ANNUAL REPORT

2002

DEPARTMENT OF

MATERIALS AND EARTH SCIENCES
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Preface

Hartmut Fuess, Dean

The year 2002 was highlighted by two outstanding events: The Sonderforschungsbereich (SFB) “Elektrische Ermüdung von Funktionsmaterialien” (Electrical Fatigue of Functional Materials) was approved by the Deutsche Forschungsgemeinschaft and the “Jahr der Geowissenschaften 2002” (Year of Geosciences) was celebrated as suggested by the “Bundesministerium für Bildung und Forschung” (German Ministry of Education and Research).

The proposal of an SFB, carefully prepared under the energetic leadership of Prof. Jürgen Rödel was evaluated in June 2002 and successfully established starting January 1, 2003. This initiative provides funding for 16 research groups for the next four years. Twelve groups of the Institute for Materials Science, two from the department of Chemistry and one each from the departments of Technical Mechanics and Engineering join efforts. But the research activities in the Institute for Materials Science were also honoured by additional equipment from external funding and by a steady increase of cooperation with industry. Figure 1 displays a distribution of external funds for the last two years.

As 2002 has been declared as the “Year of Geosciences” by the German Ministry of Education and Research, most of the Geo-Institutions in Germany went public with various activities. Darmstadt decided to concentrate on information for young people and consequently offered lectures about geotopics for schools. More than a dozen high schools took part in the program. As a special contribution the volume “Applied Geosciences at Darmstadt University of Technology” (321 pages, ISBN 3-932537-15-7) was published, reviewing the various research activities of the Institute and its historical development. The public was invited to visit the Institute on a Sunday in November and hundreds of visitors came to see the laboratories and to listen to lectures. Together with the geo-institutions in Frankfurt and Mainz the Darmstadt Institute of Applied Geosciences presented an exhibition entitled “Adventure Earth” at Frankfurt Airport which attracted more than 8.000 visitors, among them 90 school classes within two weeks.

A number of changes in the staff and some promotions have to be reported: In summer 2002 Dr. Rafael Ferreiro Mählmann, formerly Basel University (Switzerland),
was appointed as Professor for Technical Petrology as the successor of Professor Peter Blümel who retired in 2001. Following the suggestion of the Federal and state ministries the Department for Materials Science appointed the first “Juniorprofessor” Dr. Karsten Albe for the field of Materials Modelling in October. Three colleagues, Dr. Doru Lupascu, Dr. Achim Neubrand (both from the Ceramics Division) and Dr. Clemens Müller (Physical Metallurgy) obtained the degree of Habilitation. Professor Matthias Hinderer (Applied Sedimentology) received a call for a chair in geology at the University of Hannover and Dr. Edwin Kroke (Dispersive Solids) got an offer for a chair in Inorganic Chemistry at the University of Konstanz.

In 2002 15 PhD titles and 16 Diploma were awarded in Materials Science, 1 PhD and 3 Diploma in Geosciences and 10 students successfully finished their studies in Geography (7 Magister, 3 Lehramt). Fig. 2 shows a comparison of the graduates of the last three years. The number of first year students has still not been satisfying in both departments despite a slight increase (43 for Materials Science, 27 for Earth Sciences) compared to previous years.

![Graduates in Materials and Earth Sciences of the last three years](image)

The Institute of Applied Geosciences joined by Frankfurt University has been the host for the annual meeting of the group of sedimentology of the German geologists and attracted 250 scientists who came to Darmstadt to participate in lectures and various field trips. The continuous discussion to relocate Geosciences into the neighbourhood of Chemistry and Materials Science on the Lichtwiese makes future planning more difficult. As a definite decision is expected in 2003, this situation is not critical.

The annual MaWi-prize for the best diploma student has been awarded to Thomas Schulmeyer (Surface Science). Dr. Christina Roth (Structure Research) received the SHE-Award of the SHELL foundation. At the occasion of the 60th anniversary of the National University of Mongolia the title of “Honorary Professor” was awarded to Prof. Hartmut Fuess.

In conclusion the year 2002 has been extremely successful for both Departments of the Faculty.
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. Modelling and numerical simulation of casting, recrystallization, sintering, forging, 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. New methods for the quantitative description of microstructure and surface morphology are developed.

Current work deals with titanium, aluminium and magnesium based light alloys, steel, solders, precious and hard metals, superalloys, fibre strengthened aluminium, soldering alloys, 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, lead free solders, and functionally graded materials as well as improvements in the understanding of solidification, remelting, ion implantation, nucleation and recrystallisation.

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, Chemistry, Technical Mechanics and Physics, as well as with other universities in Germany (Kaiserslautern, Aachen, Chemnitz, Dortmund) and abroad (Australia, South Africa, India, Switzerland, France, The Netherlands and others) as well as with industry (Acheson, Adam Opel, Daimler-Chrysler, Degussa-Hüls, Heraeus, Hirschvogel, OMG/dmc2, 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

Influence of Stress State and Friction on Surface Modification and Damage during Sheet Forming (DFG, 1997-2002)


Crack Growth and Crack Closure in Functionally Graded Materials (DFG, 1998-2002)

Fatigue Strength of Magnesium Alloys (Adam Opel, Rüsselsheim, 1998-2002)

Characterization of Chip Formation at Short Time Loading during High Speed Cutting (DFG, 1998-2005)

Development of Lead Free Solders (ESEC, Cham, Switzerland and OMG, dmc2 division, Hanau, 1999-2002)

Recrystallization in Particle Reinforced Materials (AvH-Foundation, 2000-2002)

Storage and Permeability of Hydrogen in Metals (Daimler-Chrysler, Ulm, 2000-2003)

Partition Coefficients in Multicomponent Alloys (DAAD, 2000-2003)

Solutal Melting (DFG, 2002-2004)

Publications


Seshacharyulu, T.; Dutta, B.; Influence of prior deformation rate on the mechanism of $\beta$ to $\alpha+\beta$ transformation in Ti-6Al-4V, Scripta Mater. 46 (2002) 673-678.


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. Processing and especially sintering of oxides and metal/ceramic composites:
   Investigations on the rheological behaviour of nanocrystalline ceramic slips are geared towards an understanding of the processing windows these slips allow as compared to microcrystalline materials. Sintering of ceramics is also 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. Metal/ceramic composites are prepared for structural and functional applications, both using a powder metallurgical route and by gas pressure assisted metal infiltration into porous preforms. Materials under consideration are ZrO₂, Al₂O₃, CeO₂ 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. Recently, an additional focus was placed on microcracking coupled with efforts on finite element modelling and damage evolution on the grain size level. Materials under consideration are ZrO₂, Al₂O₃, Al₂TiO₅ and Al₂O₃/Cu.

3. Ferroelectric materials:
   Two scientific questions are of interest for this group. 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. Point defects are speculated to contribute to the electrical fatigue effect. In order to investigate the reduced domain – boundary mobility, acoustic emission is used for polycrystalline ceramics. In parallel, Barkhausen pulses and acoustic emission studies are performed on single crystals used as model systems. The second branch is concerned with mechanical properties of ferroelastic materials. Crack propagation depends on crack – and specimen geometry and is experimentally determined and correlated. These investigations consider both a thermodynamic crack equilibrium as well as subcritical crack growth. The process zone in ferroelastic materials is investigated using a liquid crystal display, an approach which was recently developed in our group. Besides mechanically loaded cracks, electrically driven cracks – as appearing in multilayer actuators -are also investigated. A strain incompatibility between electrically active and inactive material gives rise to the initiation and propagation of cracks at electrode edges. Electric cyclic loading without
any mechanical preload is also studied as it has been shown to provide a mechanical driving force for crack propagation also. Materials under consideration are PZT as well as PMN-PT.

