb is a conventional s-wave superconductor (S), YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) is an oxide d-wave superconductor (D), Au is a normal metal (N), and Ca$_{1-x}$Sr$_x$CuO$_2$ (CSCO) is a quasi-two dimensional Heisenberg AFM, where the quasiparticle spin direction alternates in the neighbor \( \{111\} \) ferromagnetic planes (see Fig. 1b). Electric and electronic paramagnetic resonance measurements of the CSCO thin films in the temperature range of 4.2-300 K demonstrate hopping conductivity and a Néel temperature \( T_N=90 - 120 \) K, respectively. Thus, the CSCO films are in a G-type antiferromagnetic Mott-insulating state within the temperature range of 4.2 – 40 K, where the electrical measurements have been carried out.

Integer and half-integer Shapiro steps at voltages \( V_n=n(hf_e/2e) \) and \( V_{n-1/2}=(n-1/2)hf_e/2e \) (\( n=1, 2, 3... \)), respectively, are observed in the \( I-V \) curves of the investigated AFM-junctions irradiated by an external millimeter-wave electromagnetic source at frequencies \( f_e=36-120 \) GHz (see the \( I-V \) curves of one of the junctions in Fig. 2 for \( f_e=56 \) GHz). The oscillating dependences of the critical current, \( I_c(I_e) \), and the amplitudes of the Shapiro steps, \( I_n(I_e) \), versus the millimeter-wave electromagnetic current amplitude \( I_e \) were derived from the \( I-V \) curves of the AFM-junctions (Fig. 3). Values of \( I_e \) were calculated as the square root of power of the external radiation. The experimentally obtained \( I_c(I_e) \) dependences follow the Resistively Shunted Junction (RSJ) model of Josephson junctions, where electrical current of the junction is considered as superposition of superconducting and quasipartical parts.

A specific feature of the AFM-junction is the additional rapid modulation of the \( I_c(H) \) pattern with a period of \( H_1=0.7 \) µT. The shape of the rapid oscillations strongly depends on the direction of the applied magnetic field. For instance, in-plane rotation of the applied magnetic field \( H \) by 90° makes the \( I_c(H) \) pattern asymmetric and doubles \( H_0 \) and \( H_1 \). Thus, the observed rapid oscillations of \( I_c(H) \) qualitatively correspond to the theoretically predicted ones in case of S/AFM/S Josephson junctions with layered AFM with alternating magnetic moments.

In collaboration with Institute of Radio Engineering and Electronics Russian Academy of Sciences; Moscow, Russia and Chalmers University of Technology, Göteborg, Sweden.

Novel half-metallic double perovskites for spintronics with tunable conductivity

Lambert Alff, Yoshiharu Krockenberger, Andreas Winkler, J. Kurian

This contribution has been selected as a ESRF-Highlight publication in 2007.

Materials with a high spin-polarisation of the conducting charge carriers are of great interest for spintronics. In particular, an ideal material with 100% spinpolarisation is called a half-metal. Such materials can be found in several materials classes: In classic oxides as magnetite or CrO$_2$, in manganites and intermetallic Heusler alloys, but also in the group of double perovskites. Double perovskites are of special interest, since within this group half-metals with above room-temperature transition temperatures are found. At the same time, within the vast perovskite family, heteroepitaxial multilayers of different functional materials as insulators, magnetic metals, and even superconductors, can be grown for future spintronic devices.

![Diagram](image.png)

Fig. 1: Simple model of the effect of $5d$ doping in Sr$_2$CrMO$_6$ with $M = \text{Ta, W, Re, and Os}$.

We have rediscovered [1] a double perovskite that has the highest Curie-temperature known so far within this group (725 K or 450°C): Sr$_2$CrOsO$_6$. It was erroneously considered to be nonmagnetic at room-temperature. Osmium is certainly an odd element with difficult metallurgy, however, one may remember that filaments in light bulbs are being made from osmium and tungsten. The role of Os in the compound Sr$_2$CrOsO$_6$ is to supply spin-polarised charge carriers. As in the light bulb filament,
one can also have tantalum, tungsten, and rhenium at the crystal site of osmium. Since these ions are in the 5+ state, they supply a number of spin-polarised electrons per unit cell, 0, 1, 2 and 3 electrons for Ta, W, Re, and Os, respectively. These spin-polarised electrons are also the glue and origin of ferrimagnetism of these compounds. In the case of Sr$_2$CrTaO$_6$ with no doped electrons, correspondingly, no ferrimagnetism is observed. With increasing number of doped electrons, the Curie-temperature of the compounds also increases: 450 K for Sr$_2$CrWO$_6$, 635 K for Sr$_2$CrReO$_6$, and finally 725 K for Sr$_2$CrOsO$_6$. With the changing number of electrons, the conductivity also changes. In Sr$_2$CrOsO$_6$ the metallic band (5d$_{t_{2g}}$) is completely filled. Therefore, Sr$_2$CrOsO$_6$ is an insulator and at the same time it still has the highest Curie-temperature. The band scheme is illustrated in Figure 1 [1]. This result is remarkable because it brings to light the possibility to tune a material in order to obtain fully spin-polarised conductivity in a desired range between a good metal and an insulator. In the future, an elegant way to tune the spin-polarised carrier density in a spintronics device would be to use the field effect.

In order to elucidate the mechanism of ferrimagnetism in the described double perovskites, it is of utmost importance to measure (separately) the spin and orbital magnetic moments at the Os (or W or Re) site. The magnetic moments of these ions are induced in the specific double perovskite structure from the magnetic Cr$^{3+}$ ions. Within a model of kinetic energy driven exchange it is expected that the induced spin magnetic moment scales with the Curie-temperature of the compound [2]. It is the merit of beamline ID12 that such measurements can be made with very high quality. In excellent agreement with neutron scattering experiments, the existence and scaling of the induced magnetic moments has been confirmed unambiguously by X-ray magnetic circular dichroism (XMCD) experiments (see data in [3]). At the Os site, a spin-magnetic moment of -0.17 $\mu_B$/formula unit (the minus sign indicates the anti-parallel orientation with respect to the Cr magnetisation) and an orbital magnetic moment of 0.015 $\mu_B$/formula unit has been measured. In addition, it could be shown that spin-orbit coupling has to be taken into account due to the heavy ionic mass of Os.

In conclusion, we have shown that the mechanism of magnetic coupling in the ferrimagnetic double perovskites also applies to insulating compounds with filled bands, where even the highest Curie-temperature is observed for this class of materials. This finding may contribute to the development of thin-film based field-effect transistors with the ability of switching between high and low conductivity that is in both cases fully spin-polarised and therefore desirable for spintronics.


Mechanistic description of gas sensing on inorganic, organic and polymeric materials is nowadays of great scientific and technological interest. The understanding of surface and bulk reactions responsible for gas sensing effects will lead to the increased selectivity and sensitivity in the chemical determination of gases and in the development of better sensors. In the last years operando and in situ spectroscopic tools have been developed and adapted to follow the physicochemical processes taking place in an active sensing element in real time and under operating conditions. Previous dreams, such as the monitoring of the processes responsible for gas sensing in the “living” sensors, no longer constitute unsolvable problems. Herein we have attempted to give an overview on in situ and operando spectroscopic techniques for the studies of gas sensing mechanism on solid state sensors.

Figure 1: Methodological approach for simultaneous spectroscopic and electrical (“phenomenological”) characterisation of gas sensors based on semiconducting metal oxides.
Summary and Outlook. Potential for the Future Development

The state-of-the-art models of gas sensing cannot explain all effects observed on operating metal-oxide-based sensors. The breakthrough in mechanistic description can be achieved only by the combination of experimental methods with the theoretical modelling. This requires developing the methodology that allow following the physicochemical processes taking place in an active sensing element in real time and under operating conditions. Hence, the improvement of the in situ spectroscopic tools / methodology and combination of in situ spectroscopic and electrical characterisation is the first part of the future research activities. The second concerns the development and the application of quantum chemical methods that allow to predict surface structure and reactivity in terms of temperature, pressure and composition of gas-phase in interaction with the surface of metal-oxide-based sensors.

They are expected to clarify the physicochemical processes on an active sensing element under working conditions and also provide new insight into mechanism of gas-solid interaction. The potential of that is, however, not fully recognised. One can expect real breakthrough in this field in the next years; this will concern (i) mechanistic understanding, (ii) theoretical advances and (iii) methodological developments. Below we will address this in several short example.
High Pressure and High Temperature Synthesis of Single Crystals of Carbon Nitride Imide, C2N2(NH)

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The main group element IV nitrides, Si\textsubscript{3}N\textsubscript{4} and Ge\textsubscript{3}N\textsubscript{4}, are well known inorganic compounds which crystallize in four polymorphs, namely in two hexagonal structures, \(\alpha\) and \(\beta\), and one cubic high pressure \(\gamma\)-phase with spinel structure as well as one high-pressure \(\delta\)-phase which cannot be recovered at ambient conditions. The homologue of the group IV element, Sn, forms a spinel-Sn\textsubscript{3}N\textsubscript{4}-phase under ambient pressure. So far there is no reliable evidence of the existence of a crystalline carbon nitride, however. In our search for C\textsubscript{3}N\textsubscript{4}, we obtained single-crystals of carbon nitride imide, C\textsubscript{2}N\textsubscript{2}(NH), by high pressure and high temperature synthesis in a laser heated diamond anvil cell at \(T > 1700\) °C and at \(P > 27\) GPa. The compound is formed from the single source precursor 1-cyanoguanidine, C\textsubscript{2}N\textsubscript{4}H\textsubscript{4}, presumably by polycondensation accompanied by release of NH\textsubscript{3}. Single crystals of C\textsubscript{2}N\textsubscript{2}NH with unusual high density \(\rho = 3.2\) g/cm\textsuperscript{3} were recovered to ambient conditions. The structure is of the defect-wurtzite type (\textit{Cmc2\textsubscript{1}}, \(a = 7.536(15)\) Å, \(b = 4.434(8)\) Å, \(c = 4.029(8)\) Å, \(Z = 4\)), closely related to the structures of silicon nitride imide, Si\textsubscript{2}N\textsubscript{2}(NH) and Si\textsubscript{2}N\textsubscript{2}O. The bulk modulus, \(B_0\) is calculated to be 277 GPa attesting a compressibility lower than \(\beta\)-Si\textsubscript{3}N\textsubscript{4}. Moreover, the atomic density of C\textsubscript{2}N\textsubscript{2}(NH) is 172.7 atoms/nm\textsuperscript{3}, which is only exceeded by the atomic density of diamond (176.5 atoms/nm\textsuperscript{3}). The novel carbon nitride imide is considered as a suitable precursor for the formation of C\textsubscript{3}N\textsubscript{4} analogous to the synthesis of Si\textsubscript{3}N\textsubscript{4} via the diimide route where Si\textsubscript{2}N\textsubscript{2}(NH) is formed as an intermediate compound.

![Figure 1: Defect wurtzite (dwur) structure of C\textsubscript{2}N\textsubscript{2}(NH).](image)
Characterization of Mo/W and V/W mixed oxide catalysts for the selective oxidation of acrolein to acrylic acid

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For the industrial production of acrylic acid, the selective oxidation of acrolein is the most important pathway. The reaction takes place under the catalytic influence of a V/Mo/W mixed oxide catalyst. The performance of the heterogeneous catalyst for this reaction is very high with conversion rates for acrolein close to 100 % and over 95 % for both the selectivity to acrylic acid and the yield of acrylic acid [1]. But still, the reaction pathway, the active phases of the catalyst and the mechanism of deactivation are controversially discussed.

The catalysts are usually prepared via spray drying of a precursor solution of the ammonia metallates and subsequent calcination, as described by Kunert et al. [2]. The resulting catalyst powders are fine grained sphere-like particles consisting of nanoscale crystallites with a high degree of disorder. Therefore, especially under operation conditions, the precise characterization of the catalysts is difficult. In order to understand the quaternary system, the ternary system V/Mo/O, which also shows considerably high catalytic performance, has already been characterized [3]. To complete this approach, the analysis of the structure and the behavior of the other two ternary systems, V/W/O and Mo/W/O, with respect to the selective oxidation reaction of acrolein is carried out in this project.

In cooperation with the Department for Technical Chemistry and Macromolecular Science, the catalysts have been tested for their catalytic potential by temperature programmed reaction experiments [4]. The results of these tests are shown in Figures 1 and 2 in terms of yield of acrylic acid. In all cases, the mixed metal catalysts show much better performance than the pure oxides which tend to be almost inactive (MoO$_3$ and WO$_3$) or too active (total oxidation with $V_2O_5$). Especially the catalysts V30W70 (30 at% V, 70 at% W) and Mo70W30 (70 at% Mo, 30 at% W) perform considerably well, reaching a selectivity towards acrylic acid of 45 % and 35 % respectively.

![Fig. 1: Yield of acrylic acid, Mo/W series.](image1.png)

![Fig. 2: Yield of acrylic acid, V/W series.](image2.png)

The structural analysis by X-ray powder diffraction of these two catalysts is shown in Figures 3 and 4. The graphs show diffraction patterns of catalysts as prepared, after
reduction under acrolein/nitrogen atmosphere at 400 °C and after three cycles of temperature programmed reactions under an atmosphere consisting of nitrogen, oxygen and acrolein at temperatures up to 480 °C.

Fig. 3: XRD patterns of Mo70W30 as prepared (1), after reduction with acrolein (2), after three cycles of temperature programmed reaction.

Fig. 4: XRD patterns of V30W70 as prepared (1), after reduction with acrolein (2), after three cycles of temperature programmed reaction.

The XRD patterns are exemplary for the corresponding catalyst series. The prepared Mo/W mixtures all display sharp reflections corresponding to well crystalline material, while the V/W series show very broad reflections indicating nanocrystalline and X-ray amorphous material respectively. During a reduction with acrolein at 400 °C, the Mo/W catalysts change their crystal structure, sometimes completely, as displayed by the Mo70W30 catalyst. On the other hand, the V/W catalysts show almost no alteration of the XRD signal after reduction. After three cycles of temperature programmed reaction, the crystal structure of the Mo/W catalysts is almost unchanged. The presence of oxygen seems to maintain the crystal structure of the catalysts while allowing a re-oxidation of the active parts of the catalysts according to the “Mars-van-Krevelen mechanism” [5], a generally accepted model for the processing of heterogeneously catalyzed partial oxidations. Also, the crystal structure of the V/W catalysts seems to be unchanged, as indicated by the positions of the reflections. But a growth of the crystallites seems to have occurred, as the width of the reflections is significantly narrowed, however not as narrow as for the Mo/W material.

The analysis of the structures and the behavior of the catalysts during the reaction is supplemented by the methods of transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS).

Literature

Ultrafine Grained Microstructure in HSLA Steel by Linear Flow Splitting

T. Bohn, E. Bruder, C. Müller

The requirements on the material properties are increasing continuously. Preferably materials would be used whose high performances do not limit the production process by exhausted formability. Therefore UltraFine Grained (UFG) microstructures with grain dimensions in the submicron range, characterized by high mechanical strength as well as high ductility, are of great economic and scientific interest [1]. Presently UFG materials are manufactured by several methods of Severe Plastic Deformation (SPD), like Equal Channel Angular Pressing (ECAP) [2], Accumulative Roll Bonding (ARB) [3] and High Pressure Torsion (HPT) [4]. All these SPD methods are characterized by high hydrostatic compressive stresses, which enable extremely high deformations in the work piece. Cells, cellblocks and microbands are formed within the grains and a subgrain structure of Low Angle Grain Boundaries (LAGBs) is created. With further deformation the LAGBs develop to High Angle Grain Boundaries (HAGBs) and lead to a grain refinement with grain sizes in the submicron range [5,6].

The new linear flow splitting technology is a process where such a microstructure appears in real components. Here, the edge of a sheet metal (sheet or coil) is formed into two flanges by splitting and supporting rolls generating the necessary hydrostatic stresses. These profiles are characterised by strongly inhomogeneous deformation resulting in microstructural and property gradients that are not characterised yet. Further details on the process principle and possible applications are presented elsewhere [7,8].

Microstructure

The HSLA steel ZStE 500 was used to investigate the microstructure and the mechanical properties of bifurcated profiles produced by linear flow splitting. Detailed EBSD-investigations on the microstructure of the as rolled flanges and the splitting center reveal a grain size gradient perpendicular to the flange surface. The elongated grains near the surface are mostly separated by HAGBs and show only marginal fragmentation. Within 50 µm to the flange surface the smallest average grain dimensions (line intersection perpendicular to the split surface) are below 100 nm. With increasing depth, i.e. distance to the split surface, the grain structure becomes coarser and more equiaxed. No microstructural gradients are observed along the splitting direction and parallel to the flanges (except at the flange tip, about 4 mm in length).

The distribution of HAGBs and LAGBs with different distances to the splitting center is illustrated in Fig. 1 on the basis of EBSD maps (inverse pole figure) with marked grain boundaries. HAGBs (>15°) are traced in black and LAGBs (2-15°) in

![Fig. 1. EBSD maps of the processing zone (inverse pole figure + marked grain boundaries) with different distances to the splitting center: (a) 650 µm, (b) 450 µm, (c) 250 µm.](image)
Mechanical properties

Hardness measurements on the split flanges from the splitting center to the flange tips (25 µm below the surface) reveal a constant hardness of 365 HV0.05 parallel to the surface over a wide range of the flange whereas the hardness of the as received material is only about 196 HV0.05.

Tensile tests reveal an increase in yield and tensile strength (744 MPa and 782 MPa) of about 60% in the flanges compared to the as received material (Fig. 2). The increased strength is associated with a reduced fracture strain and marginal uniform elongation as it is typical for UFG microstructures. Note that due to the samples thickness (0.8 µm) the tensile specimens include a microstructural and hardness gradient perpendicular to the loading direction. On the basis of hardness measurements the yield strength in the surface area of the flanges can be estimated to about 1000 MPa [9].

Summary

Linear flow splitting leads to the formation of UFG microstructures at the surface area of the split flanges. The UFG microstructure develops by the formation and fragmentation of a dislocation cells. The resulting grain size decreases with increasing deformation and the fraction of HAGB increases. This leads to a process characteristic ultrafine grain size gradient perpendicular to the split surface.

Due to the formation of UFG microstructures a steady state is reached in the process zone, where increasing deformation (i.e. splitting depth) has no more or little influence on microstructure and resulting properties. Thus work hardening and the related reduction of formability are no limiting parameters for the splitting process.

The flanges exhibit extremely high yield stress combined with an acceptable ductility. Hardness and yield stress gradients perpendicular to the split surface are a consequence of the process characteristic microstructure.
Thin film lithium ion batteries are currently investigated intensively due to their enormous technological potential as integrated power supplies on micro devices, such as implantable medical devices, CMOS-based integrated circuits, as well as smart IC packages or chips. The interest in the layered LiMO$_2$-type oxides (M= Co, Ni) as 4V-cathode materials for thin film batteries is originated in its superior properties, like capacity and (cycle-) stability, compared to other candidates for thin film applications. These qualities and also the well known electrochemical behaviour favour the model system character for fundamental intercalation studies.