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Research Projects

Coordination of core program “Graded Materials”, (DFG, 1995-2002)

Fracture toughness and crack propagation in graded materials (DFG, TU Karlsruhe, Dr. Fett, 1999-2002)

Formation and extension of single and multiple cracks in ferroelectrics due to electrical poling: experiment (DFG, TU Dresden, Dr. Bahr, 1999-2002)

Mechanical properties and fracture of metal-ceramic composites (DFG-SFB 298, TUD, Prof. Gross, 2000-2002)
Sintering of ceramic films (DFG, 2000-2003)

Electrical fatigue in actuators (DFG 2001-2003)

Crack growth in ferroelectrics driven by cyclic electric loading (DFG and NSFC, 2002-2004)

Defects in ferroelectrics (DFG, 2002-2003)


Processing and thermo-mechanical properties of AlN-Al matrix composites (Phase II) (VW-Foundation, Prof. Jayaram, Bangalore, India, 2002-2004)

Functional metal-ceramic composites (Freudenberg, 2002-2003)

**Publications**


Electronic Material Properties

The division *Electronic Materials* (ELMA) has been founded to introduce the aspect of functional materials and their properties into the Institute of Materials Science. 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 properties of organic semiconductors,
- Charge transport and polarization in organic dielectrics, and
- Photo- and photostimulated luminescence in inorganic phosphors.

In the field of organic semiconductors a worldwide interest exists in the use of organic semiconductors in novel electronic devices, such as displays and organic electrical circuits. An already commercialized application is a multicolor car radio display supplied by Pioneer Corporation consisting of vacuum-deposited layers of functional small organic molecules. Applications reaching further into the future will be simple organic circuits based on semiconducting polymers. These will be found in communication electronics such as circuits on chip cards, barcodes and maybe one day in an electronic newspaper where the information is continuously renewed via local area networks (LAN). The activities of ELMA are concerned with the characterization of organic materials properties. In this respect a set of experimental techniques for the evaluation of functional electronic properties are installed and will be refined in the future. Two major aspects are addressed: the first one is the detection and characterization of electronic traps in organic semiconductors and their correlation to charge transport properties, such as carrier mobility number of trapped charges, etc.. The second one is to understand the limits of electronic conduction in highly ordered and intentionally disordered organic semiconductors.

In the field of charge transport and polarization in organic dielectrics the necessary measuring equipment is presently installed. This includes poling equipment such as corona charging, and thermal charging under high electric fields as well as techniques to study the charge transport in dielectric films such as the pressure-pulse-step method to determine the spatial distribution. A thermally stimulated currents setup to investigate the energetic trap structure in dielectrics is already functioning. Also a high voltage switching equipment for ferroelectric polymers has been introduced which is able to apply up to 4000V in 150ns with poling currents as high as 60A. Presently investigations are directed towards the basic understanding of polarization buildup and stabilization in PVDF which is scientifically still under debate. Further a project on piezoelectric foams as a novel class of piezoelectric materials has been started.

The field of photo- and photostimulated luminescent materials (phosphors) is concerned with the synthesis and characterization of suited inorganic compounds. Such materials are utilized as wavelength converters in fluorescent lamps and in scintillating and information storing crystals. Challenges are the sensibilization of such phosphors in respect to the radiation energy under investigation which can range from ultraviolet to hard γ-rays or thermal neutrons. Present work is focussed on materials suitable for the detection of thermal neutron images as needed in
radioactive waste monitoring, medical treatments and neutron diffraction in materials science. Scientifically the energy transfer process from the absorption of thermal neutrons to the generation of photostimulable centers has to be understood and optimized. This does not only imply the optimization of the phosphors but also the optimization of the detecting layers in respect to spatial resolution and detection efficiency. Started is a new research topic in this field of quantum cutters. These are materials that emit two light-particles (photons) upon the absorption of one high energy photon. Such materials are foreseen to be essential components in future high efficiency energy saving lamps which will function without mercury and so have a low environmental impact.

In respect to teaching ELMA contributes to the topics of electronic properties of organic and inorganic materials. The understanding of electrical, optical, dielectric and magnetic properties of matter and their relation to structural properties such as crystalline and amorphous phases are the dominant tasks. The basic understanding is to give students the intellectual tools at hand to utilize the relation between function and structure to design special materials for special properties and applications.

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**Research Projects**

Development of Field Effect Transistors from Organic Thin Films (DFG, 2000-2002)

Impurities in Organic Semiconductors I (DFG, 2000-2003, Chemical Analysis)

Impurities in Organic Semiconductors II (DFG, 2000-2003, Chemical Analysis)

Improvement of Detective Quantum Efficiency of Neutron Image Plates (DFG, 2000-2003)

Piezoelectric sensor materials from porous polymers (AiF, 2000-2003, DKI)

Development of Neutron Image Plates (Forschungszentrum Jülich, 2000-2003)

Charge Storage and Piezoelectricity of Porous and Cellular Electret Films (VW-Stiftung, 2001-2004)

Development of Functional Polymers for Integrated Organic Circuits (PODOS), (BMBF Project with Siemens, 2001-2004)

Characterization of traps in organic semiconductors by Thermally Stimulated Current (TSC) (BMBF Project with Covion, 2001-2003)


Injectionlaser (EU-Project 2002-2004)

Interface alignment in organic field effect transistors (2002-2004)

Publications


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 and interfaces in cluster tools. The main research interest is directed to devices using novel polycrystalline compound semiconductors and interfaces between dissimilar materials. The perspectives of energy converting devices as e. g. solar cells are of special interest. In addition, the fundamental processes involved in chemical and electrochemical device engineering 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 semiconductors and ion conductors.

- **Van der Waals semiconductor heterojunctions and multilayers**
  The aim of this research activity is the testing and development of 2D-semiconductors (layered chalcogenides) for optoelectronic devices. In addition, van der Waals layers are investigated as passivating layers for 3D semiconductors and as buffer layers of lattice mismatched materials combinations. Furthermore the decisive factors, which govern the electronic properties of heterojunctions, are studied.

- **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 solar cells are to be characterized on a microscopic level to understand and to further improve the empirically based optimisation of solar cells.

- **Surface analysis**
  The UHV-surface science equipment and techniques using different and versatile integrated preparation chambers are 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 members 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**


Interfaces and inhomogeneities of polycrystalline CdTe thin film solar cells (BMBF, 1999-2002)


ZnO for Thin Film Solar cells; Materials and Interface Research (BMBF, 2001-2003)

Photovoltage optimization of II-VI compound thin film solar cells (BMBF, 2001-2004)
Silicon-organic pigment material hybrids for photovoltaic application (VW-Stiftung, 2002 – 2005)

Publications


Hunger, R.; Pettenkofer, Chr.; Scheer, R.; Dipole Formation and Band Alignment at the Si(111)/CuInS$_2$ Heterojunction; Journal of Applied Physics 91(10) (2002), 6560 – 6570.


Thin Films

The scientific program of the Thin Films Division combines the synthesis, the characterization with the determination of the properties and the theoretical modeling/simulation of nanostructured materials. Nanostructured materials with structural features in the nanometer range can be found in the form of clusters, thin films, multilayers and nanocrystalline materials often expressed by their dimensionality of 0, 1, 2 and 3. The ultimate goal of the research program is to achieve a better understanding of the fundamental atomistic processes and properties of materials which are dominated by grain boundaries and interfaces. In selecting the materials and the properties, the potential for technological applications is considered. 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 nanocrystalline materials. Most synthesis techniques are based on vapor phase processes such as Molecular Beam Epitaxy (MBE), Chemical Vapor Deposition (CVD) and DC- and RF- Magnetron Sputtering for thin films and multilayers and Chemical Vapor Synthesis (CVS) for clusters and nanocrystalline materials. The high quality and reproducibility of the materials are achieved by establishing clean conditions such as ultra-high vacuum environments, computer control of the synthesis parameter and in-situ analysis techniques such as Reflection High Energy Electron Diffraction (RHEED) or Aerosol Mass Spectrometry. The characterization of the materials is performed in part in collaboration with research groups in the Materials Science Department and other institutions using modern analytical methods. These include X-Ray Diffraction (XRD), High Resolution Scanning Electron Microscopy (HRSEM) and Transmission Electron Microscopy (HRTEM), Electron MicroProbe Analysis (EMPA), Secondary Ion Mass Spectroscopy (SIMS), Atomic Force and Scanning Tunneling Microscopy (AFM/STM), Mössbauer Spectroscopy (MS) and Depth-sensitive Conversion Electron Mössbauer Spectroscopy (DCEMS), Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Ion Scattering Spectroscopy (ISS), nitrogen adsorption and in cooperation with several national and international research facilities, e.g. Small Angle Neutron Scattering (SANS) and Extended X-ray Absorption Fine Structure (EXAFS). In addition, several accelerator facilities are used for ion beam analysis, such as Rutherford Backscattering Spectroscopy (RBS) or Nuclear Reaction Analysis (NRA), of thin film structures and nanocrystalline materials after ion implantation and ion beam modification. A wide range of optical, electronic, magnetic, mechanical and catalytic properties of these materials are investigated. For example, the giant and tunneling magnetoresistance effects (GMR, TMR) and atomic transport in multilayers and in nanocrystalline materials, have been studied intensively. An understanding of the atomistic processes can be deduced from the knowledge of the detailed microstructure and of the structure/property relationships leading to optimized engineering properties for applications. These include materials for resistive gas sensors based on semiconducting oxides, catalysts and calorimetric gas sensors based on noble metals on nanocrystalline oxides and motion sensors for automotive applications based on the GMR-effect in multilayers and granular thin films. Atomic scale computer simulations are in the focus of the materials modelling activities. The main tool is the Molecular Dynamics (MD) method. Large scale computer simulations of several million of atoms can be performed on the recently
installed 18-processor parallel cluster computer (DAMASCOS). The development of reactive analytical potentials allows the simulation of a variety of elemental and compound systems. Total energy calculations within the density functional theory are used for materials characterization, kinetic Monte-Carlo methods for studying materials processes on time scales, which are not accessible by the MD-method. In late 2002, the research efforts in atomistic simulations have been concentrated in an independent “Junior-Professorship - Materials Modelling”.

Besides the teaching of mandatory undergraduate and graduate courses, the Thin Films Division offers several elective courses for students of Materials Science, Physics, Chemistry and Engineering:

- Synthesis of novel high-technology materials;
- Modification and analysis of materials using ion beam techniques;
- Magnetic properties of novel nanostructured materials;
- Phase transformations in solids;
- Introduction to high resolution scanning electron microscopy.

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Research Projects

Local Structure of nano perowskites (DFG, 1999-2002)

Critical Behavior of FeBO$_3$-layers and particles close to the Néel-temperature (DFG 2001-2003)

Novel layered structures for fuel cells (DFG 2000-2002)

Designed synthesis of nanoparticles, conditioning and applications (DFG 2001-2002)

Functionalization and modification of nanoparticles in the gas phase (DFG 2002-2004)

Depth sensitive characterization of thin films by Mößbauer spectroscopy (DFG 2001-2002)

Synthesis and characterization of magnetic Fe-Pt nanoparticles and their self-organized two dimensional arrangement (DFG 2002-2003)

Atomistic computer simulation of elemental processes during gliding of grain boundaries (DFG 2001-2003)

Defect evolution, grain growth and phase transitions in nanocrystalline ceramics under heavy ion irradiation (GSI 2001-2004)


BMBF Project on transparent conducting nanocrystalline oxides (Klares Sigma) (BMBF 2000-2002)

BMBF Project on Magnetoelectronics (BMBF Bosch 1997-2002)

PPP-Finland - Project related exchange of personnel (DAAD 2002)

Innovatec – guest professorship for innovative studies at German universities, (DAAD 2002-2003)

Publications


Dispersive Solids

The research is based on the development of strategies for producing novel inorganic, oxidic, and non-oxidic materials. The main focus is the synthesis of ceramics with properties which exceed the present state of the art. Synthesis methods like the sol-gel-technology, polymer pyrolysis and chemical vapour deposition (CVD) are used and continuously further developed. Moreover molecular, oligomeric, and polymeric ceramic precursors as well as inorganic materials derived therefrom are synthesized and characterized. Further emphasis is put on the transformation of the precursors into ceramic components (for example layers, fibers, bulk materials, composites, membranes) and the characterization of their chemical and physical materials properties. The aim of our research activities is to correlate those properties with the composition and structure of the molecular precursors.

The present projects include the following four main topics: material synthesis, properties, modelling, and processing & applications.

In 2002 the group has organized or co-organized the following seminars, symposia and workshop:

- **DGM Hartstoffseminar, April, 2nd – 4th**
- Symposium Polymer Derived Ceramics, 104th Annual Meeting of the American Ceramic Society, St. Louis, April, 28th – May, 1st
- Symposium Structure and Properties of Advanced Nitrides and Electronic Nitrides, 104th Annual Meeting of the American Ceramic Society, St. Louis, April, 28th – May, 1st
- 1st International Workshop on *Spinel Nitrides and Related Materials* in Rüdesheim/Rhein, September, 1st – 5th

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- Dipl.-Ing. Marcus Schwarz
- Dipl.-Ing. Frank Hönack
- Dipl.-Ing. Wolfgang Völger
- Dipl.-Ing. Elisabeta Horvath-Bordon
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Dr. Mathilda Zemanova, University of Bratislava, Slowakei
B. Tech. Rajneesh Verma, Institute of Technology, Banaras Hindu University, India

Research Projects

High pressure synthesis of SiCN-materials (DeBeers, Johannesburg, South Africa, since 2000)

Electrical properties of precursor-derived ceramics in the system Si-O-C (Robert Bosch GmbH, Stuttgart, since 1996)

Precursorkeramik (DFG-SPP): Synthesis and high-temperature stability of amorphous ceramics in the system Si-B-C-N from polymeric preliminary stages and their application for carbon-fibres coatings about the fluid-coating-method (DFG, with Prof. Dr. U. Klingebiel, Inorganic Chemistry, Univ. Göttingen; Prof. Dr. R. Gadow, Fertigungstechnologie keramischer Bauteile, Univ. Stuttgart; Dr. H.-J. Kleebe, Materialforschung, Univ. Bayreuth, since 1997)


Precursorkeramik (DFG-SPP): Novel nitrogen rich ceramic materials in the binary system C/N (DFG, since 1997)

Precursorkeramik (DFG-SPP): Oxidation und corrosion of Si-(B)-C-N materials from polymeric precursors (DFG, Prof. Dr. K. G. Nickel, Mineralogy, Petrology & Geochemistry, Univ. Tübingen, since 1998)

Microstructure components for the information technology and more functional, high temperature stable sensors using preceramic polymer: Development of filled functionalized polysiloxane systems for the manufactur of microstructured ceramic prefabricated parts (Robert Bosch GmbH, Stuttgart, since 1999)

Hochtemperaturstabilität von polymerbasierter SiOC Keramik (Robert Bosch GmbH, Stuttgart, since 1999)

SiCO-ceramics with titanium containing fillers (since 1999)
Synthesis of novel materials and improvement of the properties for the application as nitrogen-oxid storing catalytic converters of modern fuel-injection engines (dmc², Degussa Metals Catalysts Cerdec, Hanau, since 2000)

Inorganic Membranes (JFCC, Nagoya, Japan)

Anorganic / organic hybrid materials and ceramics on the base of non-oxide carbodiimid-gels (DFG, since 2000)

Superhard materials (scientific technologic cooperation with South Africa, since 2000)

III-V-Group semiconductor materials (Merck, Darmstadt, since 2001)

PACVD-synthesis and characterisation of Si(B)CN hard material films for tribological applications (DFG, since 2001)

Nitridation of SiO₂-glass in order to increase its high temperature stability (since 2002)

Synthesis of Si₃N₄/SiC-nanocomposites from precursors prepared using a sol-gel process (since 2001)

Synthesis of novel nitrides of type A₃₋ₓBₓN₄ (A, B =Ti, Zr, Hf, C, Si, Pb; 0 < x < 3) in laser-heated diamond high-pressure anvil cell and their properties (DFG, since 2002)