A controversially discussed topic in the field of lithium ion batteries is the mechanism of charge transfer during the deintercalation reaction. The removal of Li$^+$ from a host materials like LiMO$_2$ (M= Co, Ni) requires the transfer of an equal amount of electrons. It is still not clarified whether the transition metal ions and/or the oxygen participate at the charge compensation and if there are differences for the substituted systems. Furthermore, it is an open question if the hybridization of the transition metal ions and oxygen changes during the different stages of deintercalation reaction.

Thin films of layered oxide materials like LiCoO$_2$, LiNiO$_2$ and Li(Co,Ni)O$_2$ have been deposited by rf magnetron sputtering [1]. The high quality of the thin films has been confirmed by XRD and Raman spectroscopy as well as electrochemical measurements.

The electrochemical deintercalation was carried out in a specific glass cell under Ar atmosphere (Fig. 1). The cell is directly connected to the solid liquid analysis UHV system.
(SoLiAS) which combines in situ thin film deposition and characterization by photoelectron spectroscopy [2]. This set-up allows a virtually contamination free transfer of the treated samples from the electrochemical cell to the UHV analysis.

![Intensity vs Excitation Energy](image1.png)

**Fig. 3.** The O K-edge x-ray adsorption near edge structures of LiCoO$_2$, LiNiO$_2$ and LiNi$_{0.5}$Co$_{0.5}$O$_2$ exhibit different behaviors upon lithium deintercalation (bottom to top). For each system a contribution of oxygen states to the charge compensation is visible. Though, the role of oxygen has still to be clarified mechanistically.

Changes of the electronic structure during deintercalation of the LiMO$_2$ cathodes have been investigated by SXPS and SXAS. This combination provides access to occupied core level and valence band density of states as well as the unoccupied conduction bands. In case of LiCoO$_2$ and Li(Ni,Co)O$_2$ a gradual oxidation (3+ to 4+) of the Co site becomes apparent during the deintercalation. This change is reflected by the change of relative intensities in the Co2p core level and Co3d like valence band emissions (Fig. 2). In comparison, the Ni2p only shows minor changes upon deintercalation for LiNiO$_2$ and Li(Ni,Co)O$_2$ (not included). The contribution of oxygen states can be derived from the x-ray absorption spectra of the O K edge (Fig. 3). At deep deintercalation levels also for LiCoO$_2$ an abrupt change can be observed, whereas for LiNiO$_2$ and Li(Ni,Co)O$_2$ the spectral changes are more continuously.

For each system a different impact on the electronic structure is observed during the intercalation reaction. Besides similar changes for the transition metal ions, distinct differences in the unoccupied oxygen states are obvious and hence a different role of oxygen states has to be assumed. In addition to the electronic changes of the materials, the highly surface sensitive core level electron spectroscopy delivers information about the formation of a solid-electrolyte interphase at the cathode surface (SEI). The investigation of these surface phases can help to understand long term stability and degradation phenomena for lithium ion batteries. Within this context the oxygen loss at the surface and the formation of defects is critical.

The applied experimental technique provides unique insights in the surface chemistry and changes of the electronic properties of electrode materials during the electrochemical deintercalation reaction. Detailed information, e.g. oxidation states of the transition metal ions, can be deduced.

**References**

Interfaces of organic solar cells
Eric Mankel, Corinna Hein, Johanna Härter, Thomas Mayer and Wolfram Jaegermann

1. Principles of organic solar cells

Providing of useable energy will be one of the most important challenges of the 21st century. Due to their unlimited availability renewables will become more and more indispensable. In particular the fast-growing fraction of solar energy conversion demonstrates the high demand on non ebbing energy sources.

Because of their low production costs, organic solar cells (OSC) promise a possible way to obtain cheap and flexible devices. Unfortunately, until now the efficiencies of OSCs are low. The prototype of bilayer-heterojunction OSCs, the so called Tang-Cell, shows an open circuit voltage of 0.44V and a short circuit current of 2.4mA/cm$^2$ leading to an efficiency of 0.8% only. By usage of interdigitating phases forming bulk heterojunctions and tandem cell device structures efficiencies of nearly 5% have been reached in the laboratory.

But why is the efficiency low? To understand this we first have a look on the working principle of a Tang-Cell which is shown in Fig. 1. Because of the low dielectric permittivity of organic materials, strong bound Frenkel excitons are formed after photon absorption. Exciton dissociation takes place at a phase boundary between a donor type material (CuPc) and an acceptor type material (BPE-PTCDI). The maximum open circuit voltage of the cell is given by the interface band gap between the HOMO of the donor and the LUMO of the acceptor molecule whereas the photo current is driven by the gradient of the electric potential at the interface ($\nabla U$) and the gradient of the charge carrier concentration ($\nabla n$) in each phase.

Therefore efficiency which is the product of voltage and current with respect to the incoming light power is directly affected by two interface parameters namely the electronic alignment (influences the voltage) and the development of the electric field at the interface (influences the current). The ideal method for investigation of these interface properties is synchrotron induced photoelectron spectroscopy (SXPS). To avoid contaminations of ambient air in-situ preparation and analysis is essential. For this we run the experimental station SoLiAS at BESSY II which can be connected to the beamlines U49/2-PGM2 and TGM7 providing synchrotron light in the range of 90eV to 1400eV and 20eV to 120eV, respectively.

2. The CuPc/BPE-PTCDI interface
In the interface experiment shown in Fig. 2 BPE-PTCDI molecules are deposited step by step on a thin film of in-situ evaporated CuPc. After each evaporation step photoemission spectra of the N1s core level line and the HOMO region in the valence band are taken at light energies of 600eV and 90eV, respectively.

The N1s core level line as well as the HOMO and the secondary edge show an energetic shift of the line position relative to the Fermi energy with increasing BPE-PTCDI coverage. This shift can be correlated to a change of the electric potential at the interface. The experimental results can be translated into a band diagram of the CuPc/BPE-PTCDI interface (Fig. 3).

The band diagram shows a band bending in both phases forming barriers of 0.12eV for electrons in BPE-PTCDI and of 0.15eV for holes in CuPc hindering the transport after the charge carrier dissociation. The width of the space charge layer in BPE-PTCDI is around 10nm as derived from the coverage. By these fields the recombination of dissociated charge carriers at the interface is favoured which could be the reason for the low short circuit current of the Tang-Cell.

A suggestion for improving of the short circuit current could be doping of the
CuPc layer. As shown in Fig. 3, the Fermi energy of CuPc is found at a mid gap position. A shift of the Fermi energy closer to the HOMO level could reduce the barrier height or reverse the band bending causing a potential gradient for the dissociated charge carriers accelerating them towards the contacts.

3. Doping of thin organic layers

Typically, shifting the Fermi energy of molecular organic layers will be performed by mixing with strong acceptor molecules. Grabbing this idea we decided to coevaporate CuPc with TCNQ obtaining blends of both materials with different TCNQ content. After coevaporation we took valence band spectra of the composites to identify the CuPc HOMO level position with respect to the Fermi level (Fig. 4).

The maximum of the HOMO level of pristine CuPc can be identified at 1.3eV binding energy. With increasing TCNQ content the maximum of the HOMO shifts closer to the Fermi level. The maximum shift we obtain is about 0.45eV. At low TCNQ contents the shape of the valence band features remains almost unaffected. At higher contents the CuPc features are overlapped by the characteristic TCNQ valence band emissions.

The experiments show that shifting of the CuPc Fermi level by mixing with TCNQ is possible but unfortunately the doping efficiency is small. The reason for this could be an interfacial dipole of 0.3eV measured by step-by-step deposition of CuPc on TCNQ possibly lowering the acceptor strength of TCNQ. Nevertheless the principle effect of systematic doping on the band alignment and the electric potential at the doped CuPc/BPE-PTCDI interface as well as the consequence on electric properties of the solar cell device will be the motivation for the next investigation steps.

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**Fig.4:** XP spectra of the secondary electron edge, the valence band and the HOMO region of CuPc/TCNQ composites with varied TCNQ content.
Oxide thin films based on the sol-gel technique are well-known for a number of favourable features, such as high hardness and chemical inertness, however, they tend to form holes and cracks. As they are chemically highly stable, they should be well-suited for corrosion protection. The drawback is that for this purpose cracks might be detrimental. The study aimed at investigating the properties of sol-gel based oxide films for their corrosion protection ability. Thin films of zirconium oxide, partially mixed with silicon oxide, were prepared by spin depositing sols of zirconium tetrapropoxide and phenyltriethoxysilane onto silicon wafers, iron and magnesium samples. The samples were heat treated (at temperatures between 100 and 900° C) to form the respective oxide coatings. Film thickness was measured as a function of spin speed, spin time, drying time and heat treatment temperature.

The results show that spin speed is a main factor determining the final thickness (Fig. 1a). Another possibility for depositing thin films is dilution of the sol-gel mother solution.

Scanning electron microscopy (SEM) images of the films showed that the surfaces are mostly homogeneous with defects only occurring above the critical film thickness of crack formation (Fig. 1b,c). It turned out that pure zirconium oxide films tended to crack at low thickness (around 200 nm), while admixture of silicon oxide reduced crack formation (with a critical film thickness > 400 nm).

The corrosion performance of the film/substrate system was evaluated by means of cyclic voltammetry in slightly acidic aqueous medium. For this purpose, polished iron substrates were coated with films of different thickness below and above the critical value to investigate the relation of thin film morphology and corrosion protection ability. For coated and uncoated iron substrates alike, cyclic voltammetry was carried out and the forward scans of the first potential scan cycles were plotted in a current density vs. potential graph (Fig. 2 left hand side). It can be concluded from the reduction of the iron dissolution current densities that the coatings protect iron samples to a certain extent from corrosive attack. The open circuit potential of coated samples shifts towards anodic values and the maximum so-called critical current density ($I_{\text{crit.}}$) of iron dissolution decreases by at least
two orders of magnitude. This means that a corrosion protection effect is obtained, however, the residual iron dissolution currents show that the films suffer from a certain microporosity. This is typical for thin films of such thickness.

Fig. 2: Results of electro-chemical measurements of a) an uncoated iron substrate and zirconia coatings with a pre-heat-treatment thickness of b) 415 nm and c) 250 nm; left graph: current density vs. potential plots; right graph: critical current densities, as extracted from the current/potential plots, as a function of number of potential scan cycles.

In order to gain information about the long-term corrosion behavior of the samples, their critical current densities ($I_{\text{crit.}}$) were plotted against the number of potential scan cycles from multiple potential scanning (Fig. 2, right hand side). After 20 cycles, which constitutes a severe corrosion attack, $I_{\text{crit.}}$ values increased only slightly and were still more than two orders of magnitude lower than for pure iron. Hence, as the films are able to stand multiple potential cycling, they prove to be stable over a longer period of corrosive attack.

As films with cracks are expected to provide less protection from corrosion, a series of samples with thicknesses above and below the critical value were prepared, heat treated and their corrosion behavior was investigated by means of cyclic voltammetry. It turned out that the films show a quite good corrosion protection effect, independent of the film thickness within the investigated region (200 to 500 nm).

When experiments with the same process parameters are carried out with magnesium substrates, the results are quite different. The metal dissolution currents are hardly reduced by the coating, indicating that the protection effect is very poor. Investigations with SEM and other methods showed that the films tend to flake off the substrate. This is an indication that, in contrast to films on iron substrates, adherence on magnesium substrates is poor. One reason for this may be found in stress, generated in the films upon cooling down after heat treatment. The thermal expansion coefficients of magnesium and zirconium oxide differ more than of the latter and iron.

Further work in this direction is in progress. Apart from single films, multi-layers are under investigation. Additionally, further precursors for the sol-gel process will be investigated, including ones for deposition of aluminium oxide.
Ion beam induced degradation of polymers used in superconducting beam guiding magnets*

D. Severin, T. Seidl, W. Ensinger

In the future high-energy and high-intensity heavy ion synchrotron SIS within the International Facility for Antiproton and Ion Research (FAIR) at Gesellschaft für Schwerionenforschung, superconducting beam guiding magnets with high fields and very short ramping times will be used. During operation, these will be exposed to high energy particles from swift heavy ions and their fragments, escaping from the desired beam trajectory.

Among the materials used in the magnets are polymers, such as polyimide and glass-fibre reinforced polyepoxy which act as electrical insulators and as construction materials. From all materials used in the magnets, these are most sensitive towards irradiation. Hence, they will define the magnets' operational life times.

For long term radiation stability tests polymer foil stacks were irradiated with swift heavy ions at a kinetic energy of 11.1 MeV/u at the UNILAC linear accelerator of GSI. Apart from the ion mass, the number of ions (fluence) to which the polymers are exposed is one of the major parameters determining radiation damage.

The mechanical degradation of polyimide induced by samarium ion irradiation at different fluences was measured with tensile strength measurements which give an indication of the stress/strain behavior. The mechanical stability of the material was analyzed by means of the standard force at break which is represented by the end of the curve when the polymer fails mechanically. Figure 1 shows the stress/strain curves of virgin and irradiated polyimide.

With an increase in ion fluence the curves become shorter. The standard force at break decreases. This shows that the material loses its mechanical stability.

The material degradation was also followed by infrared and UV/Vis spectroscopy. IR spectroscopy shows details of the degradation of the polymer backbone. Irradiation leads to an overall decrease of the absorbance of all bands, such as carbonyl, aromatic carbon and cyclic imide.

* in collaboration with materials research group of GSI (Dr. C. Trautmann, Prof. R. Neumann)
UV/Vis spectroscopy shows the radiation induced graphitisation, leading to an increase in light absorption. Figure 2 displays the UV/Vis spectra of virgin and irradiated polyimide foils. An increase in fluence leads to a decrease of the transmission level. The absorption edge is shifted towards larger wavelengths. Upon irradiation, the polymer is strongly discoloured. The colour changes from amber to dark grey. The reason for this observation is carbonization of the polymer. The polymer looses small molecule fragments, forms conjugated C/C-bonds and eventually graphitizes. The remaining carbon-rich network shows a dark color and strongly enhanced electrical conductivity. This is particularly detrimental, as this polymer serves as electrical insulator. Even more radiation-sensitive than polyimide is polyepoxy. As mentioned before, it is the resin phase of a composite material consisting of woven glass fibres and cured polymer. Fig. 3 shows the UV/Vis-spectra of polyepoxy, irradiated with uranium ions. In analogy to polyimide, the absorption edge shifts to a larger wavelength as a consequence of ion exposure.

![Fig. 3: UV/Vis-spectra of polyepoxy sample before and after irradiation with uranium ions](image)

![Fig. 4: Normalized shift of the absorption edge as a function of dose for ion-irradiated polyepoxy and polyimide (Kapton)](image)

Results of both polyimide and polyepoxy can be compared when energy, deposited in the material by the ions, and shift of the UV/Vis absorption edge are normalized. In Fig. 4, the abscissa gives the radiation dose in Gray, determined by the energy transfer of the ions to the polymer and by the ion fluence. While polyimide shows a threshold of degradation at around 1000 kGray, it is only in the order of 100 kGray for polyepoxy. The results show that polymers are heavily radiation damaged by irradiation with heavy ions and that the damage threshold strongly depends on the type of polymer, with an order of magnitude between the most radiation hard polymer polyimide and a weaker polymer such as polyepoxy.

The next steps will include the characterization of the glass-fibre containing material and the use of light fragment particles (deuterons, protons, neutrons).
Optical properties of a dielectric photonic composite with a superconducting surface layer

H. Rauh, Y.A. Genenko

The interaction between electromagnetic radiation and matter is amongst the most fundamental sources of dynamics in nature; it brings about phenomena like the absorption and emission of photons or the scattering of light. Despite its fundamental character, this interaction can be controlled by means of photonic crystals, i.e. regularly structured, synthetic composites made up of materials with different refractive indices.

In this work, the effect of a strongly anisotropic superconducting surface layer on the transmittance, reflectance and absorptance of a one-dimensional, layered dielectric composite with periodically alternating, isotropic constituents for linearly polarized, normally incident electromagnetic radiation, as depicted in Fig. 1, is studied both analytically and numerically.

![Fig. 1: Schematic view of the layered photonic composite with dielectric constituents a and b covered by a superconducting surface layer s. The normally incident electromagnetic radiation is symbolized in the case of (a) TE polarization with the electric field (dark bold arrows) oriented parallel to the x-axis, the magnetic field (light crossed circles) oriented parallel to the y-axis and (b) TM polarization with the magnetic field (light bold arrows) oriented parallel to the x-axis, the electric field (dark crossed circles) oriented parallel to the y-axis of a Cartesian coordinate system x, y, z.](image)

The underlying model of the electric permittivity of the superconducting constituent accounts for photonic excitation at frequencies both below and above the superconductor pair breaking frequency as well as thermal and normal scattering right up to the superconductor critical temperature. The optical properties addressed reveal traits such as band-like patterns of the transmittance and reflectance, but also step-like or smeared-out patterns of the reflectance and absorptance, displaying a marked reference on the particular type of polarization by virtue of the anisotropy of the superconducting layer covering the dielectric composite.

To appraise the effect of a superconducting surface layer on the optical properties of the layered photonic composite, we propose that its dielectric constituents are made from almost cubic perovskites, whose electric permittivity can be widely tuned by proper doping and which allow nearly perfect epitaxial growth. Moreover, we imagine that the superconducting layer consists of a single-crystalline, highly anisotropic and very pure
yttrium-barium cuprate epitaxially grown on the composite substrate such that its (electrically 'light') crystallographic $a$-axis and its (electrically 'heavy') crystallographic $c$-axis coincide, respectively, with the $x$- and $y$-axes of the chosen Cartesian coordinate system $x, y, z$. Our numerical predictions of the transmittance, reflectance and absorptance, displayed representatively in Fig. 2, rest on geometrical and materials data causing the range of frequency discussed here (with its maximum centred in the infrared.

![Fig. 2: Transmittance $T_\nu$, reflectance $R_\nu$ and absorptance $A_\nu$ of the coated dielectric composite as a function of the normalized frequency $\omega d/2\pi c$, where $d$ signifies the primitive translation of the dielectric composite and $c$ denotes the vacuum speed of light, for a superconducting surface layer of normalized thickness $d_s/d = 0.25$ at the nitrogen temperature $T = 77\,K$ in the case of (a) TE polarization, where $\nu = x$, and (b) TM polarization, where $\nu = y$, assuming on-axis propagation. The normalized pair breaking frequency here is $\omega_s d/2\pi c = 0.189$.](image-url)
part of the spectrum of electromagnetic waves) to encompass the pair breaking frequency of the superconducting constituent at all temperatures; the respective plasma frequencies, however, lie outside this range for either type of polarization.