Precursors for ternary wide band-gap semiconductors based on gallium nitride (Materials Department of the University of California, Santa Barbara, USA, April – October 2002)

Synthesis and thermal stability of ceramic materials in the quaternary system of Si-B-C-O (scholarship of the land Hessen, since Aug. 2002)

Correlation of pyrolysis parameter, gas mixture and property profile of ceramic composites (Robert Bosch GmbH, Stuttgart, since Oct. 2002)

Development of mechanical and oxidation resistant coatings for ceramic substrates (EADS, Munich, since Nov. 2002)


Development of ceramic oxidation resistant coatings for Ni-based-alloys (Alstom, Mannheim, since Nov. 2002)
Publications


Structure Research

The central activity of the Structure Research group is the study of the correlation between materials properties and the corresponding crystal structure. The detailed characterization of structure and nanomorphology at an interatomic length scale requires different types of radiation. Therefore a variety of diffraction and microscopic techniques have been established in our group. In this background almost any structural defect or any type of material has successfully been studied, ranging from crystalline samples and amorphous solids to surfaces and interfaces. In addition, we operate two powder diffractometers at large scale facilities; one dedicated for experiments with synchrotron radiation at the HASYLAB laboratory in Hamburg, the other for neutron diffraction at the research reactor FRM II in Munich.

Among the main objectives in structure research is the selective improvement of novel but also already industrially applied materials. In this context materials for heterogeneous catalysis are investigated and optimised by systematic analysis of the respective structure-property relationship. Simultaneously, magnetic materials and ionic conductors play an important part in current research activities. Materials under present investigation are anode catalysts in PEM and direct methanol fuel cells, magnetic alloys, as well as complex oxides and pigments in collaboration with Merck, Darmstadt. Together with OMG, Hanau, projects on three-way- and diesel catalysts are in progress.

The funding of the research activities is based on the infrastructure provided by the university. The actual projects are mainly supported by public science organisations (BMBF, DFG) and to a large extend by cooperations with industry. These joint ventures proved to be beneficial to both partners in the past.

The scientific staff is involved in basic teaching of the department’s curriculum and offers special courses in crystallography and X-ray diffraction. Additionally, more application-oriented topics, e.g. battery materials as well as spectroscopy and diffraction in applied catalysis, are presented in lectures.

Staff Members

<table>
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<tr>
<th>Head</th>
<th>Prof. Dr. Hartmut Fueß</th>
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Prof. Dr. Michiyoshi Tanaka, Tohoku Univ. Sendai, Japan (Humboldt-prize)
Prof. Dr. Vytautas Balevicius, Univ. Vilnius, Litauen

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Prof. Dr. Roman Boča, Univ. of Bratislava, Slovakian Republic
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Prof. Dr. Delegiin Sangaa, National Univ. Ulaan Batar, Mongolia
Dr. Mustafa Öksüzoglu, Selcuk Univ. Konya, Turkey

Research Projects
Resonant and high-resolution powder diffraction on polycrystalline materials at
HASYLAB in Hamburg (BMBF, 2001-2004)

Ternary rare-earth rhenium oxides (DFG, 1998-2002)

Ternary rhenium oxides with alkaline-earth metals (BMBF, 1998-2002)

Chemical composition, nanomorphology and electrolytic activity of catalytic materials
for direct methanol fuel cells (DFG, 1998-2004)

Design and realisation of a neutron powder diffractometer at the FRM-II at TUM in
Garching (BMBF, 1998-2004)
Inelastic neutron scattering investigation of lattice dynamics in nitrided metals (BMBF, 2000-2003)

Research and development of catalysts for engines operated with diesel fuels (DMC2, 2000-2003)

Ion traces in polymers (GSI, 1998-2002)

Ion traces in insulators (GSI, 2001-2004)

Development of novel interference pigment materials (Merck, 1999-2002)

Function and dynamics of oxygen in Mo / V mixed oxides catalytic materials for partial oxidation of aldehydes (DFG in collaboration with Prof. Dr. H. Vogel, TUD and Prof. Dr. M. Martin, RWTH-Aachen, 2000-2004)

Design and investigation of new oxygen storage systems to be used in three-way-catalysts (OMG, 2001-2004)

Structural characterization of silicon monoxide SiO (DFG, 2000-2003)

Lattice dynamics of superionic copper selenide (DFG, 2001-2003)

In-situ studies of intercalation batteries (DAAD, 2002-2003, with the Universidad San Pablo, Madrid, Spain)

Oxygen conductivity in rare earth / lanthanum - gallium oxides (DAAD, 2001/2002 with the Univ. of Lviv, Ukraine)

Correlation between properties and structure in niobates (1999-2002)

Publications

Atakol, O.; Nazir, H.; Durmus, Z.; Svoboda, I.; Fuess, H.; Crystal structure of a symmetrical heterotrinuclear Ni$^{	ext{II}}$-Mn$^{	ext{II}}$-Ni$^{	ext{II}}$ complex: Bis(\(\text{N,N}'\)-dimethylformamide)(\(\mu\)-acetato) \(\mu\)-\(\text{N,N}'\)-bis(salicylidene)-2-hydroxy-1,3-propanediamine) nickel(II))manganese(II), Analyt. Sci. 18 (2002) 493-494.


Ehrenberg, H.; Dinçer, I.; Elmali, A.; Elerman, Y.; Fuess, H.; Magnetic and crystal structure correlations in PrMn$_{1.5}$Co$_{0.5}$Ge$_2$: a synchrotron diffraction study, Solid State Comm. 124 (2002) 429-432.


Ellouze, M.; Boujelben, W.; Cheikhrouhou, A.; Fuess, H.; Madar, R.; Vacancy effects on the crystallographic and magnetic properties in lacunar Pr$_{0.7}$Ba$_{0.3-x}$MnO$_3$ oxides, Solid State Comm. 124 (2002) 125-130.


Chemical Analytics

We are active in the following fields:

- **Corrosion phenomena**
  - High temperature corrosion of iron- and nickel-based PM-ODS superalloys
  - Corrosion of graphite tube assemblies in atomic absorption spectrometry
  - Corrosion of metals in polymer technology
  - Corrosion of vessel materials for ultratrace analysis
  - Corrosion of medieval glasses

- **PM-technology**
  - Investigations of the reduction process of MoO$_3$ by hydrogen
  - Surface chemistry of water atomized aluminium alloy powders
  - Effect of trace impurities in hard metals

- **Particle characterization**
  - Single particle characterization mainly by electron probe methods of
    - environmental particles
    - industrial aerosols for occupational health evaluation
    - wear particles in polymer technology (in co-operation with the DKI)
    - Diesel soot from Otto- and Diesel-engines (Prof. Hohenberg, Department of Mechanical Engineering)

- **Process analytics**
  - Development of a fast and simple method for the determination of toxic metal traces in industrial waste waters
  - Fast materials identification by X-ray fluorescence analysis including the Compton scattering and statistical principal component analysis (Merck, Darmstadt)

- **Analytical methods development**
  - Development of a portable µ-XRS with polycapillary optics and drift chamber detector for cultural and forensic applications

- **Wear studies**
  - Study of the wear process of cutting of compacted graphite iron used for high compression Diesel motors (Production Engineering and Machine Tools, Department of Mechanical Engineering)

- **Activation analytical techniques**
  - Particle induced gamma-ray emission, charged particle activation analysis and neutron activation analysis techniques for the determination of fluorine, boron and of other elements in human bone samples (IAEA Vienna)
Staff members

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Dipl.-Ing. Jamila Saroukh

Student
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Gunther Kraft
Selma Temiz

Research Projects

Quantification of wear in extruders for polymer production by continuous and time-resolved x-ray fluorescence analysis (AIF, Deutsches Kunststoffinstitut, 2000 – 2002)

Analytical investigations on graphite corrosion in electrothermal atomic absorption spectrometry (in co-operation with the Institute for Analytical Chemistry, University of Warsaw and the Department of Chemistry, Federal University of Santa Catarina, Florianopolis, Brazil, since 1996)