A comparison of the optical properties of the coated dielectric composite with those well known for the corresponding bare composite reveals obvious similarities, but even more substantial differences depending on the thickness of the superconducting layer, frequency, temperature and polarization of the incident electromagnetic radiation. Thus, since the band modes only propagate, finite transmittances solely appear across the photonic bands, with zero transmittance due to the evanescent modes over the photonic gaps. One can observe a monotonic increase of the maxima of the transmittance $T_y$ with the number of the bands in the case of TM polarization, whereas the transmittance $T_x$ is depressed by 5 to 10 orders of magnitude, depending on both frequency and temperature, in the case of TE polarization. Taken together, these facets yield a maximum optical selectivity $\left(\frac{T_y}{T_x}\right)_{\text{max}}$ of the order of $10^9$ in switching from TE to TM polarization, for the nitrogen temperature $T = 77$ K. The reflectance $R_y$ shows minima at frequencies within the photonic bands, their depth increasing monotonically with the number of the bands, in the case of TM polarization; by contrast, the reflectance $R_x$ in the case of TE polarization is almost unity throughout, but reveals a smeared-out fall around the pair breaking frequency of the superconducting constituent. The absorptance, originating from electromagnetic dissipation in the superconducting constituent, builds up with temperature, as does the density of the normal electrons, irrespective of the thickness of the superconducting layer and type of polarization. Yet, for a fixed thickness of this layer and a given frequency and temperature, it is stronger in the case of TE polarization than in the case of TM polarization owing to the higher normal conductivity, and hence the higher normal current density, along the $x$-direction as opposed to the $y$-direction.

In conclusion, when switching from TE to TM polarization, the maximum optical selectivity can become gigantic, given an appropriate thickness of the superconducting layer, with a moderate dependence on temperature. This fact offers unique possibilities regarding practical applications of such a novel photonic composite as an efficient polarization filter for electromagnetic radiation tunable via the thickness of the covering layer and temperature.
Finite-element simulations of the Meissner state in a magnetically shielded superconductor strip

Y.A. Genenko, H. Rauh, N. Narayanan

Thin type-II superconductor strips are deemed promising elements for both large-scale power and microelectronic device applications. An important characteristic regarding their use is the critical current, i.e. the maximum loss-free current that can be carried by the strips. This is commonly improved through the introduction of suitable pinning centres which suppress the flow of magnetic flux and the consequential dissipation of electromagnetic energy. There are, however, further ways to increase the superconductor current-carrying capability based on the shielding effect of magnetically susceptible environments.

The idea of guiding the magnetic flux with the help of magnetic shields in order to improve superconductor performance has been advanced before. Thus, magnetically sheathed single or multifilament superconductor cables yield a reduction of the strength of the magnetic fields exerted upon the superconductor filaments, in the case of both external fields and current-induced fields, by decoupling the filaments. For planar superconductors like thin superconductor strips, resorting to soft-magnetic environments of special shapes admits intricate control of the magnetic flux and of the current density too. Reducing the high intensity of the magnetic flux near the edges of the strip by means of convex magnetic shields entails a pronounced decrease of the self-field influence on the strip.

Here, we simulate field and current distributions in a thin type-II superconductor strip surrounded by shielding magnets of finite, practically relevant geometries, addressing soft-magnetic materials as industrially used, with the aim of examining whether superconducting states distinguished by total transport currents much higher than those in an unshielded strip may occur under these circumstances as well. When studying the variation of the sheet current $J$ over the width of the superconductor strip for particular magnetic shields, we assume strip protection against entry of magnetic flux owing to an edge barrier typified by the sheet current value $J_b$, which ensures that the strip remains flux free provided that $J < J_b$ at the edges of the strip. Our focus is the Meissner state carrying the maximum total transport current possible, whence $J = J_b$ at the edges of the strip, with or, respectively, without a shielding magnetic environment. To this end, we call upon ANSYS, a commercial finite-element software programme for computing scalar and vector fields, though not originally designed for modelling superconducting states, by exploiting magnetostatic-electrostatic analogues.

A representative example of the distribution of the magnetic field $H$ around a superconductor strip of half-width $w$ in a soft-magnetic environment is shown in Fig. 1. The pattern of field lines differs greatly from that in the absence of magnetic shields, and so does the sheet current in the strip, $J$, whose distribution for different values of the distance $a$ between the edges of the strip and the magnets is displayed in Fig. 2. A central maximum of the sheet current at short distances $a$ associated with a wide region in which the sheet current transcends the edge barrier critical value $J_b$ is clearly discernible. This characteristic gives rise to the total transport current exceeding the maximum value achievable in an unshielded strip by possibly several times.
Fig. 1: Distribution of the magnetic field $H$ induced by the transport current in the superconductor strip, with two bulk magnets present, as computed using ANSYS. The area occupied by the magnets is shown by white contour lines. The strength of the magnetic field is characterized stepwise by the colour depth as shown at the bottom of the figure. The relative distance between the edges of the strip and the magnets equals $a/w = 1$, the relative permeability of the magnets is $\mu = 1000$.

Fig. 2: Distribution of the sheet current $J$ over the superconductor strip in the Meissner state, normalized with the edge barrier value $J_c$, referring to the configuration of Fig. 1, for the relative distance between the edges of the strip and the magnets $a/w = 0.33, 0.67, 0.83, 1.17$ and infinity, as indicated at the curves. The relative permeability of the magnets is $\mu = 1000$. 

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The predictions of our simulations of the Meissner state of a magnetically shielded superconductor strip are in plausible agreement with previous analytical and numerical results concerning idealized shields; they demonstrate redistributions of the current towards the centre of the strip for both convex and concave magnetic environments, yet show markedly stronger enhancements of the total current in the case of convex geometries. The effect of current redistribution is highly sensitive to the distance \( a \) between the superconductor strip and the magnetic shields and reveals saturation for values of the relative magnetic permeability \( \mu \geq 100 \), as in earlier studies addressing semi-infinite magnetic shields. The present simulations, on the other hand, with their emphasis to restricted geometries and finite permeabilities, even disclose two new, essential traits due to the said effect: (i) non-monotonicity with distance \( a \); (ii) distinct sensitivity to small values of the relative magnetic permeability \( \mu \). Taken together, these facts suggest a possible optimization of the magnetic environment with respect to dimension and morphology, so as to achieve the maximum enhancement of the total current possible.

Although our simulations do not take account of pinning of magnetic vortices at internal defects, it is known from Bean’s model of the critical state that a magnetically shielded strip carrying a total transport current much higher than that in an unshielded strip exhibits similar sheet current distributions, by which only infinitesimal regions near the edges of the strip are penetrated by magnetic flux, the major part of the strip remaining flux free. In such a case, the effective edge barrier \( J_{eb} = d j_c \) for a strip of thickness \( d \) is determined by the pinning critical current density \( j_c \). This enables the results of our simulations to be used to estimate the enhancement effect for the critical state too.

In conclusion, exploiting magnetostatic-electrostatic analogues allows successful applications of ANSYS for the purpose of optimizing magnetic shields and opens up new possibilities for achieving higher transport currents in superconductor/magnet heterostructures.
Molecular dynamics simulation of deformation mechanisms in nanocrystalline fcc metals

Y. Ritter, A. Stukowski, K. Albe

Materials with a grain size of less than 100nm exhibit unique mechanical properties: nanocrystalline (nc) metals are characterized by an extraordinary strength and the occurrence of superplasticity; enhanced ductility is found for ceramics at nano grain sizes and nc-coatings stand out due to highly improved wear, friction and corrosion behavior. The outstanding mechanical properties found for nc metals are a result of the mechanisms relevant for plastic deformation at small grain sizes, which fundamentally differ from those present in coarse grained metals. Plastic deformation of nanostructured metals is thought to arise from the intricate interplay between dislocation and grain boundary (GB) processes. The underlying concepts and fundamental mechanisms of this complex interplay, however, have still not been fully exposed [1], although nc metals have been studied intensively since the synthesis of the first nc metals in bulk form about 20 years ago [2]. The interest in the mechanical properties of nc metals has been highly increasing over the last years, which is as well attributed to the enhanced computer performance allowing more and more realistic numerical models. In the past, molecular dynamics (MD) simulations lead to substantial progresses in understanding plastic deformation of nc metals [3].

In this study we investigated the plastic deformation of nc materials by MD simulations using bicrystal models of face centered cubic (fcc) metals (Al and Cu) containing different high angle CSL (coincidence site lattice)-boundaries.

![Graphs](a) and (b)

Fig. 1: Time dependencies of the shear stress displaying the stick-slip character of GB sliding for (a) Cu and (b) Al bicrystals containing a $\Sigma 7(111)$ twist boundary.

Grain boundary sliding, induced by an applied shear deformation with a constant strain rate, has been shown to occur by the cooperative movement of all GB atoms for a $\Sigma 7(111)$ twist boundary. The barriers for the process were found to be rather high, a sliding mechanism carried by intrinsic GB dislocations, however, appeared to be even less favorable for the system. The relative movement of the two grains was observed to occur on different paths resulting in different sliding barriers (see Fig. 1). Furthermore it has been shown that, depending on the stacking fault energy, the GB slides from one distinct minimum energy to another (like for Al with a high SF energy), or the GB slides over a
smooth energy hypersurface with several local minima (like for Cu with a low SF energy). For a $\Sigma 33(225)$ tilt boundary with a dissociated boundary structure, GB sliding has not been observed. Instead intrinsic stacking fault (ISF) facets were found to be emitted from the boundary, when the bicrystals were exposed to a shear deformation. When the ISF facets reached their maximum elongation, stress-induced grain growth occurred. The atomistic mechanisms during the dissociation process and the structural changes in the interface due to the shear deformation were monitored and the influence of the SF energy was analyzed.

![Fig. 2: Dislocation nucleation at a $\Sigma 7(111)$ copper bicrystal interface under tensile deformation; (a) top and (b) perspective view. Atoms in an fcc environment are deleted, black = hcp environment, grey = unordered environment.](image)

When subjected to a tensile deformation, a statistical dislocation nucleation process was found for the $\Sigma 7$ (111) twist boundary. The effect of thermal activation has been investigated and the nucleation mechanism has been studied on an atomic scale. It has been found, that Shockley partial dislocations were emitted from the boundary on the (11-1), (1-11) and (-111) slip planes building tetrahedra of stacking faults (see Fig. 2). The emission of partial dislocations has been observed for the $\Sigma 33(225)$ interface as well, the nucleation sites, however, were not occurring randomly. The structural units within the interface due to the GB dissociation served as preferred locations for the emission of dislocations. Hence, the stresses required for the nucleation of the first partial dislocation were found to be lower than for the $\Sigma 7$ boundary.


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Solid nitrogen under pressure

Jani Kotakoski and Karsten Albe

Experiments have recently confirmed [1] the theoretical predictions [2,3] on nitrogen forming a polymeric solid under pressure, although nitrogen is traditionally considered as chemically inert due to the strong triple bonds in dimers, which form the well known molecular solids. After the first prediction of polymeric nitrogen with cubic gauche (N-cg) structure [3], which was confirmed by the experiments [1], several theoretical groups have proposed new possible structures which could be more stable or easier to synthesize than N-cg. However, a consistent comparison reviewing all the suggested phases has been lacking.

In our studies [5], we have used first principles calculations within the density-functional theory in trying to provide an overview of the pressurized solid nitrogen structures. For example, we have found that the N-cg with another insulating phase [4] with covalent bonds in all three dimensions are thermodynamically favored at pressures 50-200 GPa, after the molecular structures have become higher in enthalpy. At 200 GPa, the black phosphorus phase, which has previously been described as the high-pressure phase of nitrogen, becomes the lowest in enthalpy. However, according to our results, this phase exhibits imaginary phonon frequencies at 200 GPa (see figure 1), which indicates instability of the structure. In fact, this phase seems to be metastable only at pressures of 100-150 GPa.

As the experiments on polymeric nitrogen are performed under high pressures using diamond anvil cells, we have also studied the effect of pressure on the electronic band structure and density of states of the most interesting polymeric nitrogen phases. The band gaps of the two insulating phases were seen to respond differently to the applied pressure - for N-cg the band gap increases up to at least 100 GPa, and again decreases after this, whereas for the other phase the band gap always decreases with increasing pressure (see figure 2).

Because of the difficulties in synthesizing the polymeric structures by starting from the molecular phases, we have also studied the possibility of using other precursor materials. One group of possible candidates for this are the alkali metal azides as in these structures the nitrogen atoms form N$_3$ molecules with bonds weaker than the dimer bond. Hence, one
could expect that breaking these bonds would be easier in order to form the single-bonded polymeric nitrogen network, as compared to the case of molecular nitrogen.

![Electronic band structures](image)

Fig. 2 Electronic band structures of the two insulating polymeric nitrogen phases with electronic density of states at different pressures.

According to our results, the solubility of lithium to N-cg is significantly lower than that of H or Na. Although the azide structures remain thermodynamically stable with respect to phase-separated polymeric nitrogen and metal, this gives hope in forming the polymeric nitrogen with mixed lithium impurities when pressurizing the lithium azide, whereas less hope is given for sodium or hydrogenic azides.

In conclusion, we have improved the understanding on the various nitrogen phases under pressure, as well as investigated the possibility of using different precursor materials for the synthesis of these structures. These studies serve as a starting point towards obtaining the high-T,P phase diagram of solid nitrogen and can help experimentalists on their task in trying to realize the potential of these materials.


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Ionomer-coated Pt/C catalysts for improved utilization

S. Zils, V. Croze, F. Scheiba, N. Benker, C. Roth

Both performance and final device cost of polymer-electrolyte fuel cells (PEMFC) are significantly affected by limited platinum utilization. Utilizations of as low as 25% have been reported in the literature indicating that up to 75% of the expensive noble metal remains inactive [1]. In this work, different methods have been developed in order to pre-coat a carbon-supported Pt catalyst with ionomer before the actual manufacturing of the membrane electrode assembly. The coating method should provide a uniform and controllable ionomer distribution, improved adhesion between electrode and membrane and also allow for easy scale-up. In this work the Pt/C catalysts were coated with the ionomer Nafion® using two different preparation routes. The XRD, SEM and TEM measurements showed major differences of the ionomer thicknesses of the two coated catalysts. These different thicknesses have a pronounced effect on the fuel cell performances during the electrochemical measurements.

Platinum is the material of choice in fuel cell catalysis, and it is used at both electrodes of standard polymer electrolyte fuel cells (PEMFC). However, as a noble metal it is neither largely available nor economic, rendering fuel cell technology expensive and commercially unattractive. Consequently, the focus of many recent activities has been on the reduction of the noble metal loading [2]. In this context, platinum utilization in the porous gas diffusion electrodes is discussed as an impeding factor, since it strongly affects both fuel cell performance and final device cost [3, 4]. One way towards improved catalyst utilization is via the development of new preparation techniques, which increase contact between proton and electron conducting phases.

Carbon supported platinum (20 wt% on Vulcan XC-72) purchased from E-TEK inc. and the Ionomer Nafion® (5 wt%) purchased from DuPont were used for the preparation of the two coated catalysts. For preparation method I the catalyst-ionomer mixture was stirred in a three-neck round-bottom flask (Fig. 1). The preparation of the coated catalyst according to method II was performed by spray-drying the catalyst-ionomer dispersion onto a heated Teflon-coated surface (Fig. 2).

Figure 3 displays transmission electron micrographs of the two different coated catalysts. A higher ionomer film thickness was observed in the TEM images of catalyst I. This higher ionomer film thickness can be well observed in the TEM images of the coated catalyst I (Fig. 3a). The ionomer film on catalyst II was not stable and was destroyed immediately in the electron beam (Fig. 3b).
To deal with this problem a movie was recorded with the attached camera. A sequence of six images shows the evaporation of the Nafion® thin film from the coated catalyst (Fig. 4).

The fast evaporation of the ionomer film on the catalyst prepared by method II implies a smaller film thickness for this catalyst. This is in good agreement with the results of the XRD and SEM measurements. According to the work of Song et al. [5] we expected higher fuel cell performances for the MEAs with the catalyst with thinner coating. The E/i curves of the four prepared MEAs (Fig 5) show higher fuel cell performances – i.e. higher open circuit voltages and higher current densities – for the MEAs with the coated catalyst prepared by method II. This confirms the thesis postulated by Song et al. [5].
The MEAs with the coated catalysts applied to the anode sides show a better electrochemical activity than the MEAs with the coated catalysts applied to the cathode sides of the MEAs. We assume that this is due to the fact that the coated catalysts feature a high hydrophobicity, which has a strong effect on the water management of the MEAs. The hydrophobicity effect of the coated catalysts on the anode sides results in a decreased proton conductivity and leads to the drying up of the membrane, as not enough water vapour passes through the coated electrode and is instead held back at the hydrophobic anode. The higher hydrophobicity on the cathode sides, however, leads in addition to the decreased proton conductivity and membrane dry up to a deteriorated water management, which causes problems with the gas transport. These hydrophobicity effects result in a diminished ohmic conductivity compared to a reference MEA prepared with the standard Pt/C catalyst on both electrodes. On the other hand the MEAs prepared with the coated catalysts show a higher open circuit voltage, which may indicate a better accessibility of the platinum particles in the electrodes. However, this has to be investigated further.

The positive effect of the coated catalysts on the fuel cell performance is more pronounced on the anode side of the MEA. The observations concerning this work led us to the conclusion that the spray coated catalyst II should be studied and improved in future work, e. g. to observe the effect of a hot pressing procedure of the MEAs after the dry spraying process.

**Literature**

4. F. C. Wu, C. C. Wan, Y. Y. Wang, L. D. Tsai, K. L. Hsueh *Journal of the*  
Electron microscopy techniques for the analysis of the polymer electrolyte distribution in PEM fuel cells

F. Scheiba, N. Benker, U. Kunz, C. Roth

Transport processes play a significant role for the proper operation of polymer electrolyte membrane fuel cells (PEMFC). In PEMFCs the reactant gases must have access to the catalytically active sites, protons and electrons must be conducted through the electrode and the reaction water must be removed from the pore system to avoid blocking of the gas diffusion paths. In the current standard electrode design each transport process is realized by a different component. Gas transport is accomplished by a network of pores in the electrode structure. Electrons are conducted by the catalyst particles themselves or a conductive support, whereas proton diffusion is realized by the addition of a polymer electrolyte. Since the various components influence each other in a non-constructive manner, optimization of the electrode structure is far from being trivial.

One of the key components in electrode design is the polymer electrolyte, because it influences proton conductivity as well as the catalysts electrochemically active surface, mass transport, electronic resistivity and electrode porosity. Several publications have focused on the effect of the polymer electrolyte concentration in the electrode [1, 2]. Beside the absolute amount of polymer electrolyte in the electrode, its distribution has a significant effect on the performance of the cell. The distribution of the electrolyte itself is mainly influenced by the preparation technique of the electrode, i.e. the catalyst ink preparation and coating procedure.

However, detailed analysis of the polymer electrolyte distribution is difficult. Mercury porosimetry, which has been widely used to study the influence of various preparation parameters on the pore size distribution, may in some cases be used to derive information on the polymer electrolyte distribution. But since mercury porosimetry probes the pore size distribution rather than the polymer electrolyte distribution itself, information on the polymer electrolyte distribution requires the choice of an appropriate reference and is based on the assumption that differences in the pore size distribution are directly correlated with the polymer electrolyte distribution.