Single particle characterization of industrial aerosols for occupational health evaluation (National Institute of Occupational Health, Oslo, since 1998)

Investigations of the wear of cutting tools on the basis of cubic boron nitride during machining of cast iron with vermicular graphite (co-operation with the Institute of Production Engineering and Machine Tools, Faculty of Mechanical Engineering of the Darmstadt University of Technology and SinterCast Inc., Clarkston, U.S.A., since 2000)

Bulk- and topochemical investigations of trace contaminations in organic semiconductor materials (DFG, 1999 – 2003, in co-operation with the group for electronic properties of materials in our department)
Determination of the morphology, size distribution, elemental and phase composition of particles from various sources (BMBF, 1998 – 2002)

Particle induced gamma-ray emission, charged particle activation analysis and neutron activation analysis techniques for the determination of F, Cu, Zn, B and other elements in human bone samples (IAEA Vienna, 2001 – 2002)

Solid sampling analytics with atomic absorption spectrometry and laser ablation ICP-OES (E. Merck KGaA, Analytical Research, 2001 – 2002)

Publications


Hoffmann, P.; Chemisch-Analytische Untersuchungen an technischen Produkten aus der mittelalterlichen Dorfwüstung Holzheim. Holzheim bei Fritzlar (Hrsg. N. Wand); Verlag Marie Leidorf, Rahden/Westf., 511-525 (2002).


Theoretical Materials Science

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 which already exist and to guide the design of new materials with properties, or behaviour, required in future engineering applications.

Modelling transition metals and related alloys, high-temperature superconductors and organic dielectrics lies at the heart of current activities. For the first 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 the intense proton beam. 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. For the second class of materials, typified by $YBa_2Cu_3O_7$ and $Bi_2Sr_2Ca_2Cu_{3}O_{10}$ 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 defects. 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. Finally, for the third class of materials, represented by $Alq_3$, emphasis is on real-time modelling of the charge transfer by injected carriers and thermally stimulated luminescence phenomena with the aim of extracting, in conjunction with experiments, information about the electronic structure of inherent traps, thereby assisting technological exploitation and further materials development. The theories underlying these investigations range from microscopic to macroscopic; their realization employs analytical as well as computational techniques.

Staff Members

Research Associate Dr. Yuri A. Genenko
Secretary N.N.
Research Projects

Electrodynamics of macroscopic magnet/superconductor heterosystems (DFG, 2002-2005)

Dynamic modelling of the charge transfer in organic semiconductors and ionic conductors (SFB Electrical fatigue in functional materials, 2002-2006, with Prof. Dr. H. v. Seggern, TUD)

Publications


Materials Modelling

In November 2002 the Materials Modelling group was started as a new research division within the Institute of Materials Science. The research activities are directed towards the investigation of materials properties and structure formation processes. Our main tool are atomic scale computer simulations. In doing so we are combining a variety of methods depending on the time and length scales involved in the corresponding problem. Quantum mechanical calculations based on density-functional theory are used for investigations of structural and electronic properties, while large-scale molecular dynamics with analytical interatomic potentials are the main tool for studying far-from-equilibrium materials processes. Additionally, kinetic Monte-Carlo simulations and cellular automatons are the methods of choice for problems on extended time scales. Our computer equipment consists of a cluster of desktop machines and a dedicated 18-processor parallel cluster. A new 32-processor machine for scientific computing is currently under construction.

The main research areas are:
- Development of realistic interatomic potentials for compound systems with mixed chemical interaction including ionic systems
- Simulation of gas phase condensation by combined MD-KMC methods.
- Simulation of thin film growth of multilayer systems and superhard materials
- Simulation of materials processes induced by ion-beam irradiation
- Investigation of mechanical properties of nanocrystalline structures

The Materials Modelling group is currently offering a 2-semester course on atomic scale materials simulations.

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Janne Nord, M.Sc; University of Helsinki, Finland
Dr. Emppu Salonen; University of Helsinki, Finland
Jonas Frantz, M.Sc.; University of Helsinki, Finland
Research Projects

Molecular dynamics simulations of atomic processes during interface gliding (DFG 2002-2003)

Atomistic studies of processes far from equilibrium (DAAD, PPP Finland, 2001-2003)

Publications


Development of Pb-free Solders for Power Semiconductor Packaging

P. Lambracht, M. Rettenmayr, B. Kempf

The replacement of Pb in electronic devices is motivated by environmental concerns: the widespread distribution of small amounts of Pb in consumer products and the contamination of landfills is a significant problem. For Pb-containing solders in the melting range below 200°C a number of alternatives is available on the basis of Sn. Imminent legal regulations and consumer pressure stimulated a project on the development of alloys that meet the criteria for soft solders in the higher temperature range (die-attach applications, see Fig. 1). Currently about 150tons/year of Pb-rich solders are used for die-attach, most of it as solder wire or ribbon.

As the die-attach is done in highly sophisticated, fully automated production lines, the Pb-free solder should be directly applicable in existing soft solder die bond equipment, i.e. avoid further investment in new system modules, or any change in the production process of electronic devices, in order to find acceptance by the appliers. Therefore, the requirements for a replacement alloy are: (i) a melting range between 260°C and 420°C, as higher liquidus temperatures could cause damage of the chip in the production process, and lower solidus temperatures would lead to (partial) remelting at later production steps; (ii) the alloy should be free of toxic elements; (iii) it must be manufacturable in form of wire; (iv) it should be “better than Pb” in terms of wettability, ductility and thermal reliability of a soldered bond, and “better than Sn” that upon alloying becomes brittle and difficult to handle.

Starting from an alloy listing with approx. 150 alloys and based on criteria that were provided from two industrial partners (solder wire producer and solder applier), computer aided development was employed to carefully select a limited number of experiments. Thus, the number of potential candidates was reduced sequentially until a class of alloys was defined that could be produced as solder wire and features the properties that are required for the die-attach application.
We started the alloy development with an alloy listing of potential candidates. Based on their non-toxic properties different binary to quaternary alloys on the basis of Al, Mg, Bi, Ag, Sn and Zn were chosen for further evaluation. The alloys were first characterized in terms of melting range using thermodynamic software, supported by DTA measurements where the extrapolation techniques appeared to be insufficiently accurate. The mechanical properties were tested in compression tests. The selection criterion for potential candidates was the comparison with the deformation behavior of a commercial alloy (Sn-Ag25-Sb10), because of its critical deformability. In a next evaluation step the alloys were extruded to wires. In parallel to the mechanical tests the wetting behavior on Cu, Ni and Ag substrates was investigated (Fig. 2).

![Fig. 2: Wetting behaviour of alloy Bi-2.6Ag on a Ni-substrate](image1)

![Fig. 3: Microstructure of alloy Bi-12Ag with primary dendritic Ag-phase (white) and interdendritic eutectic](image2)

The alloys that passed the series of tests were based on Bi-Ag (Fig. 3), with further minor additions. This was surprising inasmuch as generally in the literature it is stated that “Bi-based alloys are unsuitable for soldering purposes”. Apparently, modern development tools and optimized production procedures could overcome the difficulties in contrast to such statements.

The reliability of the Bi-Ag alloys was tested under application conditions with equipment and parameters used in technical applications. The newly developed solder equals or surpasses the properties of the traditional Pb solders. The tentative exception for Pb-rich solders in the upcoming legal regulation about the application of Pb because of the absence of a technical solution appears thus to be obsolete.
Sintering stresses and Sintering Viscosities

R. Zuo, E. Aulbach and J. Rödel

Both the sintering stresses and the sintering viscosities are key functions to understand and predict sintering of thin films and of layered structures. Both of them can be functions of sintering temperature, grain size, relative density and so on. Experimental determination of both parameters becomes necessary considering that theoretical research has been carried out extensively, predicting different functional dependences on relative density.

Hot forging experiments have been considered as a standard procedure to experimentally determine these two parameters based on the viscoelastic analogue of the stresses and the strain rates. In this case, a uniaxial load is employed during isothermal sintering so that concurrent creep deformation and sintering densification can be measured in radial and axial directions of a cylindrical sample. In our group a loading dilatometer assisted by two high-resolution lasers has been recently developed and applied for experimental research on ceramic oxides and low temperature cofired ceramics (LTCC) materials. A schematic of this apparatus is shown in Fig. 1. A constant uniaxial compressive load can be activated whenever the required density is achieved so that a continuous or discontinuous (intermittent) hot forging experiment can be performed.

![A schematic of a loading dilatometer](image)

In this study, high purity Al₂O₃ powder with grain size of about 200nm was made into cylinders by first conventional uniaxial pressing and then cold-isostatic pressing. The experiments were performed at 1250°C under different uniaxial compressive loads ranging from 0N to 700N. Our preliminary experimental results found that the anisotropy of microstructure (preferred pore orientation along z-axis) and the discrepancy of grain size occurred between freely sintered and hot forged samples with the same density, which are, however, strictly required in the analysis using this approach. It was considered that the effect of uniaxial loads on the microstructure has challenged this experimental approach.
Recently, a discontinuous hot forging technique was developed where the sample is first allowed to sinter freely to prescribed densities, then the uniaxial load is applied and the instantaneous radial and axial strains measured. The experiments were performed under different loads starting from varying starting densities. Using the linear response of the axial strain rates to the applied compressive stresses, the sintering stresses and the sintering viscosities can be measured, as plotted in Fig. 2 and Fig. 3. As seen from Fig. 2(a) and Fig. 3(a), the biased microstructure caused by uniaxial loads can be avoided by intermittently applying a load, which was reflected in the dependence of the as-measured values on the loading procedures. The longer the load was applied, the more serious the anisotropy of microstructure tends to be and the smaller the grain size is, due to the shortened sintering time. The reported experimental result could be the best experimental determination so far. The technique is being further employed for determining the viscous Poisson’s coefficient.
Photo-stimulated luminescence of calcium co-doped BaFBr:Eu$^{2+}$ x-ray storage phosphors

M. Schlapp, E. Bulur and H. von Seggern

Storage phosphors provide a means for two-dimensional position-sensitive detection of x-rays when used in image plates. The phosphor with the best storage and read-out properties known today is Eu$^{2+}$ doped BaFBr. During x-ray irradiation electrons and holes are created and stored separately at different trap sites thereby forming a latent image of the applied x-ray exposure. Upon stimulation with visible light, the electrons are liberated from their traps and recombine with the holes. The recombination energy is transferred to the activator ion Eu$^{2+}$ that emits the characteristic 4f5d emission at 390 nm, called photo-stimulated luminescence (PSL). The spectral dependence of the PSL is mainly determined by the spectral dependence of the absorption cross-section of the electrons in their traps which are called colour centres (F-centres). In BaFBr: Eu$^{2+}$ two basic types of colour centres have been reported, the fluorine vacancy based F(F$^-$)-centres and the bromine vacancy based F(Br$^-$)-centres. Although the stimulation maxima of the F(Br$^-$)-centres at 590 and 495 nm are substantially red-shifted compared to F(F$^-$) centres at 470 nm, practical requirements would still favour an even more red-shifted PSL spectrum in order to match the wavelengths of practically used HeNe lasers or semiconductor laser-diodes. In this work the optical properties of the F-centres in calcium co-doped BaFBr:Eu$^{2+}$ are investigated in more detail and are compared to non-doped BaFBr:Eu$^{2+}$.

The PSL spectrum of a sample without Ca co-doping exhibits the typical double peak structure of F(Br$^-$)-colour centres slightly disturbed by F(F$^-$)-centres which can be expected in the UV part of the spectrum. In samples with increasing Ca content no strong shift in the stimulation maxima compared to the BaFBr:Eu$^{2+}$ sample was observed. However, broadening of the PSL spectra transforming from the double-peak spectrum of BaFBr towards a single broad almost featureless peak which extends more to the long wavelength side as calcium concentration increases is a striking observation to be noted. Measuring the PSL before and after bleaching at certain wavelength and using the known spectral dependencies of F(Br$^-$) and F(F$^-$)-centres to fit the difference plot, it was possible to show that the broadening is due to a new type of colour centre with maximum stimulabilities at 670 and 540 nm. The symmetry of the new centre seems to be the same as that of the F(Br$^-$)-centre. It is therefore probable that the here obtained F-centre is a disturbed $F_A(Br^-, Ca^{2+})$-centre related to the Ca-doping, since the magnitude of these centres depends on
the Ca-concentration. An interesting feature to notice is that although the sample contains only 0.5 mol% Ca, nearly half of the colour centres are perturbed. This tendency increases even more with higher calcium co-doping and is due to an easier formation of storage defects at the already existing lattice distortions around calcium ions situated on barium lattice sites.

The observed red shift of the F(\text{Br}^-,\text{Ca}^{2+})-centre when compared to a F(\text{Br}^-)-centre is related to an increase in size of the anion vacancy resulting from the replacement of the larger barium ion by the smaller calcium ion. A correlation between defect size “a” and the stimulation energy $E$ of the electron is given by the Mollwo-Ivey relation which is based on the particle-in-a-box model.

In order to measure the optical absorption cross-sections of the colour centres, the method of linearly modulated photo-stimulated luminescence (LM-PSL) was applied to BaFBr for the first time. The method is based on the linear enhancement of the stimulation light intensity from zero to a value $I_{\text{max}}$ and results in a peak shaped luminescence curve rather than a decay curve with time obtained from stimulation with a constant intensity. The parameters of the LM-PSL curve for monomolecular kinetics are related to physical properties of the phosphor and the luminescence intensity in the following way:

$$L(t) = \sum N_i \sigma_i I_{\text{max}} \frac{t}{P} \exp \left[ -\frac{\sigma_i I_{\text{max}} t^2}{2P} \right]$$

where $N_i$ and $\sigma_i$ are the numbers and optical absorption cross-sections of the F-centre of type $i$, $I_{\text{max}}$ the maximum exciting light intensity, $t$ the exposure time and $P$ the time interval to ramp the light intensity from zero to $I_{\text{max}}$. Fitting the $L(t)$ curve to the experimental results allows one to determine the essential parameters of the involved F-centres, namely the absorption cross-sections and the number of involved centres.

Eq.1 was fitted to the LM-PSL curves of Fig. 2. It turned out that the assumption of three F-centre types was sufficient to quantitatively describe the measured results. Inset to Fig. 2 displays an example of a comparison of an original LM-PSL curve (0.5 mol\% Ca) at 590 nm with the fit by Eq.1. In addition, the calculated LM-PSL curves of the three delete F-centres are displayed. Measuring in addition the light intensity $I_0$ one can determine the optical cross sections $\sigma_i$. One can recognise from the involved F-centres that at 590 nm the PSL centre related to the F(\text{Br}^-)-centre is the fastest bleaching component. When stimulating at 780 nm one realises that the fastest component is due to F_\text{A}(\text{Br}^-,\text{Ca}^{2+})-centres.
The influence of chain alignment on the field-effect mobility of polyhexylthiophene based transistors


Polymeric functional materials indicate a great potential for low cost electronic devices. The most important element of such devices is the field-effect transistor whose performance strongly depends on the achieved field-effect mobilities. The secret of such high mobilities is the molecular order and hence the global alignment of molecules or polymer chains in the charge transport channel. This work reports on the influence of mechanically aligned regioregular head-to-tail coupled poly (3-hexylthiophene) P3HT films on the transport properties of a bottom gate organic field effect transistor. Alignment properties of treated P3HT films are investigated utilizing polarized absorbance measurements. These results will be directly correlated to field effect mobilities of equally treated P3HT films.