Scanning electron microscopy (SEM), which is also commonly used for structural characterization of the electrode, may in principle be used to obtain direct information on the polymer electrolyte distribution if it is combined with energy dispersive X-ray analysis (EDX). However, SEM on bulk electrodes has a number of limitations. Therefore, the elemental information obtained by the X-ray signal cannot be quantified correctly and elemental maps obtained by this method may not correspond to the real elemental distribution in the sample. When comparing SEM to TEM, TEM has a number of advantages. TEM allows imaging of all parts of the electrode structure including the nanometer sized catalyst particles, which are in general not accessible by SEM. As samples need to be thinned to less than 100 nm to be transparent for the electron beam, pores between the catalyst agglomerates appear as voids in the catalyst structure and can therefore be imaged, too. Moreover, with energy filtered transmission electron microscopy (EFTEM) another powerful technique is available for elemental mapping. However, sample preparation for TEM is a major obstacle, especially for highly porous systems such as PEMFC electrodes.
Blom et al. proposed a sample preparation technique which is generally used for biological samples [3]. To stabilize the structure of the MEA, it is embedded in epoxy resin and then cut with an ultramicrotome. However, for the analysis of the polymer electrolyte distribution, embedding of the sample has a significant drawback. Since the polymer electrolyte and the embedding resin have almost identical scattering contrast, the polymer electrolyte cannot be distinguished directly.

There are basically two different approaches to solve this problem, and results will be presented below [4]:

- Enhancement of the scattering contrast by selective insertion of heavy metal ions (referred to as *staining techniques*).
- Elemental mapping of an element that is characteristic for either the polymer electrolyte or the embedding resin (referred to as *mapping techniques*).

**Figure 1:**
TEM bright field images of an unstained a) and Cs⁺ stained b) membrane electrode cross section. Both images were taken at the membrane electrode interface.

*Staining techniques*

To significantly increase the scattering contrast of the polymer electrolyte the staining agent should have a high electron density and a low charge to introduce as many additional scattering centers as possible. Figure 1 shows cross sections of an unstained and Cs⁺ stained MEA in comparison. In both images the interface between the membrane and the electrode appears sharp indicating that penetration of the membrane into the catalyst layer is low. A clear effect of the staining can be seen on the membrane of the cesium treated sample. The membrane of this sample appears to be speckled and stripes of more or less strongly contrasted regions can be found close to the electrode interface. Also the electrode of the stained sample appears to be darkened, when compared to that of the unstained sample. The staining in the electrode layer is most pronounced around the carbon support indicating that the Nafton® ionomer is mainly covering the catalyst support particles but is not flooding large pores.
Mapping techniques
Elemental mapping techniques are an elegant alternative to staining experiments, as they do not require the insertion of a staining agent and are therefore less prone to artifacts. Instead, differences in the chemical composition can be used to distinguish the polymer electrolyte from the resin. Electron microscopy allows the use of two different elemental mapping techniques, namely energy dispersive X-ray analysis (EDX) and energy filtered imaging (EFI). Both methods have advantages and limitations that are rather complementary to each other and therefore they are best used in combination to characterize the polymer electrolyte distribution.

Figure 2 shows the SE and BSE image of a thin section of a fuel cell electrode as well as elemental maps for carbon (C), fluorine (F), platinum (Pt) and ruthenium (Ru). In the lower half of the image a part of the membrane is visible. Since the fluorine signal recorded from the membrane was much more intense than that of the electrode, a log-transform of the image intensity was necessary to visualize the fluorine content in the electrode. Close to the interface with the membrane, a slightly higher fluorine concentration can be observed. The platinum and ruthenium maps of the electrode reveal that the catalyst is not homogeneously distributed throughout the electrode layer. In particular, the platinum distribution shows agglomeration and some void regions that do not correspond to holes in the electrode structure.

Literature
La$_x$Sr$_y$MnO$_3$ (x+y≤1) perovskite (LSM) is the traditional SOFC cathode material showing excellent catalytic properties, electrical conductivity, thermal and mechanical stability [1]. However, the negligible ionic conductivity limits the overall cathode performance. The electrochemical performance of cathode layers depend largely on the microstructure of the triple point boundaries (TPBs), which in turn depend on the starting powder characteristics such as particle size and shape as well as their size distributions. In order to improve the performance of the LSM cathode, the addition of a solid electrolyte, namely yttria stabilized zirconia (YSZ), has been investigated by many researchers to enlarge the area of TPBs and extend them into the bulk of the cathode [2-4]. The rapid progress in thin-film technology, as well as the identification of alternative electrolyte materials with higher ionic conductivity such as gadolinium-doped ceria (GDC), has significantly reduced the ohmic loss the electrolyte. Thus, the development of thin film cathodes with high catalytic activity becomes increasingly critical for the intermediate temperature-solid oxide fuel cell (IT-SOFC) [5].

Material synthesis and cost effective fabrication of thin film nano-sized LSM-GDC composite cathodes was the major aim of the work in 2007. A nanocrystalline single phase LSM powder with fine microstructure and very high specific surface area was synthesized via a unique spray pyrolysis process. The powder has been characterized by various methods like in-situ high temperature X-ray diffraction (HTXRD) and Ex-situ nitrogen adsorption (Fig.1.), inductively coupled plasma-optical emission spectroscopy (ICP-OES), high resolution scanning electron microscopy (Fig.2.), and Zeta-potential measurements. Morphological improvement of the as prepared powder was achieved by ultrasonic treatment of water based dispersions. LSM-GDC composite cathodes were prepared by adding commercial nanopowder of gadolinium-doped ceria to the stabilized LSM dispersion. The stabilization of the nanocomposite dispersion was carried out successfully by a electrosteric approach. Thin films (500nm) of nano-sized composite cathode were prepared by a single step spin coating of the dispersion on yttrium stabilized zirconia (YSZ) substrates. Area specific resistances (ASRs) obtained from electrochemical characterization of thin film cathodes by impedance spectroscopy are comparable to the lowest reported ASRs of this material system for which the thickness of the functional layer is about 20 times higher.

To our knowledge, this procedure for preparation of thin film composite cathodes for functional layer of SOFC is reported for the first time. Cost-effective single step coating, high catalytic activity at a very low thickness of the cathode functional layer (about 500nm) and low sintering temperature are supposed to be advantageous for the application in thin-film IT-SOFCs.

A thin film of LSM nanoparticles deposited on the YSZ substrate and subsequently sintered at 850°C shows an ASR of 0.89 Ωcm$^2$ at 850°C which is 2.5 times lower than the value for the finest commercial LSM powder sintered at 1150°C in this study (Fig.3.).
decrease of the ASR for LSM nanoparticles confirms the increase of TPB at the cathode/electrolyte interface. This also indicates the need of lowering the sintering temperature in case of LSM nanoparticles as it is also evident from HRSEM micrographs that even at low sintering temperature a good connection between LSM nanoparticles and the electrolyte is achieved. This is due to the fact that nanopowders have the advantage that sintering processes are activated at considerably lower temperatures and thus retain a high specific surface that is equal to a high density of TPBs.

Further improvement of the electrochemical activity by a factor of 2.8 (ASR=0.32 Ωcm²) has been achieved by applying a thin film interlayer of GDC nanoparticles between the LSM functional layer and the YSZ substrate. This again shows the enhancing effect of nanoparticles on the contact area between cathode and electrolyte. Besides the effect of morphological improvement GDC also has a higher electrochemical activity.

Significant enhancement of the electrochemical activity has been achieved by introducing GDC nanoparticles into the LSM nanostructure. The dependency of the ASR on the percentage of GDC in LSM-GDC nanocomposite electrodes is shown in Fig. 3. The minimum ASR of 0.14 Ωcm² has been achieved at a composition of LSM-15wt.%GDC. This result indicates that with the addition of GDC to the nanosized LSM electrode an enlargement of the TPB length was realized so that the oxygen ion transfer step could be accelerated. However, further increase in GDC content to a value higher than 15wt.% results in higher interfacial polarization resistance. This may be due to a decrease of the electrical conductivity of the cathode as a result of losing contact between LSM particles and hence an increase in polarization resistance.

In this work we have demonstrated the versatility of spray pyrolysis for the synthesis of lanthanum strontium manganite with a very high specific surface area of 70m²/g. The application of ultrasonic energy improved the morphology for the utilization as IT-SOFC functional cathode material. A new approach for the preparation of thin film functional cathode layers by spin coating of nanocomposite dispersions has been performed for the first time. This offers a time saving single step coating process which is also very cost effective compared to conventionally applied methods for thin film fabrication like pulsed laser deposition (PLD) and metal organic chemical vapor deposition (MOD). The thickness (<1µm) is at least 10 times lower than the cathode layers prepared by screen printing which means a considerable reduce in material costs. The electrochemical properties reveal lower polarization resistance than physically mixed composites and functionally graded cathodes. Other authors reported lower ASR achieved by impregnation methods. However, from industrial point of view impregnation methods are extremely time consuming.

Fig. 1. Thermal Stability of LSM powder synthesized at 1000°C

Fig. 2. HRSEM Graphs (a) as prepared Powder. (b) LSM functional layer coated on YSZ substrate

Fig. 3. Area Specific Resistance vs. Temperature
Electrochemically-gated field-effect transistor with highly conducting nanoparticles as channel*

S. Dasgupta, S. Gottschalk, R. Kruk, H. Hahn

‘Low-tech’ field effect transistor (FET) devices have gained increasing commercial interest for inexpensive applications with lesser demand of performance compared to conventional high-performance electronics. Thin Film Transistors (TFT) with organic semiconductor channels are favored due to their suitability for direct printing. High mobility organic semiconductors with a field effect mobility of the order of 10 cm²/Vs have been reported recently. However, most of the plastic electronic materials are unstable in air and quickly degrade their performance. On the other hand, all-inorganic devices other than amorphous Silicon FETs have shown high mobility and better promise recently. In contrast, there are only few reports on nanoparticulate channel devices.

We have fabricated a field effect transistor (FET) device based on Indium Tin Oxide (ITO) nanoparticles as a channel with metallic conductance and a solid polymeric electrolyte as a gate. Polymer electrolyte gating has been reported previously in the field of single-wall carbon nanotubes (SWCNT) [1] and organic semiconductors [2]. However, these approaches mostly involve electrochemical doping (redox reactions), as opposed to the present study where the gate voltage was restricted within the adsorption-free capacitive double layer region. The use of a non-adsorbing supporting electrolyte and a finite potential window with negligible adsorption ensures high reversibility and long term reproducibility of the device. ITO belongs to the group of transparent conducting oxides (TCO) and is a degenerative semiconductor with a carrier density as high as 10²¹ cm⁻³ and a resistivity as low as 10⁵ Ohm-cm. A FET device with metal-like conductance is always favored for the low dimensions of the device as it allows a high on-state current. However, the metallic conductance yields only a very short penetration depth (less than a nanometer) of the electric field applied by the gate, which is not enough to produce an acceptable device performance. In contrast the present study shows that an electronic device is still feasible with a metal-like oxide, if a nanoparticle channel combined with electrochemical gating is used.

The device consists of passive structures like source, drain (sputtered ITO film with 310 nm thickness), active channel (ITO with 5 at% Sn, Evonik GmbH, Germany, applied as a dispersion) and a composite solid-state polymer electrolyte composed of polyvinyl alcohol, potassium fluoride and water (35:35:30). High surface area (> 1000 m²/g) activated carbon cloth (kynol) and a freshly prepared Ag/AgCl wire are used as the counter and quasi-reference electrode, respectively. The optical micrograph (a) and the schematic cross-section (b) of the actual device are shown in Fig. 1, respectively.

All the measurements were performed at room temperature. Fig. 2(a) shows the I-V characteristic of the device. Careful selection of adsorption free potential window was carried out by slow scan (5×10⁻⁴ Vs⁻¹) cyclovoltammogram. While varying the electrode/gate potential with slow scan
cyclovoltametry a constant current of 0.1 µA is applied and the potential drop is measured. A change of resistance by more than three orders of magnitude (on/off ratio = 2×10³) is observed when the potential of the working electrode is varied between -0.45 and 0.65 V (Vg = -0.65 to 0.45 V) with respect to the Ag/AgCl reference electrode (Fig. 2b). At the negative potential applied to the working electrode (positive gate potential) positive ions (i.e. K⁺ ions) come close to the surface of the ITO nanoparticles. As a result, electrons in the ITO nanoparticles are attracted towards the surface to build the charge double layer. Therefore, a positive gate potential increases the carrier (electron) concentration of the ITO nanoparticles resulting in a decrease of the resistance of the channel. In case of positive electrode potential (negative gate potential) negative ions, (i.e. F⁻) form the charge double layer which repels the electrons away from the surface-electrolyte interfaces. Accordingly, the electron density of the channel decreases with a corresponding increase of the resistance. Therefore, the positive or negative ions of the charge double layer at the solid/electrolyte interface work as a gate and the channel gets narrower and broader with the negative and positive gate voltage, respectively, making the device analogous to a normally-on junction field effect transistor (JFET). Fig. 2(c) shows the response of the device with the gate potential switched between 0.45 and -0.65 V. The resistance of the channel is measured in 100 ms time intervals.

The device shows a different transfer characteristic (Fig. 2a) compared to a regular JFET. The fairly constant rate of change of drain current over the entire gate voltage is attributed to a continuous change in double layer capacitance (DLC) along with the change in carrier concentration in the channel upon charging. Similar differential DLC values with different electrode potentials were previously reported for CdSe semiconductors [3].

The field effect mobility of the device is calculated by modifying the abrupt-junction long-channel JFET equation given by Sze [4] to fit the present geometry of nanoparticulate channel where gate/electrolyte surrounds the particles. The calculated field-effect mobility (μ) is 24.3 cm²/Vs which is comparable with the intrinsic carrier mobility (20-60 cm²/Vs) of ITO nanoparticles as reported by Edarth et al. [5]. The calculated saturated drain current at zero gate bias, (I_DSS/W = 5.5 µA/µm) and transconductance (g_m/W = 22 mS mm⁻¹) of the device, are orders of magnitude higher than most of the oxide semiconductor FETs reported. Another important device parameter, subthreshold swing (S) is obtained to 230 to 425 mV dec⁻¹ for the present device. For a nanoparticle channel an electrochemical gating seems to be very efficient (gating efficiency = 0.26) compared to a gate dielectric. This type of systems can represent a valuable contribution to the printable/flexible electronics community, particularly for the growing number of researchers who are switching their efforts in this
area away from traditional, heavily explored organics to new classes of materials, including nanostructured inorganic materials.

References:

* Cooperation between Gemeinschaftslabor Nanomaterialien at Technische Universität Darmstadt and Institute for Nanotechnology at Forschungszentrum Karlsruhe

Oxygen diffusion in ferroelectric materials
Stefan Hummelt, Sebastian Gottschalk and Adam G. Balogh

Perovskite-type ferroelectric oxides such as lead zirconate titanate (PbZr\(_{1-x}\)Ti\(_x\)O\(_3\)) are of technological interest for many sensor, actuator or non-volatile ferroelectric random access memory (FeRAM) applications because of their piezoelectric, electro-optic, and pyroelectric properties.

Unfortunately these devices suffer from polarization fatigue (loss of reversible polarization \(P_R\)) under switching cycles. In the last 15 years polarization fatigue in ferroelectrics has been under intense study. There are many fatigue scenarios discussed, e.g. the electromigration of oxygen vacancies and the formation of defect agglomerates or the formation of an interfacial dead layer near the electrodes. Other mechanisms invoke the pinning of domain walls at defects, blocking of domain wall nucleation as well as conversion of Ti\(^{4+}\) into Ti\(^{3+}\) states.

There is still no consensus on the exact mechanisms in the literature and many details remain unclear. However there is general agreement that defects and especially charged defects play an important role. The polarization fatigue is known to be refreshed by applying e.g. asymmetric dc-electric field, heat treatment, poling, or light illumination. This suggests that the trapping, detrapping, migration and redistribution of charged point defects (mainly the oxygen vacancies) appear to play a key role. However, experimental data for the oxygen vacancy mobility in technological relevant perovskite oxides at temperatures near application relevant temperatures are not available in the literature. Therefore, measurements have been performed to achieve a better understanding of the oxygen kinetics and defect mobility in technological relevant polycrystalline samples.

Fig. 1: SIMS depth profiles of O\(^{18}\) tracer at different loading temperatures (shown is the natural logarithm value of the O18/O16 ratio)
PZT samples have been loaded in a glass vessel filled at 250 mbar of $^{18}$O gas (95% isotope enrichment, provided by Campro Scientific) at temperatures between 250° and 400°C for 30 min. The concentration depth profiles of the tracer atoms were obtained using secondary ion mass spectrometry SIMS using 8 keV O$^-$ primary ions (Cameca ims 5f).

Fig. 1. shows a typical concentration depth profile as obtained from the bulk polycrystalline samples. It can clearly be distinguished between a slow bulk diffusion and a faster grain boundary diffusion components. ($D_{\text{bulk}}/D_{\text{GB}} < 10^{-2}$). In order to determine the bulk diffusion coefficient $D_{\text{bulk}}$ the near surface region of the concentration depth profile was fitted to the respective solution of the diffusion equation.

From the fits an Arrhenius graph, shown in Fig. 2., was determined. The two distinct diffusion processes for the volume diffusion and the faster grain boundary diffusion path can be distinguished clearly. The activation enthalpies were determined to be 0.87 eV and 0.66 eV, respectively.

Fig. 2: Arrhenius representation of the bulk ($D_{\text{bulk}}$), grain boundary ($D_{\text{GB}}$) diffusion coefficients and the surface reaction barrier $E_R$. 
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Hildebrandt, Erwin; Oxygen Deficiency and Ferromagnetism in Hafnium Oxide Thin Films Grown by Reactive Molecular Beam Epitaxy, Dezember 2007

Hirsch, Stefan; Einfluss der Katalysatorschichtdicke auf die Brennstoffzellen-performance unter Verwendung des Decal-Verfahrens für die Elektrodenherstellung; Dezember 2007

Kamwa Domkam, Joel; Herstellung neuer Wismut-Lithium Keramiken, März 2007

Keller, Tobias; Einfluss einer Kohlenstoff-Diffusionsschicht auf die Wasserstoffversprödung des Stahls 1.4301, Juni 2007

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Trummlitz, Mark; Alternative Rückkontakte für GaAs-Feldeffekttransistoren: Versuche zur Gasphasenabscheidung von Vanadiumdisulfid, September 2007

Tullney, Sarah; Einfluss von galvanischen Zinkschichten, DLC Schichten sowie Kohlenstoffdiffusionsschichten auf die Wasserstoffversprödung von Stählen, Oktober 2007

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Ell, Jürgen; Gasinduziertes optisches Schaltverhalten dünner Magnesium-Nickel-Schichten, August 2007

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Gassenbauer, Yvonne; Untersuchung der elektronischen und chemischen Oberflächeneigenschaften von Zinn-dotiertem Indiumoxid im Honblick auf die Funktion in organischen Leuchtdioden, August 2007

Giebeler, Lars; Einfluss von Wolfram als Dotierelement auf die Eigenschaften von V2Mo8WxOy-Katalysatoren zur Selektivoxidation von Acrolein zu Acrylsäure, September 2007

Maurer, Florian; Textur und Feldemission metallischer Nonodrähte, März 2007

Meyer, Daniel; Herstellung und Charakterisierung von codotiertem und SrAl12O19- verstärktem Zirkoniumdioxid, November 2007

Mazilu, Irina; Einkristallzüchtung und Konstitutionsuntersuchungen von magnetisch geordneten Seltenerd-Übergangsmetallverbindungen, Januar 2007

Mircea, Julian; Interfacial Fracture Toughness and Adhesion of Brittle Coating on Ductile Substrates, Juni 2007
Müller, Michael; Atomistic Computer Simulations of FePt Nanoparticles: Thermodynamic and Kinetic Properties, Februar 2007

Nikolowski, Kristian; In situ Strukturuntersuchungen an Li(Ni,Co)O₂ als Kathodenmaterial für Lithiumionenbatterien, April 2007

Schlegel, Thorsten; Elektrische Leitfähigkeit und piezoelektrisches Verhalten von Bismutferrit-Bleiititanat, Juli 2007

Schönau, Kristin; In situ Synchrotron Diffraction of Lead-Zirconate-Titanate at its Morphotropic Phase Boundary, November 2007

Schwarz, Björn; Kristallchemie, Struktur und magnetische Eigenschaften von Cu(MoxW1-x)O₄-Mischkristallen, Juni 2007

Späth, Bettina; Rückkontaktbildung von CdTe-Solarzellen: Mechanismen und elektronische Eigenschaften, Juli 2007

Trots, Dmytro; Structure and Lattice Dynamics of Copper- and Silver-based Superionic Conducting Chalcogenides, Mai 2007,
Mechanical Workshop

The mechanical workshop of the Institute of Materials Science is designing, manufacturing and modifying academic equipment for a broad range of projects. In the year 2007 the workshop was involved in the following major projects:

- Design and realisation of a new neutron structure powder diffractometer (SPODI) at the FRM-II, TU Munich, Garching
- UHV-preparation chambers dedicated for MBE, CVD, PVD and (electro)chemical treatment
- Design and manufacturing of a protection chamber for x-rays with up to 150keV photons

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In the solar system, Earth is an unique rocky planet with an ocean and an atmosphere. It is inhabited by bacteria since about 4 billion years and by higher life - plants and animals - since ca. 600 million years. Organisms, air, water, and rocks are interconnected in an unending cycle of matter and energy: *The Earth System*.

The crustal plates of Earth are driven by radioactive heat. This causes creation of new crust at mid-ocean ridges at rates of several centimetres per year. On the other side, plate margins collide, become subducted into the mantle again, or fold up vast mountain ranges like the Alps and the Himalayas, combining rocks of very different origin. During subduction the basaltic crust is partially melted generating more felsic magmas which rise to form continental-type plutons and to cause lines of andesitic volcanoes such as occurring around the entire Pacific rim. This is called the *endogenic cycle* of rocks.

At the same time Earth receives solar radiation which moves air and water in gigantic cycles around the planet. Specifically the water cycle causes the denudation of mountains by mechanical erosion and the leveling of plains by chemical weathering, the latter aided tremendously by vegetation and their CO$_2$-input to soils. This is called the *exogenic cycle* of rocks.

This exogenic cycle is increasingly impacted by mankind. The radiation balance of the atmosphere has been upset by the emission of carbon dioxide, methane and other tracegases, Earth is warming. Industrially produced chlorinated hydrocarbons have risen to the stratosphere, threatening the protective ozone layer. Dust from traffic, industry and agriculture produce reagents which alter the air chemistry, causing unprecedented interactions with the marine realm, with vegetation and even with rocks through acidification, excessive deposition of nutrients and salts. Dry and wet deposition of anthropogenic (i.e. produced by humans) particles can be measured world-wide. The population explosion caused the intensification of agriculture and the alarming loss of topsoil and cuts down on the extent of natural ecosystems at the same time. The artificial fertilization of soils causes wide-spread nitrate pollution of shallow ground waters and urbanization alters the water cycle above and below ground. Local leakage and accidents with chemicals impact soil, rivers and ground water. Civil engineering, discharges and denudation cause alterations in almost all rivers world-wide and even coastal seas show increasing eutrophication, siltation and ecosystem changes in the water column and in the shallow sediments. The scars left by the mining of minerals and fossil energy are visible everywhere and cause increasingly problems. Everywhere man has changed the rate of natural processes. He spreads ever further into the landscape, utilizing regions and building in areas which should not be used considering their natural risks. Therefore damages through natural catastrophes rise traumatically endangering the world insurance system.
All these processes and changes and their consequences are topics of *Environmental Geology*. Understanding *global change* and accepting the responsibility of mankind for this planet and its resources for future generations are prerequisites for the planning of a sustainable development.

The division of Physical Geology and Geological Cycles at the Institute for Applied Geosciences addresses several questions important to environmental geology both in the present and in the geological past. These can be summarized as follows:

- **Paleoclimatology** (through the study of varved sediments in the Dead Sea Basin/Jordan and in Lake Van/Turkey and through the study of speleothems)
- **Carbonate geochemistry through time** (through the study of alkaline crater lakes, stromatolites and through modeling of early ocean conditions also for other planets and moons of the solar system)
- **Karst and cave development** (through the studies of cave development in limestone, gypsum and lava and through the study of cave deposits and their paleontological content and geochemical composition)
- **Biogeochemistry of rivers** (through the study of the biogeochemistry of rivers such as the Ebro and Rhine or in Patagonia).

Currently two German research funded projects are pursued, the reports of which follow below.

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### Research Projects

Geomorphology and Paleoclimatology of Lake Lisan Terraces, Dead Sea, Jordan (DFG, DAAD).
Stable isotopes investigations of Late Glacial and Early Holocene brown bear finds from caves in the alpine region (Eurospel Project Ecp 2007-03).

The Impacts of Eurasian Dust Storm Events and Anthropogenic Emissions on Atmospheric Nutrient Deposition Rates in Forested Japanese Catchments and adjacent Regional Seas (DFG, 2007).

**Publications**


Books


Hydrogeology

The Hydrogeology group focuses on 3 main research areas, (I) the fate of organic contaminants in the subsurface, (II) the development of novel methods to remediate soil and groundwater contaminations, and, (III) on water resources management on a regional scale.

(I) The fate of organic contaminants in soils and sediments is especially affected by sorption/desorption processes as well as by abiotic and biotic degradation reactions. These processes are studies on a laboratory scale and in the field. We have a modern hydrogeochemical laboratory with standard equipment for chemical analysis of organic and inorganic compounds (GC-MS, HPLC, IC, ASE, AAS) and we are currently implementing compound specific stable isotope analysis (CSIA) as a tool to monitor degradation reactions (D/H, $^{13}$C/$^{12}$C, $^{37}$Cl/$^{35}$Cl) of organic compounds.

(II) We are developing remediation methods especially for waters contaminated with chlorinated organic compounds. Palladium based catalyst systems are used for the destruction of these compounds in flow-through reactors. Currently two field installations are in operation were the long term performance of this technique is studied. To tackle more complex groundwater contaminations a mobile pilot treatment plant is under construction in cooperation with the Helmholtz Centre for Environmental Research – UFZ that will serve as a research platform over the next years.

(III) In 2007, Dr. Irina Engelhardt joined the Hydrogeology Group to strengthen our competence in the field of groundwater modeling. Her research will mainly focus on water resources management, one of the key activities of the hydrogeology group. The qualitative and quantitative assessment of regional water resources and their sustainable use is of overriding importance, especially in arid countries around the world. Projects in Germany and Saudi Arabia were acquired that will serve as a reference for the further development of this area.

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Research projects

Reversibility of sorption processes in natural and synthetic sorbents (DFG: 2005-2007)

Diffusion, sorption and reactions in micro- and mesopores (DFG: 2005-2007)

SAFIRA 2: The treatment train approach (BMBF: 2007-2008)

The hydrogeology of the Taunus area, Hessia (HLUG: 2007-2009)

Publications


Patents

Engineering Geology

Engineering Geology is an applied earth science and a branch of the applied geology which requires not only multidisciplinary knowledge within the natural sciences (geology, chemistry, physics, mathematics), but still the engineering sciences. The common aims of all special subjects contributing to engineering geology are the investigation, the use, the protection and the remediation of the upper parts of the earth's crust.

Regarding the worldwide rising importance of renewable energy resources, Engineering Geology as the sciences which deals direct with the use of geothermal energy is one of the future's most important applied geosciences. A highly qualified geothermal lab and experimental hall began to realize in 2007 with first equipments.

Engineering Geology seizes the behaviour of rocks and rock masses according to the genetic material properties and their earth-history development. It quantifies the mechanical, physical and hydro mechanical characteristics and the behaviour of soils and rocks in detail and in the assembly.

Important corresponding special subjects are the soil and rock mechanics, civil services, foundation engineering, tunnel and cavity construction, drilling technology, measurement engineering and applied subjects of hydrology and hydrogeology, petrology and geochemistry. Engineering geology has thus strong relations with the geotechnical engineering. It translates the results and knowledge of the geosciences into the engineering requirements.

Thus, Engineering Geology contributes to the fact that buildings of all kinds can be constructed and heated surely and economically. For this purpose the building ground and other underground conditions for engineering structures, such as geothermal power plants, traffic routes, e.g. roads, bridges, tunnels as well as other infrastructure such as caverns, dams, pipelines as well as buildings such as high rise buildings, halls, wind power stations as well as water-structural plants such as water gates, dams, dykes, are investigated.

Most recent activities are focused on the HydroThermikum, a research and education lab which combines the various techniques such as:

- **ICP-MS and RFA with laser ablation**
- **Optical heat scanning system for hard rocks (installed 2007)**
- **Heat measuring system for soft rocks (applied for in 2007)**
- **Thermo-Triaxial-Press (applied for in 2007)**
- **Thermal column test rig**
- **Fibrer optical temperature logging device**
- **Uni axial press for high temperature testing**
- **Heat Pulse Probe (applied for in 2007)**

with existing laboratory capacity.
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Dirk Arndt
Daniel Hempel

Guest Scientist
Dr. Sven Rumohr, Hessian Agency for Environment and Geology

Research Projects

Ongoing projects

Interaction of adhesive soils, e.g. clays and steel construction for boring tools e.g. tunnel boring machines
The adhesive behaviour of cohesive soils e.g. clays may cause an immense decrease of the advance rate of tunnel boring machines or of a boring process. The chemical and physical properties of soils which causes adhesion are in research to understand the processes of the jamming of boring tools.

Environmental and geotechnical behaviour of polymeric organic additives for drilling fluids for tunnel boring machines
To reduce or to eliminate the jamming effects of adhesive soils, a polymeric organic additive must be implicated to boring fluids. The additive has to be chosen according to geotechnical criteria, which is affected by geological, hydro-geological and boring aspects. After use, this boring fluid, mixed with soil, has to be deposited. This is actually a huge environmental problem due to the additive, so that the research in this filed should bring up a clear understanding of the elute process.

Investigation on in situ degradation of urban organic lake deposits using biodegradable polymers
Organic lake deposits reduce the capacity of water storage reservoirs. To decrease the capacity reducing volume of organic lake deposits, a polymer can be added to the lake water. The biochemical effects are not well known yet. Therefore a research project is in process using a lake in the city of Darmstadt. The research content a broad field and laboratory test program on the lake deposits as well as the monitoring of the volume of the lake deposits.
**Determination of hydraulic properties of sintered HD-PE well screens**

Sintered High Density Polyethylene well screens are hydrophobic. The sintering process allows control the pore sizes and tortuosity of pores. Additionally HD-PE filters offer a large open entrance area for the filtrandum (groundwater). In this project the hydraulic properties were investigated in laboratory scale and in the field. To investigate the porosity in the well screen, a three-dimensional Computer-Tomography with very high resolution of $1 \times 10^{-6} \text{ m}$ was used. A difference of the porosity between the centre of the well screen and their border areas was stated. The production process was optimized to these results.

**Infiltration map of Dieburg**

The infiltration potential of the city of Dieburg as a basis for the planning of infiltration systems for new real estates is determined by infiltration tests and Ground Penetrating Radar (GPR). To generate infiltration potential maps, infiltration tests are performed punctually. Additionally, the geology and the land use are used to interpolate between these tests. This information can be extracted from maps and other available geotechnical, geological and other data and reports. The results of the infiltration tests are often varying even though the geology and the land use are looking similar. These variations are generated by small scaled discontinuities of the soils structure and the composition in the shallow subsurface. To achieve a high resolution spatial extrapolation of the results from infiltration tests, the structure and composition of the shallow subsurface must be investigated with a high resolution GPR.

**Finalized projects**

**Geothermal rock database for Hesse, Hessian Agency for the Environment and Geology**

Geothermal rock properties (e.g. thermal conductivity and permeability) are necessary characteristics for the planning of geothermal systems. Therefore a literature study about thermal conductivities of rocks was carried out. The results were merged in a database.

**Determination of geothermal properties of soils and rocks in the city of Calw**

For the planning of Borehole Heat Exchangers, knowledge of thermal properties of soil is needed. Actually only few data about these properties are existing. Therefore laboratory determination for the soils in the area of Calw (Germany) had been carried out and a geothermal potential map had been developed.

**Determination of the lake deposits of Steinbrücker Teich**

Lake deposits reduce the capacity of water storage reservoirs. To assess storage capacity of the Steinbrücker Teich, a lake in woods near Darmstadt, the thickness of the deposits were determined using Ground Penetrating Radar (GPR) o a boat. The results show that there was no serious reduction of the storage capacity.

**New projects**

**3D-Model of the deep geothermal potential of the federal state Hesse / Germany**

The scope of the project is the development of a three-dimensional model of the deep geothermal potentials in Hesse. The project is funded by the Hessian Ministry for Economics, Transport, Urban and Regional Development and in cooperation with the Hessian Agency for the Environment and Geology.
Water supply with horizontal wells, Biberach an der Riss, scientific consulting, private client
The water supply system at Biberach an der Riss has to be modernized. Therefore, new horizontal wells must be installed. The hydraulic design and the construction techniques of the wells in glacial deposits is very complex. The geotechnical investigations (laboratory and field investigation) will be performed under scientific consulting of the chair of engineering geology.

Geothermal potential mapping, city of Altensteig
Related to the Project “Determination of Geothermal Properties of Soils and Rocks” the new area “City of Altensteig” is investigated to determine the geothermal potential for Borehole Heat Exchangers.

Scientific consulting and supervision of an enhanced hydrothermal power plant system, Upper Rhine Valley, private client, confidential
The upper Rhine valley is one of the world’s most interesting regions for producing electricity and heat using geothermal resp. hydrothermal energy. A feasibility study to assess the risks and the prospects of the installation of a hydrothermal power plant in this region will be carried out.

Geothermal construction kit (Fraunhofer Magdeburg/Fasa e.V.)
Goal of the NEMO project “Geothermie-Baukasten” (geothermal construction kit) is the development of a geothermal component system for the planning and the construction of geothermal plants. The network wants to offer a full service over the entire life cycle of a geothermal plant starting with the preliminary planning followed by detail planning up to the realisation. Therefore necessary tools will be developed.

Determination of adhesivity of the Lauenburger Ton for a microtunneling project, Ems-crossing, private client, confidential
The Ems River near Knock in northern Germany must be crossed by a small-diameter tunnel driven by a microtunneling machine. The Lauenburger Ton, a very plastic clay, in which this tunnel is traced out is renowned for his adhesive properties. There may occur serious problems caused by clogging of this clay on the machinery equipment due to the adhesive properties. The adhesivity of the Lauenburger Ton will be investigated by a new developed laboratory test to assess the risks of clogging.

Projects in review

DIN-Innovation of normalisation and standardization
Currently no equipment for the standardized measurement of thermal conductivities of soil or cuttings exists. Thermal conductivity is one of the most important parameters for the dimensioning of Borehole Heat Exchangers, so that with missing values only a rough interpretation can take place. This is not acceptable particular for larger projects, since thereby the danger of an under-sizing of the plant exists or unnecessarily high construction costs may occur. It is planned to develop a measuring instrument which supplies reproducible results under defined soil mechanical conditions. This method should in the future take place in soil-mechanical laboratories with the use of their usual methods.
DBU "Entwicklung von Filterelementen für geothermale Brunnenanlagen" (Development of screens for geothermal wells)

DFG SA1802/2-1: Dependence of geothermal parameters on carbonate facies

Thermal-Triaxial press for research and lecture funded by GTZ, Potsdam
A cooperation with the GTZ, Potsdam is intended. The cooperation comprises the loan of Thermal-Triaxial press for laboratory tests on rock samples. The behaviour of rock in geothermal conditions can be determined in these tests.

Publications


Applied Sedimentology

Sedimentary rocks cover about 75% of the earth’s surface and host the most important oil and water resources in the world. Sedimentological research and teaching at the Darmstadt University of Technology focus on applied aspects with specific emphasis on hydrogeological, engineering and environmental issues. However, also research related to oil exploration is carried out with a speciality in palynology and reservoir characterization. To predict groundwater movement, pollutant transport or foundations of buildings in sedimentary rocks a detailed knowledge about the hydraulic, geochemical or geotechnical properties is needed which often vary about several magnitudes. This kind of subsurface heterogeneity can be related to distinct sedimentological patterns of various depositional systems. In addition, changes of depositional systems with time can be explained by specific controlling parameters e.g. changes in sea level, climate, sediment supply and are nowadays described by the concept of sequence stratigraphy. The research in applied sedimentology also includes modelling of erosion and sediment transport and its implication for the management of rivers and reservoirs with the help of GIS and gOcad.

In 2002, georadar equipment has been established as a specific method for shallow subsurface investigations. Results of these non-invasive 3-D structural clarification and 4-D monitoring of subsurface heterogeneities are frequently applied and further developed in the exploration of soils, rocks and unconsolidated sediments of aquifers, alluvial fans, debris flow cones and river dikes in various national and international projects. In the meantime, the Universities of Frankfurt (Applied Geophysics), Tuebingen (Applied Sedimentology), Gießen (Soil Sciences), Aachen (Neotectonics and Georisks), Mainz (Geophysics) industrial partners and the TU Darmstadt (leadership) have founded a centre of near surface investigation methods. Within the centre an instrumental pool is shared, regular meetings are organised and research projects are initiated. In 2005, self-constructed facilities for permeability measurements of soil and rock materials in the laboratory went into operation.