In order to be able to perform the optical studies, 20nm thick P3HT films were coated on quartz substrates. Polarization dependent transmission spectra for virgin spin-coated films show isotropic behavior, which is shown in the inset of Fig. 1. No dichroism was observed. Rubbing the active layer about ten times at a temperature of 100°C with a piece of velvet results in a considerable difference in amplitude and spectral shape of the absorbance for light polarized parallel to the rubbing direction (0°) compared to light polarized perpendicular to the rubbing direction (90°) (see Fig.1). After a subsequent heat treatment at 100°C for a period of one hour without rubbing a further increase in the dichroic ratio was observed. A dichroic ratio for the two polarization directions of 5.1 at a wavelength of 557nm was achieved.

In order to study the effect of alignment of the polymer chains on the transport properties two identical transistors with 20nm thick films of P3HT were fabricated. The P3HT film was spin coated on the substrate followed by an annealing step in a glove box. Thereafter both transistors were rubbed at 100°C in one process to ensure that both devices are exposed to the same rubbing pressure. One of the transistors was rubbed perpendicular to the source-drain contacts and the other parallel to the source-drain contacts whereby the perpendicular direction is equivalent to the charge transport direction in the field-effect transistor. The output and transfer characteristics for the parallel rubbed transistor (T1) are displayed in Fig. 2. In both cases the output characteristics for $V_G=-40V$ and the transfer characteristics for $V_{DS}=-40V$ are depicted. In the output and transfer characteristics the ID drops substantially due to the rubbing process. As in the case of the optical measurements the transistor was annealed a second time for one hour at 100°C. The resulting characteristics are also depicted in Fig. 2. They show a small rise due to the additional annealing step. After the rubbing process the mobility has dropped by a
factor of 17 and increases by a factor of less than 2 due to the annealing procedure. The transistor (T2) rubbed perpendicular to the source-drain electrodes shows a large increase of the source-drain current ID due to the rubbing procedure (see also Fig. 2). The field-effect mobility increases by a factor of nearly 4 from $2.20 \times 10^{-4}\text{cm}^2/\text{Vs}$ to $8.25 \times 10^{-4}\text{cm}^2/\text{Vs}$. After annealing at $100^\circ\text{C}$ for one hour a further significant mobility improvement to $1.78 \times 10^{-3}\text{cm}^2/\text{Vs}$ was observed, so that the overall improvement due to rubbing and annealing amounts to more than 800%. The observed mobility improvements due to rubbing seem to be easily understood. After rubbing in the charge carrier transport direction the polymer backbones are more orientated perpendicular to the source-drain contacts and therefore fewer barriers to neighboring molecules have to be overcome. The annealing induced improvements can be explained by further increased alignment or ordering close to the insulator interface induced by the aligned molecules on the rubbed surface, which agrees with the optical studies. On the other hand the observed decrease in case of rubbing parallel to the source-drain contacts can have different reasons: First, if the rubbing direction is parallel to the source drain contacts the polymer backbones are forced to arrange in the rubbing direction so that the side chains may be aligned in the charge transport direction and act as large tunnel barriers for the charge transport. Second, cracks in the polymer layer caused by the rubbing procedure may interrupt conduction in the channel.

![Fig. 2: Output (a) and transfer characteristics (b) of a P3HT transistor for $V_G = -40\text{V}$ or $V_{DS} = -40\text{V}$, respectively. The virgin transistor as well as the same transistor rubbed before and after annealing is displayed. (a) and (b) show the transistor rubbed parallel to source drain contacts and (c) and (d) the transistor rubbed perpendicular to source drain contacts.](image-url)
Commissioning of the Solid/Liquid Analysis System
SoLiAS at BESSY

R. Hunger, M. Lebedev, Th. Mayer, W. Jaegermann

The SoLiAS experimental station at BESSY is a versatile preparation system dedicated to the investigation of solid/liquid interfaces with synchrotron radiation induced photoelectron spectroscopy SXPS. During 2002 the system was installed at BESSY and successfully commissioned at beamlines TGM 7 and U49/2. With the SPECS Phoibos 150 analyser an overall resolution below 200 meV is reached (Fig. 1). The Phoibos 150 is retractable allowing free rotation of a VG ADES 500 ARUPS analyser installed in addition. In order to adapt the station to various beamlines it can be inclined horizontally versus its frame by 7°.

![Fig. 1: Uncorrected width of Ag Fermi edge at RT measured with the Phoibos 150 analyser at beamline U49/2 with pinhole 1mm x 1mm. 1st harmonic red, 3rd harmonic blue.](image)

The UHV analysis of solid/liquid interfaces may be performed with SoLiAS via three complementary routes:

i) synthesis of a model electrolyte in vacuo by coadsorption of solvent and redox species onto LN₂ cooled sample surfaces,

ii) emersion of a specimen from a liquid electrolyte and transfer to vacuum under inert (N₂) atmosphere,

iii) creation of frozen electrolytes by cooling emersed samples before pumping to UHV conditions.

Interface engineering by means of electrochemical processes is of great technological importance. For the analysis of solid/solid interfaces SoLiAS is equipped in addition with

iv) vacuum preparation facilities for heat treatment, sputtering, or PVD/CVD of contact materials.

Thus by ii) SoLiAS allows to analyse surfaces after technologically relevant wet preparation processes like etching, electrochemical oxidation and reduction, or electrodeposition of contact materials. While wet chemical processes may be complex reaction sequences and ii) allows for the analysis of a final situation only, emersion experiments may be complemented by adsorption experiments i). By adsorption the interaction of a defined single electrolyte species with a surface may
be investigated, by coadsorption of solvent and redox species the cooperative interaction with a specimen is accessible and may provide insight into intermediate reaction steps. Furthermore the interaction of the solvent and an electrolyte species may be investigated by coadsorbing electrolyte constituents on inert surfaces. Cooling of the sample before evacuation iii) allows to analyse soluble and volatile reaction products. In addition iii) allows to measure the occupied electron states of real, albeit frozen, electrolytes. Not only the impact of wet chemical processes on interface formation may be analyzed by UHV deposition iv), but also a comparison of wet chemically produced interfaces to vacuum deposited interfaces may be drawn. The unique combination of integrated preparation options of SoLiAS is complemented by a fast entry load lock permitting high flexibility in sample usage.

While the data of the cited references were taken at different experimental systems with one of i)-iv) preparation facilities temporarily in use at a beamtime, all four are now permanently available at the same time. The presented data of fig. 1 to 5 were actually taken with SoLiAS, exemplifying its versatility. LN$_2$ cooled transfer between adsorption chamber and analysis chamber is demonstrated by H$_2$O adsorption onto a vacuum cleaved WSe$_2$ single crystal. Fig.2 shows the valence band emissions of orbitals 1b$_2$, 3a$_1$, and 1b$_1$, the fingerprint of molecularly adsorbed water. The spectra were taken with a photon energy of $h\nu=30$ eV at beamline TGM7.

![Fig. 2: Valence band spectra of H$_2$O adsorption on a LN$_2$ cooled WSe$_2$ crystal. The emissions 1b$_2$, 3a$_1$, and 1b$_1$ indicate molecular adsorption. Spectra taken at beamline TGM7.](image)

SPS on emersed samples is demonstrated by etching off the natural oxide of a GaAs (100) wafer surface in a solution of 3% HCl in water. The As and Ga 3d core level spectra of Fig.3a and b were taken at the TGM7 with highest surface sensitivity. The etched surface is covered with a layer of elementary As and As-H. Some remnants of intermediate AsCl and GaCl reaction products are found which can be rinsed off by deionized water as we have shown before.
Electrochemistry on defined vacuum-prepared surfaces immersed and emersed under clean N\textsubscript{2} atmosphere without contact to ambient air is demonstrated by a GaAs (100) surface vacuum cleaned by sputter-anneal cycles. Detailed comparison of the surface composition after contact to the solvents water or isopropanol is shown. In January 2003 also the freezing in of volatile reaction products (AsCl\textsubscript{3}) by cooling of an emersed GaAs electrode etched in HCl could be demonstrated.