In 2007, activities of the Applied Sedimentary group continued by the DFG projects in Mexico and Uganda with field campaigns and conference participations. The latter is part of the Rhein-Main research unit Riftlink in which the universities of Frankfurt, Mainz and Heidelberg cooperate. In both cases, students were involved to work on their study theses. Other international activities were going on in the south-western USA with a diploma thesis and a study thesis in cooperation with the University of Munich (LMU). In February, Prof. Hinderer visited the Ministry of Water and Agriculture in Riyadh (Saudi Arabia) together with Dr. Schiedek and Prof. Schüth (Hydrogeology). They gave a presentation of sedimentological and hydrogeological research at the TU Darmstadt. A scientist from the ministry has started now his PhD on aquifer reservoir characterisation in south-western Saudi Arabia (Wajid Sandstone Group) and will visit Darmstadt in the summer semester 2008 for three months. In September 2007, Dr. Hornung and Prof. Hinderer participated in a DFG supported Sino-German workshop on geosciences in NW China (Xinjiang). Together with partners from the Jilin University at Changchun we did geological field research in the Junggar and Tarim basins. Within this project another PhD student started his work in order to analyse the formation of reservoir rocks in this area. He is a guest scientist in January 2008 at the Department for Applied Geosciences. In September 2007, two proposals to the EUCORES initiative TOPOEurope were submitted. Both were positively ranked in the evaluation process.
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Research Projects

Sedimentary geology in general and reservoir characterisation:

- Linking source and sink in the Ruwenzori Mountains and adjacent rift basins, Uganda: landscape evolution and the sedimentary record of extreme uplift: Subproject B3 of DFG Research Group RIFT-LINK “Rift Dynamics, Uplift and Climate Change: Interdisciplinary Research Linking Asthenosphere, Lithosphere, Biosphere and Atmosphere” (DFG HI 643/7-1)
- Volcaniclastic successions at the southern margin of the Transmexican Volcanic Belt as witness of the Miocene plate reorganisation of the western Mexican coast (DFG HI 643/5-1)
- The geology of raw materials, sequence stratigraphy and palynology in the “Muschelkalk” of south Germany and Hungary. (Cooperation with University Halle PhD thesis, DFG GO 761/1-1).
- Upper Triassic to lower Jurassic sedimentary record in the south Junggar and the North Tarim basin (China) – implications on tectonics and climate.
- Alluvial fans in the Death Valley (USA): A review to depositional patterns and a new sequence stratigraphic approach.

Quarternary sedimentary geology and surface processes:

- Sediment budget and sequence stratigraphy of Pliocene and Quaternary unconsolidated deposits of the Rheingletscher area, Swiss midlands and the Upper

- Carbon burial in and CO$_2$ evasion from Europe`s lakes and reservoirs (DFG 2004 - 2007) – Hi 643/4-1.
- Genesis of alluvial fans and bajadas according to tectonical uplift and climate change in the central Andes, Peru.
- 3-D architecture, depositional patterns, sediment-mass partitioning and climate triggered sediment fluxes of an alpine alluvial fan (Samedan, Switzerland).

**Hydrogeology, engineering-geology:**

- Characterisation of periglacial debris layers with ground penetrating radar in terms of sedimentology, hydrogeology and soil-science. (PhD thesis).
- Reconstruction of Holocene, Roman and modern sediment yield from valley and reservoir fillings in the Huerva catchment, Ebro basin, Spain. (PhD thesis financed by DAAD).

**Publications**


Geo-Resources and Geo-Hazards

Since 2007 more than 50 % of the global population is living in urban settlements. Cities have a metabolism which needs, amongst others, water and mass resources from the environment and discharges high amounts of fluids and waste with a possible hazardous potential for the current and future generations. Furthermore, cities need additional material to grow and expand. In many cases, this material is loam and clay for bricks as well as sand, gravel and limestone for concrete. For instance, it may be astonishing at first sight to know that sand and gravel is the most extracted resource on our globe. Cities often seal the resources they need for their own growth without knowing it. It still occurs in industrialized and non-industrialized countries because the knowledge of geoscientists is regarded as too complex by many decision makers. This fact should motivate geoscientists to put in efforts to translate and visualize their knowledge for these persons.

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Research Projects

The chair of geo-resources and geo-hazards participates in a joint inter- and trans-disciplinary effort of almost a dozen colleagues from the Technische Universität Darmstadt on the “Eigenlogik der Städte”. The principal idea of this group says that cities can be analyzed following its inherent laws based on historically development and material properties which determine future developments. One of three groups (with Andreas Hoppe as speaker) concentrates on “urban environments – routes and roundabout routes to sustainability”. It will mainly investigate geology, water/waste water and energy as well as the handling of institutions and decision makers during the last decades with the necessity of a sustainable development.
The reconstruction of the geological architecture on the Cenozoic terrestrial Hanau-Seligenstadt Basin between the Odenwald and Spessart Mts with its important geo-potentials for the Rhine-Main Area has been finished by Stefan Lang who defended his findings in a dissertation in February. Dipl.-Geol. Ina Spottke started as research assistant at the same time to investigate the hydraulic regime of the area. Target is an optimizing of 3D reconstruction with the software gOcad by an understanding of interrelations between sedimentological models and hydraulic data.

The evaluation of geo-resources and geo-hazards in the Ebro Basin in the surroundings of Zaragoza (Spain), the fast growing capital of the Province of Aragón, has been concluded and defended in a dissertation in February by Teresa Lamelas Gracia.

The ongoing project in the northern periphery of Belo Horizonte (Minas Gerais, Brazil) aims at evaluating geo-resources and geo-hazards for a sustainable growth of the city. In the last year, the focus was on multitemporal analysis of sand extraction and gully erosion modelling.

During a visit of Andreas Hoppe as short-time lecturer at the Universidad Autónoma de Nuevo León in Monterrey (Mexico), cooperation has been agreed with the colleagues in Linares in the field of geo-hazards. The city of Monterrey has actually more than 2 ½ million inhabitants; it is growing fast and developing with suburbs into its surroundings dominated by the steep hills of the Sierra Madre Oriental.

In March 2007 Dr. Rouwen Lehné joined the group and concentrates on various, GIS-supported projects, especially about neotectonics. A project to translate local geology for tourists was started (for the “Barfußpfad” of Bad Sobernheim in Rheinland-Pfalz which is visited by more than 100.00 persons per year). During his visit at Technical University of Tallinn (Estonia) in August 2007 he agreed on projects in the field of geo-resources.

In Darmstadt the group accompanied the construction of the “Darmstadtium”, the city’s science and congress centre, by investigating the underground. The congress centre is situated upon the eastern master fault of the Upper Rhine Graben. In order to detect future movements between Odenwald and Rhinegraben, a geodetic measurement device was installed in cooperation with the Czech Academy of Sciences (Prague) which will detect horizontal and vertical displacements at $10^{-2}$ mm scale.

In an interdisciplinary seminar Andreas Hoppe discussed together with the historian Dieter Schott natural catastrophes. As speaker of the Evenarí Forum for German-Jewish Studies at TUD he organized together with historians an excursion to Israel under the aspects of “natural history – history – politics” and at TUD a series of Evenarí Lectures on “cultures”. In addition, he served as chief-editor of the “Zeitschrift der Deutschen Gesellschaft für Geowissenschaften” (ZDGG); the journal is indexed in Science Citation Index now.

**Publications**


Geomaterials Science

Geomaterial Science (Applied Mineralogy) explores the formation/processing conditions, composition, microstructure and properties of minerals, rocks in addition to synthesized compounds, while the study of the latter material group focuses on industrial applications. Research activities include a comprehensive characterization of relevant natural and synthetic phases, their performance under pressure, temperature, deformation and local chemical environment as well as tailored synthesis experiments for high-tech materials.

The experimental studies comprise the crystal chemistry of minerals and synthetic materials, in particular, their crystal structure, phase assemblage, deformation behaviour and microstructure evolution. The microstructure variation (e.g., during exposure to high temperature) has an essential effect on thermo-mechanical and electrical properties of synthetic materials as well as natural minerals, which in turn can be used to reconstruct the mechanical and thermal history of rock formation during sub- or obduction processes.

An important facet of the Fachgebiet Geomaterial Science at the Institute of Applied Geosciences is the application of transmission electron microscopy (TEM) techniques for the detailed micro/nano-structural characterization of solids. TEM in conjunction with spectroscopic analytical tools such as energy-dispersive X-ray spectroscopy (EDS), electron energy-loss spectroscopy (EELS) and energy filtered imaging (GIF) are employed for detailed microstructure and defect characterization. High-resolution imaging of local defects on the atomic scale in addition to chemical analysis with high lateral resolution (down to a few nanometers) is similarly applied to high-performance ceramic materials and natural minerals.

Recent research projects involve topics such as fatigue of ferroelectrics, re-calibration of the clinopyroxene-garnet geothermometer with respect to small variations in the Fe$^{2+}$/Fe$^{3+}$-ratio, defect structure in Bixbyite single crystals (and their corresponding exaggerated grain growth), morphology of In$_2$O$_3$ nanocrystals, transparent ceramics (spinel, YAG), interface structures in polycrystals, high-temperature microstructures, and the study of biomineralisation and biomaterials.

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N.N.; Fe-Mg Geothermometer
N.N.; Electro-Corrosion of SiC
Jens Kling; SFB-595 (co-supervision with Prof. H. Fueß)

Guest Scientists
Prof. Dr. Wolfgang F. Müller
Research Projects

Microstructure Characterization of Boron Suboxide, B$_6$O (scientific cooperation 2006-2008 with Prof. Jack Sigalas, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, Gauteng, South Africa).


Polymer-derived SiCO/HfO$_2$ and SiCN/HfO$_2$ Ceramic Nanocomposites for Ultrahigh-Temperature Applications, SPP-1181 (DFG 2007-2009).


Temperature and Pressure Dependence of the Fe$^{2+}$/Fe$^{3+}$-Ratio in Omphacite for Recalibration of the Fe-Mg Geothermometer (DFG 2007-2009).


Planar Defects in Bixbyite, (Mn,Fe)$_2$O$_3$; A Prominent Diffusion Path (scientific cooperation 2005-2008 with Dr. Alexander Rečnic, Jožef Stefan Institute, Ljubljana, Slovenia).

The Effect of LiF Addition on the Sintering Mechanism of Spinel, MgAl$_2$O$_4$ (scientific collaboration 2005-2008 with Prof. Ivar E. Reimanis, Colorado School of Mines, Golden, CO, USA).


Publications


Technical Petrology
with emphasis in Low Temperature Petrology

The scientific and educational field within the applied geosciences is based on indispensable knowledge in magmatic, metamorphic (greenschist facies to ultra-metamorphism) low-temperature (studies in diagenesis and sub-greenschist facies metamorphism) and hydrothermal petrology but also in geothermal geology and sediment petrography. On these fundamentals it is possible to evaluate the mechanical, chemical and physical properties of rocks and the determination for their technical use in engineering geology, in environmental sciences, in geo-material and thermal-energy sciences. The determination of the genetic history and evolution of rocks through time and space gives, e.g., basic information on the study of rock and ore deposits for prospection and exploitation interests. To understand mineralization, re-crystallisation and petrogenesis of rocks an important effort is focussed on tectono-thermal research, tectonophysics and structural geology (from the kilometre to nanometre scale). Furthermore, many natural processes are catalytically controlled by deformation. A better understanding of these processes can be recorded from deformation versus crystallisation and deformation versus metamorphism/heating studies in the field and by experimental simulations. Therefore technical petrology is strongly field-oriented and linked to mineralogy, structural geology and also to geochemistry. Technical petrology at the TUD has strong relations to geomaterial science (applied mineralogy), applied sedimentology, geothermal science and chemical analytics four other fields of principal interest at our department.

Low Temperature Petrology is a 40 years young geoscience branch and covers a broad field of studies: - on diagenesis with application in hydrocarbon, hydrothermal and geothermal exploration, - on clay and carbonaceous materials related with applied clay and organic petrology studies, - on sorption properties of carbonaceous and clay materials, - on the determination of graphitisation nano- and microstructures (refractory quality), - on the improvement of forward numerical geothermal, maturity, and basin-analysis models (studies on hydrocarbon and fluid migration) - or on the synthesis of graphite structures and organic matter maturity related to technical aspects among other applications. It is important to understand the chemical and physical parameters of natural systems to be able to recognize the differences caused by anthropogenic changes.

In the low-temperature range, neoformation of macroscopic and mesoscopic phases is very rare and the minerals to be studied have a very small grain-size. Also stable thermodynamic conditions are scarce and metastable phases and chemical disequilibria conditions are very common. Therefore a broad analytical spectrum must be applied.

In the FG Technical Petrology, general microscopy (MPV coal reflection microscopy, fluorescence microscopy, transmitted light microscopy in the Joint Research Microscopy Laboratory, installed in 2004 and supported by the Mineralogisch Petrographisches Institut Basel, CH) and basically XRD powder and texture studies (Clay and XRD Laboratory installed in 2005, and a research XRD Laboratory recently installed with thankful help by Merck KGaA) can be combined with ICP-AES, TOC, AOX and gas chromatography (GC-ECD, GC-MS) in the Organic Geochemical Laboratory (2006 installed with thankful help by the Hessische Industriemüll GmbH). DTA, TGA, AEM, TEM, HRTEM, Raman spectroscopy, EELS and XAS studies give important hints to low temperature petrologic
researches (in collaboration with research groups of the GEO-initiative Rhein-Main –
Darmstadt, Mainz, Frankfurt).

The main research interests of the study group of R. Ferreiro Mählmann (head of the
group since August 2002) are concentrated in the petrological and petrographical study of
tectono-metamorphic orogenic terrains (Alps, Vosges, Carpathians, Andes, New
Caledonia). The major aim is to discriminate specifically between pre-, syn- and post-
kinematic metamorphic events to get a better understanding of the orogenic processes
that were active during subduction, collision, stacking and exhumation in several parts of
mountain belts. More specifically research is concentrated on diagenesis and very low-
to low-temperature metamorphism, dealing primarily with pelites and rocks rich in organic
matter. Here the principal interest is focussed on the study of vitrinite, bituminite and
secondary macerals, important constituents of coals and the main source for oil and gas
formation and economic reservoirs. In low-grade metamorphic studies reaction-
disequilibrium is a frequent factor and is documented through the irregularity of the
alteration processes of mineral and organic matter reactions. The research is concentrated
on the application of field-petrology and mineralogical laboratory methods to problems
related to equilibrium and disequilibrium conditions.

R. Le Bayon (assistant since December 2004) focuses his research on the metamorphic
petrology concerning silicate bearing-rocks and on organic matter.

Vitrinite reflectance (VR) measurement in organic carbonaceous material-bearing rocks is
of great interest in metamorphic petrology. This stems from the ability of VR to constrain
paleotemperature conditions and maturity degree of organic matter in very low- to
low-grade metamorphic terranes. However, considerable discrepancy still exists concerning
the role of pressure and time on VR evolution. Consequently, we carry out a laboratory
rate study to understand and estimate the effects of pressure and time on the development
and kinetic evolution of VR (associated with G. Brey – University of Frankfurt am Main, D;
L. Nasdala – University of Vienna, A; W.G. Ernst – University of Stanford, USA). We
conducted a series of maturation experiments at 400°C in a closed system at pressures of
2, 10 and 20 kbar employing a high-pressure piston-cylinder apparatus and cold-seal
pressure vessels. Experiments were performed on dry (no water added) xylite of swamp
cypress and involved run lengths from 0 second to 80 days.

The experimental results demonstrate for the first time that pressure ($P$) greatly enhances
the elevation of VR. Moreover, VR is confirmed to increase with run time ($t$) at each $P$
during isobaric experiments. However, an increasing deceleration with $t$ of the VR isobaric
kinetic evolution at each investigated $P$ is found despite rapid initial kinetics. Nevertheless,
we clearly observe a lesser deceleration with $t$ of the VR kinetic evolution with increasing
$P$. To quantify the relationship between VR, $P$ and $t$, we fitted our experimental fraction of
VR ($X_{VR}$) results at each pressure by the method of weighted least squares to a parabolic
equation of the form

$$X_{VR(P,t)} = \left(k(P) \ t \right)^{n(P)}$$

where the rate constant $k(P)$ is found to decrease with $P$. This kinetic equation supports
all our qualitative observations. With the exponent $n(P)$ increasing regularly with $P$ and
$0 < n(P) < 1$, our parabolic equation calls for a larger increase in VR and a lesser
deceleration with $t$ of the VR isothermal kinetic evolution with increasing $P$. We regard our
kinetic formulation as providing a step toward a general equation describing the VR evolution as a function of pressure, time and temperature.

**Fig. 1:** Variation of VR fraction ($X_{VR}$) with effective heating time ($t$) at 400°C and 2, 10 and 20 kbar. The solid curves labelled with pressures are the least-squares best fits to the data using the power law equation $X_{VR(P,t)} = (k(P)t)^{n(P)}$ that satisfactorily describes the isobaric $X_{VR}$ evolutions with effective heating time ($r^2_{2\text{kbar}} = 0.88; r^2_{10\text{kbar}} = 0.93; r^2_{20\text{kbar}} = 0.95$).

The studies of H. Hofmann (assistant since August 2004) are based in the research field of applied clay mineralogy, e.g. geochemical processes related to the formation of bentonites by the low-grade alteration of volcanic ashes and tuffs.

Bentonites, namely the swelling smectites, are most important to a large number of industrial and technical applications due to their special physico-chemical properties like sorption capacity for water, cations and organic complexes, as well as high swelling- and sealing capacity. Possible technical and geotechnical applications related to these properties are located in the pharmaceutical – and oil industry, and since a couple of years in the secure disposal of radioactive waste. Each of these applications requires different material properties. Despite the fact that most of the properties of smectites are quite well known physically and chemically, it is not yet clear where they originate from and how fast material properties can change if the environmental conditions change. To be able to predict if and how the material will change under extreme conditions like they are present in a nuclear waste disposal site, it is essential to know how fast the material can adapt to new environmental conditions. Bentonites are formed by alteration of volcanic ashes and tuffs, partly millions of years ago. However, it is not well known, when under which conditions the alteration process initiated, and how much time is required to form the swelling clays. It is attempted to determine the kinetics of the reaction progress and the controlling factors of physico-chemical property changes responding to different environmental conditions.
Staff Members

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**Technical Personnel**  Josef Kolb died in 02.11.2007
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Research Projects

Experimental kinetic study of organic matter maturation: an appraisal of pressure, temperature and time effects on reflectance properties of vitrinite. - (DFG grant BA 3527/1-1, Cooperation with University of Frankfurt a. M., D; University of Vienna, A and Stanford University, USA).

Geochronology and tectono-thermal history of the Penninic-Austroalpine boundary (Arosa Zone) in Eastern Switzerland; a multi-methodical comparison of methods. - (SNF, Willkomm Fond, cooperation with University of Bern, CH and Departement für Zivilschutz, Bern, CH).

Deformation, fluid flow and mineral reactions along the Glarus overthrust and along the extensional Turba Mylonite Zone, eastern Swiss Alps, Switzerland. Effects of tectonic shear strain on phyllosilicates and organic matter. - (SNF, OTKA Hungary, August Collin Fond cooperation with University of Basel, CH; University of Genève, CH; University of Budapest, HU; Johns Hopkins University Baltimore, USA).

Bituminite parameters to determine thermal metamorphism - field data and experimental studies. - (cooperation with University of Chile, Santiago de Chile, CL; Institutul Geologic al Romaniei, Bucharest, RO; University Complutense, Madrid, E; Stanford University, USA; University of Gießen, D; Peking University, China and ETH Zürich, CH).

Colaboration of H. Hofmann in the Projekt: Size distributions, mass concentrations, chemical and mineral composition and optical parameters of the boundary layer aerosol at Tinfou, Morocco, during SAMUM 2006 (s. Division of Environmental Mineralogy).


Colaboration of H. Hofmann in the Projekt: Ice nucleation properties of the most abundant mineral dust phases (s. Division of Environmental Mineralogy).

Colaboration of H. Hofmann in the Projekt: Stratigraphy and age of the Miocene Tepoztlán Formation, Central Mexico (s. Division of Applied Sedimentology).
Acid rock drainage and the ecologic impact at the CJV E18 Grimstad-Kristiansand PPP-project in Norwegian (cooperation with Bilfinger Berger Civil, D and PIHL, DK).

Publications
Environmental Mineralogy

Environmental mineralogy focuses its research on the characterization of individual aerosol particles by electron beam techniques (high-resolution scanning electron microscopy, transmission electron microscopy, environmental scanning electron microscopy).

We study individual aerosol particles in order to derive the physical and chemical properties (e.g. complex refractive index, deliquescence behavior) of the atmospheric aerosol. These data are of great importance for modeling the global radiation balance and its change due to human activities.

We are also interested in studying the particulate matter exposure at working places and in urban environments. As aerosol particles may have adverse effects on human health, the knowledge of the particle size distribution and the chemical and mineralogical composition of the particles is of prime importance in order to derive the exact mechanisms of the health effects.

Our research is carried out in cooperation with the following national and international partners: Max Planck Institute for Chemistry (Department of Biogeochemistry) in Mainz, Institute for Atmospheric Physics (University of Mainz), Forschungszentrum Karlsruhe (Institut für Meteorologie und Klimaforschung), Institute for Tropospheric Research in Leipzig, Paul Scherrer Institut (Laboratory of Atmospheric Chemistry) in Villigen (Switzerland), National Institute of Occupational Health in Oslo (Norway), and McDonnell Center for the Space Sciences in St. Louis (USA).

Other fields of research include kinetics of mineral reactions and cosmochemistry.

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Research Projects

Environmental scanning electron microscopical studies of ice-forming nuclei (SFB 641; “Die troposphärische Eisphase”).

Electron microscopy of Saharan mineral dust (DFG Forschergruppe SAMUM).

Source apportionment of rural and urban aerosols.

Characterization of working place aerosols (National Institute of Occupational Health, Oslo, Norway)

Environmental scanning electron microscopical studies of the hygroscopic behaviour of individual aerosol particles.

Publications


Introduction

Bones of brown bears from caves in the Alpine region in Germany, Austria, Italy and Switzerland were examined and dated in the last years (Doeppes & Pacher, 2005). The finds originate from the transition from the Late Glacial to the Early Holocene. Since some years stable isotopes of the carbon (13C) and nitrogen (15N) are used to correlate the relationship between predator and prey and in further consequence the habitat at that time. To descriptions to this method we refer to Ambrose (1990) and Bocherens & Ducker (2003).

Preliminary work

Nineteen sites of brown bears are dated by radiocarbon method. The serial numbers of the sites used in the text correspond to the numbers used in the general map (Figure 1). The produced ages reach from the Pleistocene – Holocene transition until the Middle Ages. The first evidence of brown bears in the Alpine region after the Last Glacial Maximum comes from the southern Alpine site Grotta Ernesto (11) and from the northern Alpine site Neue Laubenstein-Bärenhöhle (9). The bear dates correspond to the Bölling-Alleröd-warming. From the Younger Dryas cold event there are no data. The radiometric dating from the Gamssulzenhöhle (2) was determined by means of U/Th-method and shows a large range of error. Nevertheless, the dating falls into the beginning of the Holocene. No brown bear data are known from the cold snap around 8.2 ka. The "optimum" of the Holocene (Atlantikum) is with six dates well documented (Allander Tropfsteinhöhle (1), Wolfshöhle (4), Schwalmis-Bärenhöhle (12), Bärenhöhle am Stoos (15), Nonstopschacht (17), Bärenfalle Silberen (18)). The third gap of our data record is in
the Subboreal. From the end of the Subboreal (Bronze Age) the data record is documented continuously to the Middle Age (Eichberghöhle (5), Wildes Loch (6), Feistringsteinhöhle (7), Bärenhöhle bei Reuthe (8), Bärenhöhle auf Bettenalp (13), Bärenhöhle am Schwarzhorn (14). Further studies will have to show, if the obtained distribution was caused by the still relative small number of dated sites.

Aim
In the last millenniums the brown bear could also have carried out a change in his diet, of carnivore in the Pleistocene to omnivore in the Holocene. These realizations serve on the one hand for the climatic reconstruction in the Late Glacial and Early Holocene and on the other hand for the resettlement in Central Europe.

Dr. Hervé Bocherens, currently Humboldt scholarship holder at the University of Tübingen (‘Ältere Urgeschichte und Quartärökologie’) would analyze the samples. By dating at bone collagen it is indirectly proven that collagen is available sufficiently in the bones so that results are to be expected in any case.

Figure 1: Dated brown bear sites from Austria, Germany, Italy and Switzerland (1 - Allander Tropfsteinhöhle, 2 – Gamssulzenhöhle, 3 – Lauffenbergloch, 4 - Wolfhöhle, 5 – Eichberghöhle, 6 - Wildes Loch, 7 - Feistringsteinhöhle, 8 - Bärenhöhle bei Reuthe, 9 - Neue Laubenstein-Bärenhöhle, 10 - Schlüssellochhöhle, 11 - Grotta d’Ernesto, 12 - Schwalmis-Bärenhöhle, 13 - Bärenhöhle auf Bettenalp, 14 - Bärenhöhle am Schwarzhorn, 15 - Bärenhöhle am Stoos, 17 - Nonstopschacht, 18 - Bärenfalle Silberen, 19 - Milchbalm-Höhle)
For the first time a more precise picture of the former habitat of the brown bears from the time span Late Glacial to Early Holocene in the Alpine region could reconstruct with the described investigation. Brown bears from caves in the Alpine region were never examined by with this method. With the indicated number of samples it is surely posed that the quantity of the analysis values can illustrate the regional difference, and in addition, similarities are statistically evaluable. Cooperation with an Australian university has also been offering the possibility to genetically investigating on the alpine brown bears from this time span.

References


Management of Regional Groundwater Resources: The Wajid Aquifer Study

C. Schüth, T. Schiedek, M. Hinderer

The qualitative and quantitative assessment of regional water resources and their sustainable use is of overriding importance, especially in arid countries around the world. In cooperation with GTZ-IS and Dornier Consulting and on behalf of the Ministry of Water and Electricity of the Kingdom of Saudi Arabia a detailed study of the Wajid Aquifer is carried out, one of the mega aquifers on the Arabian peninsula. This project acts as a pilot project to further develop our activities in the water resources management area.

The Wajid aquifer is the most important groundwater resource southwest Saudi Arabia with an approximated area of 200,000 km² and thickness between 200 m and 900 m. It consists mainly of coarse grained cross-beded sandstones of cambrian to ordovician age. Since the 70th of last century the aquifer is extensively used, mainly for irrigation in agriculture (Fig. 1). As a consequence, the aquifer is overexploited leading to falling groundwater tables and a deterioration of groundwater quality.

Main aim of the Wajid aquifer study is the evaluation of the hydrogeological situation and the development of instationary 3D groundwater model. With this, the fundamental base for the establishment of a water management plan can be delivered.

In order to set-up a conceptual groundwater model, the permeabilities of different rock units have to be studied systematically. This is done in a detailed sedimentological study of the Wajid Sandstone Group which is completely missing until now. The study includes field work such as logging of sedimentary sequences and mapping of geometries of rock bodies, so called architectural elements. γ-ray measurements are useful for correlations and the identification of these bodies in bore wells. This work is supplemented by lab work in Darmstadt on stratigraphy (palynology), diagenesis (microscopy, XRD analysis) and porosity as well as permeability measurements.

Fig. 1: Areal picture of southwest Saudi Arabia close to Sulayyil. Irrigation using groundwater and center pivots. The circular irrigated areas have diameters between 500 m and 1 km.
Predictions and correlations of geobodies and sequences are largely based on the interpretation of past depositional environments. The Wajid group was deposited over almost 300 Million years from the Upper Cambrian to the Lower Permian as a marginal clastic sequence of an intracontinental basin with low subsidence at the northern edge of Gondwana. Due to a repeated drift of the Arabian Plate from equatorial position to low latitudes and back, depositional environments experienced different climates and thus transport and sedimentation modes. Among those are river plains, deltas, shallow marine settings, and deserts. Because the Arabian Plate was in a low-latitude southern position during paleozoic glaciations, also glacial and fluvio-glacial deposits are present. Towards the east marine intercalations become more frequent which give potential for aquicludes and/or oil-generating organic rich shales. The sedimentological research is carried out by a PhD student enrolled at TU Darmstadt who is member of the Saudi Arabian Ministry of Water and Agriculture.

The results of the field and laboratory work as well as already existing data on the Wajid aquifer will be integrated in a digital 3D georeferenced subsurface model. The subsurface structures will be interpreted as hydrofacies units enabling the transfer of the data into the instationary 3D groundwater model, based on the software Modflow.
Modelling of geochemical and isotopic changes in a column experiment for degradation of TCE by zero-valent iron

C. Schüth, H Prommer

Zero-valent iron (ZVI) permeable-reactive barriers have become an increasingly used remediation option for the in situ removal of various organic and inorganic chemicals from contaminated groundwater. In this study a process-based numerical model for the transport and reactions of chlorinated hydrocarbons in the presence of ZVI has been developed and applied to analyse a comprehensive data set from laboratory-scale flow-through column experiments.

The model formulation includes reaction network for the individual sequential and/or parallel transformation of the chlorinated hydrocarbon tetrachloroethylene (TCE) by (Fig. 1), for the resulting geochemical changes such as mineral precipitation, and for carbon isotope fractionation occurs during each of the transformation reactions of the organic compounds. The isotopic fractionation was modelled by formulating separate reaction networks for lighter ($^{12}$C) and heavier ($^{13}$C) isotopes.

The code PHT3D was used to formulate and incorporate the reaction network for TCE degradation by ZVI media and the corresponding geochemical changes. PHT3D uses the transport simulator MT3DMS. to account for advection and dispersion of aqueous components, while using PHREEQC-2 for the computation of the reactive processes. The model was then subsequently used to simulate the transport of TCE-contaminated groundwater through the experimental column filled with the iron filings.

Fig. 1. Reaction network for the degradation of TCE by zero-valent iron:

Fig. 2: Observed and simulated isotope fractionation of TCE, acetylene, ethane and ethane along the column length.
The study illustrates the successful simultaneous simulation of kinetic isotope effects for a complex network of degradation reactions. Similar to concentration data, the simulated carbon isotope ratios of TCE and its daughter products were in good agreement with observations (Fig. 2). The modelling approach for quantifying isotopic fractionation is readily applicable for comparable problems involving ZVI but, perhaps more importantly, also for multi-dimensional field-scale problems, for example, where TCE undergoes natural attenuation by reductive dechlorination and where transformation products such as DCE, VC and ethylene and their isotopic composition need to be analysed.

Numerical modelling of such systems will assist to distinguish between simple dilution of compounds and to estimate the systemic environmental assimilation and degradation of contaminants.
Is there a correlation between permeability and thermal conductivity? – Interpretation of characteristics in anisotropic formations

Ingo Sass, Arne Buß

The relationship between thermal conductivity and porosity was already examined. However a systematic analysis of permeabilities and thermal conductivities (fig. 1) is missing. The relationship between thermal conductivities and permeabilities represented in figure 1 is taken from relevant literature. From the latest results of the Institute of Applied Geosciences, TU Darmstadt (IAG) becomes clear that an increased permeability of dry drill cores does not correspond necessarily with an acceptance of the dry thermal conductivity.

The planning of enhanced deep geothermal plants cannot rely frequently on direct sampling. Exploratory drilling can not be financed in early stages of geothermal investigation. The prognosis of geothermal formation and rock characteristics for target horizons is to be supported by characteristic value determination at easily accessible samples. This can be done with outcrop studies etc. This requires a statistically secured basis of rock data. More than 8.000 single results of rock samples about geothermal parameters extracted from literature (Rumohr & Sass 2007) just show only for 13 hard rock samples with both permeability and thermal conductivity data.

For the determination of the heat conductivity the Optical Scanning Method (Popov et al 1999) was selected, since it can be accomplished at drill cores of most different quality on the one hand relatively fast and on the other hand the anisotropy of the heat conductivity can be studied nearly arbitrarily in detail.

A heat source heats a rock sample surface. The surface temperature of the sample is measured contactless by two infrared temperature sensors. The heat source and the sensors move with constant speed and constant distance to each other. The light and radiant heat are focused on the surface of the sample, whereby the sample is heated. The temperature is measured before and after heating.

Fig. 1: Thermal conductivity versus permeability - literature values a. Haefner et al. (1992), Gehlin (2002) and Pannike et al. (2006)
The determination of heat conductivity is based on the comparison of the difference of the temperature of reference samples with defined and well-known heat conductivity and those sample material with unknown thermal conductivity. The measurement can be performed on rectangular as well as on cylindrical samples, both under dry and water-moistened conditions with an accuracy by up to ±3 %. The method can be used under certain soil-mechanical conditions also for the regulation by heat conductivities at loose rock samples (Homuth 2007, Mack 2007).

The measurement of the permeability took place with a combined column and mini permeameter with conditioned compressed air as measuring medium. With the mini permeameter, developed at the IAG, a smooth rock surface can be measured punctually. An injection nozzle is pressed over a sealed adapter with constant contact pressure right-angled to the drill core axis on the sample surface. Compressed air is pressed by the ring opening with a diameter of 4 mm into the rock sample. After relatively short time a specific stationary flow adjusts itself. The measuring error of the arrangement in principle amounts to up to ±5 %.

The relationship between permeability and thermal conductivity shows deviating from the porosity/thermal conductivity relationship a smaller dispersion (fig. 2 exemplarily shown at samples of drill cores of the middle Buntsandstein).

![Graph showing permeability versus thermal conductivity and porosity](image)

**Fig. 2:** Permeability versus thermal conductivity and porosity (middle Buntsandstein)

The systematic measurements of the thermal conductivity at drill cores, take place lineful with an optical thermal scanner, the permeability regulations take place with one at the IAG developed gas pressure mini permeameter. Both measurements can be accomplished at several points on a sample. Thus a direct comparison of thermal conductivity and permeability anisotropy with consideration of lithological, sedimentological and other characteristics is possible.
Sedimentary analysis of a lacustrine to fluvial environment and its depositional dynamics  
(Haojiagou-valley, Junggar Basin, NW-China)

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Summary

In the Haojiagou valley (40km W of Urumqi, Xinjiang-province) the fluvial to lake-deltaic sedimentary inventory of the Middle Triassic Huangshanjie and the Upper Triassic Haojiagou formation comprises gravely channel bodies, sheet like sandy and clayey units, as well as ferrocrete horizons and coal seams. In some areas of the Junggar-Basin these units act as important hydrocarbon reservoirs and seals. Also, the up to 10m thick coal seams play an important economic role. So, as the succession may represent an important outcrop analogue for these raw materials it was quantitatively logged and characterized in terms of lithofacies and architectural element analysis, depositional trends, sequence stratigraphic cycles and natural gamma ray, porosity and permeability trends (not published here).

Statistical evaluation of channel body size, geometry, interconnectedness and stacking patterns was done at a 600 m thick and 1 km wide two-dimensional section, which was composed from hundreds of small scale outcrop photos with a spectacular mounting and photo-surveying technique. Seal distribution, sand and gravel body stacking patterns show typical fingerprints for each sedimentary environment as well as for regional allochtonous controls.

Depositional trends and stratigraphic cycles show a clear four-fold hierarchy, while only the macro- and overall scale reveals sequence stratigraphic relevance. Micro- and meso scale cycles are considered to be governed or masked by autocyclic processes.

This data set may be used as an outcrop analogue to establish time lines at a regional scale and for prediction of facies transitions, geobody architecture and their properties in comparable subsurface areas where less information is available or interpolation schemes for existing data sets are needed. In terms of distribution of coal deposits and hydrocarbons this data set can be used for prediction and characterisation purposes of reservoir properties and so it could have an enormous economic value.

The fluvial sedimentary system

A dominance of alluvial processes is recognized during deposition of the upper Haojiagou formation.

Typical architectural element successions (Fig. 1)
Fluvial channels are topped by prominent crevasse deposits followed by thin and silty near channel floodplain successions, which can intercalate with swamp coal beds. The swamp coal beds contain mostly higher amounts of clay and silt so they can not be identified in the gamma ray log. On top of this succession again crevasse splay units follow or exceptionally levee beds are preserved.

**Environmental interpretation, facies model (Fig. 2) and sequence stratigraphic interpretation**

Due to the lack of lateral accretion, the river system is interpreted to have straight and less bended channels with small braided individual channels and bars in a narrow channelbelt (100’s of meters). Interchannel areas are dominated by crevasse and near channel floodplain successions, which implies that distances from channels are never very far (km’s). Channel shifting takes place by avulsion-processes, lateral dislocation by erosional processes was not observed. Although the preservation potential is high due to plenty of accommodation space, only levees, which were shed into the lower floodplains, can be preserved, so if they occur they can be found always beneath a channel. Fluvial depositional cycles at micro or meso scale are not suitable for any sequence stratigraphic interpretation because they are locally developed and have no regional significance. In contrast, macro scale cycles can be used as they are demonstrating stacking patterns of several fluvial cycles.

**The delta-plain sedimentary system**

The lower Haojiagou formation is characterized by the deposition of coal seams, which are considered to have developed in the delta plain.

**Typical architectural element successions (Fig. 3)**

The architectural elements of ‘swamp’ and ‘floodplain’ are frequently interbedded. The individual floodplain units often show a slight fining upward trend which indicate that they may represent event layers where suspended load settles down from a waterbody over some time due to grain size variations or decrease in stream power. The swamp-floodplain units are up to 10-12 m thick and intercalate with crevasse splay successions which may contain also crevasse and river channels.

**Environmental interpretation, facies model (Fig. 4) and sequence stratigraphic interpretation**

As the coal swamps are regionally spread and positioned in the middle part of all depositional cycles it is likely to assume a very shallow flooding of the coastal plain. This makes it possible to create large areas with dense vegetation. The biomasses can accumulate vertically and the following progradation of fluvial sediments seals and conserves it. The macro-scale depositional cycles spans over approx. 20 to 25 m thickness and the meso-scale cycle over approx. 80 m. Additionally macro and meso scale cycle hierarchies are regionally traceable, which makes it reliable to assume a regional control e.g. by lake level fluctuations. So, thick, grouped and clean coal beds can be used as proxy for the maximum retreat of the fluvial systems or the maximum influence of the lake environment, which means a base level rise to fall turnaround point. Vice versa the coarsest clastic units in between mean a fall to rise turn around point.

**The delta-top sedimentary system**

The upper Huangshanjie formation shows a significantly different depositional pattern due to dominance of clean, traceable sandy units and downcutted channels. This pattern is considered to be formed at delta shorefaces.
**Typical architectural element successions (Fig. 5)**

Through stratigraphy, mouth bars typically follow channels which itself may interfinger with rippled sand sheets and towards higher positions with coastal mud flats. Beaches are associated with rippled sand sheets and mouthbars.

**Environmental interpretation, facies model (Fig. 6) and sequence stratigraphic interpretation**

Due to brown coal deposition and a dominance of thick and coarse grained gravely channel units in the lower part of the section it is likely to assume a fluvial system feeding the more downdip located delta at that time. Interchannel areas consist of floodplain mud, crevasse splays and small coal swamps (see Fig. 5, facies model of upper Huangshanjie-form.). The middle parts of the section show the transition into deltaic conditions. This fluvial system retreats more and more towards deltaic conditions as indicated by intercalations of mouth bars and rippled sand sheet units. Further towards coastal mudflats develop which indicates the maximum lateral or updip retreat of the alluvial system. Overall it can be stated that baselevel fall turnaround points can be set at maximum grain size of channels or alternatively at mouth bar deposits. A base level rise is represented by rippled sand sheets as pure shallow lacustrine deposits.

The lacustrine dominated sedimentary system

The lower Huangshanjie formation is characterized by highly variable lacustrine dominated conditions, which may represent delta lobe switches and lake level/sediment supply fluctuations.

**Typical architectural element successions (Fig. 7)**

Subaqueous channels are interbedded with delta foreset and subaqueous fan sediments. Channel margins are flanked by levees or show a gradual transition into delta foreset sediments. In a majority of cases subaqueous channels show a slight downcutting into those sediments.

**Environmental interpretation, facies model (Fig. 8) and sequence stratigraphic interpretation**

As most of the observed architectural element successions belong to the subaquatic realm, it is likely to assume a dominantly lacustrine environment where clastic input is distributed by bottom- or surface-flows in the lake. The clastics settle down from the water column related to grain size forming the drape-like delta foresets. Bottom-flow conditions may form a subaqueous continuation of the river channels. Also slope failures occur and form a turbidite like system with subaqueous channel-fan complexes. The depositional cyclicity displays a retreat or advance of the delta or even fluvial system while channels indicate an advance and the most distal fan sediments the retreat (see Fig. 12). This can be also interpreted as a lateral facies shift, so progradation or lake transgression in a sequence stratigraphic sense can be done only by correlations throughout the whole delta, in an overall stratigraphic scale or best by regional correlations of different delta systems in order to quantify the lake level fluctuations independently from local changes in sediment supply.
Fig. 1: Typical alluvial succession of the upper Haojiagou-formation with isolated channels (CH) embedded in floodplains (FF) and swamps (SW) containing crevasse splays (CS) and levees (LV). Height of outcrop approx. 10m.

Fig. 2: Depositional model of the fluvial successions (upper Haojiagou-formation).

Fig. 3: Typical architectural element succession of the delta plain system: Coal seams (SW) intercalate with floodplain fines (FF) and crevasse (CS).

Fig. 4: Depositional model of lacustrine coastal swamp successions.

Fig. 5: Typical delta top succession of architectural elements. Coastal mudflats (CM) are topped by mouth bar sequences (MB).

Fig. 6: Depositional model of lacustrine delta top successions.

Fig. 7: Architectural element association of the deeper lacustrine environment dominated by turbidite activity and suspension fallout.

Fig. 8: Depositional model of lacustrine delta slope successions.
Displacements at the eastern master fault of the Upper Rhine Graben in Darmstadt

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The Upper Rhine Graben in Germany is a still subsiding tectonic unit with an active sinistral strike slip component (Fig. 1). This is accompanied by recent isostatic rebound which results from the still ongoing back-formation of a mantle plume that originated in Cretaceous times. This plume can be deduced for that area where during Cretaceous times, with a very high sea level, no sediments have been deposited. The further development resulted in a smaller plume and a failed rift and subsidence.

The Upper Rhine Graben is also a densely populated area with a higher hazard of earthquake and intense construction activities. High precision measurements on dividing planes like faults and joints can help to decipher micro-movements and their mechanisms. Most suitable for such high precision measurements (i.e. 3D-monitoring) are dividing planes which are known as recent active. Outcrops to install such devices are rare. So it has been an opportunity to install a measuring station for the 3D monitoring of displacements when in the city of Darmstadt the eastern master fault has been exposed recently.

Embedded in an already existing system of long term monitoring in Europe working successfully for more than 25 years [1] the Rhine Graben allows the comparison of tectonically active regions with more stable parts of the European crust like Bohemia where a measuring program by the Czech Academy of Sciences has been started recently.

Fig. 1: Outline of the Science and Congress Centre “darmstadtium” and the master fault [2] and kinematic model [3] of the Upper Rhine Graben for the Pleistocene and Holocene.

The device (Fig. 2) is a development of the Czech Academy of Sciences (Košťák 2006) and detects displacement rates even in the order of $10^{-1}$ to $10^0$ mm a$^{-1}$. First
measurements (Fig. 3) show such displacements, but it should be stressed that these actually may not be related in any case to tectonic movements or isostatic rebound resp. as during the measurement intervals, intense construction activities in the building and its surroundings took place! It is hoped, that future measurements under normal conditions will detect the geological components.

Fig. 2: A dilatometric measurement station was installed in May 2007 between sediments of the Rhine Graben and the crystalline rocks of the Odenwald.

Fig. 3: First measurements on the master fault at the Darmstadium in 2008. Please note that these movements may be caused by construction activities of the Science and Congress Centre during that time.

Transmission electron microscopy of ultra high temperature ceramics
Laura Silvestroni, Hans-Joachim Kleebe, Stefan Lauterbach

Borides and carbides of the fourth group of the transition metals belong to a class of materials called ultra high temperature ceramics (UHTC’s), because of their high melting temperatures (>3000°C), high hardness (20-26 GPa), high thermal and electrical conductivities and high stiffness (400-500 GPa). They find applications in refractory linings, electrodes, microelectronics and cutting tools. Potential applications of zirconium and hafnium diboride and carbides have been also considered for aerospace manufacturing as, for example, the leading edge parts on hypersonic re-entry spacecrafts.

Despite their good properties in aggressive environment, the use of monolithic material is limited due to the poor sinterability. To obtain dense materials, metallic and non-metallic additives have been added, but often the secondary phase segregate at the grain boundaries and make the material collapse at high temperature. Recently, MoSi2 has been disclosed as a sintering aid even for densification without the application of pressure. It possesses a high melting point (~2030°C), excellent oxidation resistance, high stiffness and it has been proved to improve the mechanical properties at high temperature as regards to monoliths.

A critical literature analysis review reveals that neither any detailed transmission electron microscopy work nor any report on densification mechanism is available for this class of materials. In order to optimize the sintering additives and sintering parameters, it is necessary to understand the mechanisms which govern the densification through a detailed analysis of the microstructure. The study of microstructure of carbides and borides of Hf and Zr with addition of 20 vol % of MoSi2 densified by pressureless sintering was carried out.

We consider the ZrC-MoSi2 composite sintered without the application of pressure at 1950°C for 60 minutes under flowing Ar. Besides the main phases ZrC and MoSi2, secondary phases were detected: SiC, ZrSi, ZrSi2 and mixed phases containing Mo-Zr-Si with excess of Mo or Zr.

From microstructure analysis we deduce that C plays a key role in the densification of this composite. The calculated C-MoSi2 pseudo binary phase diagram indicates that one of the main equilibrium products between carbon and MoSi2 is the SiC and, above 1700°C, it will form at any C/MoSi2 concentration ratio in the liquid-solid phase transformation process. As a matter of fact, SiC was always found embedded into MoSi2 phase and it showed an uneven morphology. Carbon is present as impurity in the starting ZrC powder (~1wt%) and may derive from the sintering environment, as both the crucible and the heating elements are made of graphite. Zirconium silicides were found at the interface between MoSi2 and SiC or MoSi2 and ZrC, as shown in Fig. 1. The very low dihedral angles suggest that these Si-based phases were liquid at the sintering temperature. According to the Zr-Si phase diagram ZrSi2 will be melt at the peritectic temperature of ~1600°C and ZrSi will be in equilibrium with the liquid phase.
from 1600°C on. The reaction paths leading to the formation of these silicides might be the following ones:

\[
\begin{align*}
\text{ZrC} + \text{MoSi}_2 &= \text{ZrSi}_2 + \text{MoC} \\
2 \text{ZrC} + 2 \text{SiO}_2 + \text{C} &= \text{ZrO}_2 + \text{ZrSi} + \text{SiC} + 2 \text{CO}
\end{align*}
\]

It is reported that surface layer of SiO\(_2\) can exist on MoSi\(_2\) particles, moreover, the MoC phase is not stable at temperatures above 1200°C, actually, during sintering tests, a 2.3 % weight loss was measured and it is attributed to the evaporation of the volatile species (MoO\(_3\), CO).

Based on the present results we can draw the conclusion that the densification of this system is assisted by liquid phases provided by MoSi\(_2\) which reacts with both Zr and C.

**Fig. 1:** BF TEM image of ZrC-20 Vol% MoSi\(_2\) sintered at 1950°C without application of pressure. Reaction products based on Zr-Si can be seen at the interface ZrC-MoSi\(_2\).
CaCO$_3$ biomineral formation and bio-inspired mineralisation in hydrogel matrices

Ingo Sethmann, Hans-Joachim Kleebe

Biomineralised hard parts, such as skeletons, teeth, and shells, are produced by organisms under cellular control, i.e., under physiological conditions. In many cases they show elaborate morphologies and ultrastructures that are adapted to specific functions. CaCO$_3$-minerals, predominantly calcite and aragonite, are among the most common biomineral phases. These mineral phases are usually intimately associated with a so-called organic matrix to form organic-inorganic composites. These organic matrices must already be present while mineral precipitation takes place. Hence, they are expected to influence crystal growth and may play a role in the controlled formation of complex, often hierarchically organised structures. However, the factors that control this morphogenesis and structure formation in biomineralisation are still not well-known. The aim of this investigation is to learn more about the role of the organic matrices.

As an example of biominerals, we investigated the sclerites that form a flexible supporting skeleton of octocoral (*Sinularia* sp.) colonies. The sclerites are mostly spindle-shaped millimetre-sized objects with tubercles on their surfaces (Fig. 1a). Structurally, the sclerites are composed of densely packed Mg-calcite fibres, which are embedded in a network-like organic matrix and largely oriented parallel to the morphological axis of the sclerite. The sclerite surfaces, however, were found to consist of nano-granular layers with a transition towards the internal bulk structure by aligned aggregation and fusion of nanogranules to form crystal fibres (Fig. 1b). This finding strongly suggests that the sclerites grow by precipitation of nanoparticles onto the sclerite surfaces in the presence of an organic matrix and subsequent transformation of the particles into calcite crystal fibres by self-assembly. Although the driving force of this elegant self-assembly of hierarchically structured material remains unclear, we assume that the organic matrix is involved in the modification of the crystal growth pattern.

As an experimental approach to a better understanding of the role of organic network matrices in biomineral formation, we carried out bio-inspired CaCO$_3$ precipitation in pH-buffered polyacrylamide (pAAm) hydrogel by counter-diffusion of calcium and carbonate.

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**Fig. 1:** Octocoral sclerites, (a) complete sclerite, (b) transition from nanoparticles to crystal fibres by aligned fusion; scanning electron micrographs (SEM).
ions in U-shaped glass tubes. The resulting calcite crystals resembled hierarchically structured aggregates of aligned rhombohedral microcrystals (Fig. 2a). Cleaved and 'premature' crystals revealed that the aggregate structure developed only after the initial crystal had been grown to a certain size. Correspondingly, the crystal surfaces of aggregate blocks showed nanogranular compositions (Fig. 2b), while those of 'premature' non-aggregate crystals were almost flat. In cleaved aggregate blocks, the internal nanogranular appearance is more pronounced directly below its growth surface than in its core. Thermo-gravimetric and differential thermal analyses (TGA/DTA) revealed that small amounts of the gel matrix became incorporated into the aggregate structure, probably wedged between the aggregate blocks. These experimental observations suggest that with progressive growth of the crystals, the gel matrix was pushed outwards and became compressed at the crystal surface, where it then formed an obstacle for crystal growth and gave rise to crystal growth with an aggregate pattern on a micro- and nanometre scale as well as to incorporation of parts of the organic network. During crystal growth, nanogranular surface aggregates seem to fuse and form the compact crystalline material of the aggregate blocks.

![Fig. 2: Calcite crystal grown in pAAm hydrogel, (a) complete crystal (SEM), (b) nanogranular crystal surface (atomic force micrograph, AFM).](image)

Although the experimental precipitation system is rather simple compared to biological systems as in octocorals, the resulting mineralised structures seem to resemble each other surprisingly well in their crystal growth mechanism, their hierarchical structure, and their composite nature. Therefore, we assume that, in addition to being a structural component of the final material, one role of organic network matrices in biomineralisation is to modify the mineral precipitation and crystal growth pattern to facilitate the formation of hierarchical structures. Additionally, controlled precipitation and aggregation of nanoparticles enable the construction of mineralised hard parts with complex and rounded morphologies.
Transmission electron microscopy characterization of polymer-derived SiCO ceramics

Hans-Joachim Kleebe, Stefan Lauterbach

The correlation between microstructure evolution and processing temperature of polymer-derived SiCO ceramics with a high volume fraction of free carbon is studied by transmission electron microscopy (TEM). The high carbon content of the SiOC ceramics was achieved by crosslinking the starting precursor polyhydrido-methyl-siloxane (PHMS) with divinylbenzene (DVB). Focus of the TEM characterization is the evolution of the carbon phase upon pyrolysis at 1000 °C and after additional heat treatment at 1450 °C. Although a continuous structural rearrangement within the bulk SiOC matrix was observed with raising temperature, samples annealed at 1450 °C remained predominantly amorphous, with the exception of a percolation network of turbostratic carbon and the precipitation of nanosized SiC particles. The micro/nanostructure observed upon thermal treatment at high temperature suggests a phase separation in small SiO$_4^-$ and SiC$_4^-$-rich regions encapsulated by carbon. This specific phase distribution is consistent with the exceptional thermo-mechanical properties reported for similar high C-content SiOC materials. Scarmi et al. reported on an unexpected observation: the viscoelastic behaviour of carbon-rich SiOC at temperatures exceeding 1000 °C. In brief, their experiment was performed as follows: when loading pure SiO$_2$ glass in compression at 1000 °C, an expected high-temperature creep deformation was monitored. However, when continuously loading and unloading the SiOC sample at a slightly higher temperature, the initial strain was recovered after the applied stress was removed from the sample. Scrami et al. proposed two different SiOC nanostructure models regarding the distribution of the carbon phase within the residual amorphous silica. In the first model, the carbon phase was embedded in an SiO$_2$ matrix as isolated individual clusters, while the second model predicted graphene cages which encapsulate the SiO$_2$ glass phase. Only the second model could explain the observed viscoelastic behaviour of the carbon-rich SiOC. High-resolution TEM imaging allowed to unequivocally confirm the latter micro/nanostructure model of C-rich SiCO ceramics, as shown in Figure 1.

Fig. 1: HRTEM image of C-rich SiCO upon HF etching. It is assumed that the etching process selectively removes the residual silica phase forming small pores (indicated by arrows) with an average diameter of 10-20 nm. The enlarged area clearly shows the formation of nanosized SiC crystallites in close proximity to the turbostratic carbon (graphene cages).
New insights into the ash to bentonite transition: A case study of Upper Cretaceous pyroclastic dykes of the Lago Pellegrini, Neuquen, Northern Patagonia

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Pyroclastic dykes occur in close association with the bentonite beds of the Upper Cretaceous Allen Formation of the Lago Pellegrini area, near Neuquen, Argentina. The dykes were sourced from a thick ash (bentonite) layer and injected upward, along sub-vertical fractures, under over pressured conditions into the overlying clastic sediments. Injections occurred during early compaction and were subsequently shortened by up to 32%. Alteration to montmorillonite probably commenced dyke emplacement, but the bulk of clay and zeolite mineral formation occurred after dyke emplacement. The mechanism of fracture formation and dyke intrusion is suggested to be of seismic origin. Earthquake activity explains the simultaneous formation of localized vertical dilational fractures and the liquification of the coarse ash material into the more compacted, fine, overlying, well bedded clastic rock sequence. These relationships constraint the importance of the seismically induced release of fluidized ash in controlling subsequent alteration history of the bentonite rocks.

The Anisian Peri-Tethys – Tethys connection: implications from clay mineralogy of Lower Muschelkalk deposits (Leuggern well, N Switzerland)

Annette E. Götz and Heiko Hofmann

During Middle Triassic times, Central Europe was subdivided into two major palaeogeographic domains: (1) the NW Tethys shelf area (Tethyan or Alpine realm) and (2) its northern, peripheral Germanic Basin (Germanic realm). Recent studies addressed the eustatic history of the NW Tethys shelf and the Peri-Tethys (Germanic) Basin by means of sequence stratigraphic interpretation of depositional series and their overregional correlation. Anisian carbonate successions of northern and central Switzerland turned out to be key sections for investigating marine ingressions from the Tethys ocean into the epeiric Muschelkalk sea. Palaeontological data strongly support the hypothesis of a western (“Swiss”) connection during the entire Anisian.

In the present study, 26 samples of the Leuggern well (N Switzerland) were analysed with respect to clay mineral distribution of the Anisian carbonate series. All samples were found to be composed of the clay minerals illite (illite/smectite), chlorite and kaolinite without showing significant stratigraphical changes depending on burial depth, composition or mineral properties. We suggest this continuity to display constant sedimentation and mineral growth conditions within the entire series. These results support the Anisian Peri-Tethys - Tethys connection via a western gate area. However, the position of this gate has still to be reconstructed by further integrated investigations.
Chemical and mineralogical composition and morphology of aged Saharan dust, marine and biomass burning aerosol at Cape Verde

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The Saharan Mineral Dust Experiment II (SAMUM II) is dedicated to the understanding of the radiative effects of mineral dust. A field campaign focussed on investigation of aged Saharan dust and admixtures of biomass burning and marine aerosols was carried out at the airport of Praia, Island of Santiago, Cape Verde. Ground-based and airborne measurements were performed in the winter season, where mineral dust from the Western Sahara and biomass burning aerosol from the Sahel region are observed to occur.

Figure 1: Secondary electron image of a soot particle with inclusions of ammonium sulfate and sodium chloride.

Samples were collected with a miniature impactor system, a sedimentation trap, a free-wing impactor, and a filter sampler. Beryllium discs as well as carbon coated nickel discs, carbon foils, and nuclepore and fiber filters were used as sampling substrates. The size-resolved particle aspect ratio and chemical composition is determined by means of electron-microscopical single particle analysis and characteristic X-ray fluorescence analysis. Mineralogical bulk composition is analysed by X-ray diffractometry.

First investigations of the collected samples confirm the presence of a mixture of sea salt, mineral dust, and anthropogenic material (see sample images). A complex aerosol
consisting of externally mixed particle types as well as internally mixed species – e. g., sea salt/mineral dust mixtures – is encountered in the marine boundary layer at Praia.

Figure 2: Secondary electron image of a complex mineral dust/sea salt mixture.

By comparison with earlier measurements in Morocco, further analyses of the samples will yield information on the change in chemical composition, particle morphology, and mixing state of the aerosol during transport from the African continent to Cape Verde.

Figure 1: Secondary electron image of an external mixture of soot and ammonium sulfate.

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