The SoLiAS project is financed through BMBF 05 KS1RD / 0
The interface between Cu(In,Ga)Se₂ (CIGS) and CdS is crucial for the performance of CIGS thin film solar cells. Cu deficient ordered defect compounds (e.g. CuIn₃Se₅, CuIn₅Se₈) exist at the CIGS surfaces and interdiffusion is known for the interface. The impact of these phenomena on interface band alignment and interface charge distribution is not clear. Furthermore, the outstanding cell performance with CdS buffer layers, in comparison to other buffer layer materials, is also not resolved. We have performed systematic studies of interface formation between Cu(In,Ga)Se₂ and II-VI semiconductors CdX and ZnX (X= S, Se, Te) using in-situ photoelectron spectroscopy.

The experiments were performed using polycrystalline Cu(In,Ga)Se₂ thin films deposited with slightly Cu-poor stoichiometry onto Mo coated glass substrates. Typically 13% energy conversion efficiencies are obtained at the ZSW with these films. After deposition the samples were cooled down and covered with a Se layer in the deposition chamber. After transfer to the integrated surface analysis and preparation system at the TU Darmstadt, the Se layers were heated off. Heating was performed in ultra-high vacuum environment by applying a current through the Mo film, which has the advantage of only little pressure rise during this decapping procedure. After decapping the surfaces are free of oxides, which is evident from the X-ray photoelectron spectroscopy and from the clear signature of CIGS valence bands determined using ultraviolet photoelectron spectroscopy (Fig. 1). Using the sensitivity factors of our photoelectron spectrometer we determine a composition of the surface corresponding to the 135 ordered defect compound (CuIn₃Se₅).

Fig. 1: (left) XP spectra of a selenium cap on a CIGS surface and a clean CIGS surface after removing the selenium cap by a temperature treatment in UHV. (right) UP spectrum of a decapped CIGS surface.
We have further studied the interface formation of II-VI semiconductors, which were deposited onto the decapped surfaces. The II-VI compounds were deposited by thermal evaporation in a deposition chamber, which is directly connected to the photoelectron spectrometer. Our spectra obtained in dependence on II-VI thickness give no evidence for chemical interface reactions. The experimentally valence band offsets are shown in Fig. 2.

![Figure 2: Experimentally determined valence band offsets of different II/VI semiconductors on CIGS. For comparison, the theoretical calculated valence band offsets of different CIGS surface formations are additionally displayed.](image)

Figure 2 also includes theoretical valence band offsets calculated by the group of A. Zunger. Different offsets are expected depending on the CIGS surface composition. This is due to the interaction of the Cu 3d with the Se 4p states, which results in an upward shift of the valence band maximum in the CIGS compound. This shift is less strong for the Cu deficient surface phases. The valence band offsets expected for the stoichiometric 112 and the Cu deficient 135 and 158 phases are indicated in Fig. 2.

The experimental valence band offsets are all very close to the calculated values, indicating transitivity of the band offsets. However, not all of the offsets agree with the values calculated for the 135 surface composition of our films. In addition, the experimental offsets are all very close to those determined for single crystalline CIGS substrates, which are expected to have a non Cu deficient 112 composition. The agreement between the offsets determined for the decapped Cu deficient surfaces and the single crystal surfaces is in direct contradiction to the theoretical prediction. This might be due to some interface modification of, so far, unknown origin. However, as it has been observed that a Cu deficient surface is formed on CIGS single crystals during interface formation, this result might also indicate, that the interfaces formed on single crystals are effectively the same as those formed on Cu deficient surfaces. Further experiment will clarify this.

We have demonstrated how a combination of state-of-the-art solar cell film deposition and in-situ photoemission studies give access to systematic studies of relevant electronic interface properties.
In the last years, the development of thin film rechargeable batteries has attracted a great deal of interest due to their reduced resistivity with respect to bulk materials, and due to the technological perspectives of integration with other thin film devices as rechargeable power supplies for implantable medical devices, CMOS-based integrated circuits, as well as smart IC packages or chips. The transition metal oxides, especially vanadium pentoxide ($\text{V}_2\text{O}_5$), are considered to be interesting materials for such technological applications. In this work the $\text{V}_2\text{O}_5$ films are deposited onto highly oriented pyrolytic graphite crystals by physical vapour deposition. Onto this substrate the Na intercalate has been deposited from commercial Na dispensers (SAES Getters). The intercalation happens instantaneously at room temperature.

In Fig. 1 XP spectra of the Na exposed $\text{V}_2\text{O}_5$ films are shown for different Na exposure times $t_{\text{D,Na}}$. The O1s spectra show a significant change for $t_{\text{D,Na}}>120\text{s}$. The O1s component at higher binding energies appears due to the formation of Na oxide and Na peroxide on the surface. For $t_{\text{D,Na}}<120\text{s}$ the V2p signal shows the V$^{5+}$ to V$^{4+}$ reduction of the V ions due to the Na to V charge transfer during intercalation. The V$^{4+}$ component is shifted by about 1.1eV to smaller binding energies. These oxidation states are only formal valencies in a simple ionic model of $\text{V}_2^{5+}\text{O}_5^{2-}$. From resonant photoelectron spectroscopy performed at the synchrotron BESSY in Berlin the compound is found to be more covalent with real valencies of $\text{V}_2^{2.5+}\text{O}_5^{-}$. From this information it is clear, that only 0.5 electrons have to be transferred to the V ion to reduce it by one formal oxidation number. For higher Na exposure times also V$^{3+}$, V$^{2+}$ and V$^{+}$ components are found indicating the decomposition of the $\text{V}_2\text{O}_5$ host material. The weak V$^{4+}$ component for the pure host material shows a slight oxygen deficiency of about 4% of the PVD grown $\text{V}_2\text{O}_5$ films. In the Na KLL Auger emission the intercalated and the surface adsorbed Na atoms can be distinguished, because the
Auger component of the adsorbed species is found at higher binding energies than that of the intercalated species. For $t_{D,Na}<120s$ a constant ratio of about 10% of the Na atoms is adsorbed on the surface, while the rest is intercalated into the host material. For $t_{D,Na}>120s$ the adsorbed Na amount increases significantly and at $t_{D,Na}=240s$ even metallic sodium is found on the surface indicating multilayer adsorption. From this data it is clear that after about 60s the host material is saturated with Na intercalate atoms and further deposition can only lead to surface adsorption. The surface adsorbate gets oxidized and the decomposition of the host material starts. From this data the stoichiometry of the stable Na saturated V$_2$O$_5$ phase has been calculated to about Na$_{1.3}$V$_2$O$_5$. For the intercalation reaction a charge transfer to the host material of about 0.4 electrons per intercalated Na atom has been found. This charge transfer leads to a shift of the Fermi level position to higher energies. This is the reason for the parallel shift of all emissions in the XP spectra to higher binding energies with increasing $t_{D,Na}$.

In Fig. 2 the UP spectra of the same samples are shown for HeI and HeII excitation. With increasing Na deposition time $t_{D,Na}$ an emission G in the band gap appears. By resonant photoemission it has been shown that emission G is originating from V3d-like conduction band states that are occupied by the Na3s to V3d charge transfer during intercalation. The fact that these states are shifted from the Fermi-level by about 0.5 eV indicates, that the filling of the conduction band cannot be explained in a simple rigid band model. The split-off of the states G from the conduction band occurs due to a structural change in the host material. But this process is not yet understood. The shape of the UP spectra changes significantly for $t_{D,Na}>60s$, also indicating a decomposition of the host material for larger Na contents. The oxidic and peroxodic Na adsorbates can also be identified. From the changes of the Fermi-level position and the work function in the stable intercalation region a stable discharge range of the sodium battery of about 0.9V has been calculated, correlating quite well with electrochemical measurements for intercalation batteries with V$_2$O$_5$ cathodes.

Fig. 2: UP spectra for HeI excitation (21.22eV) (left) and HeII excitation (40.8eV) (right).
Structural and Magnetic Properties of Fe/C Nanoparticles

S. Bhattacharya, M. Winterer, B. Stahl, T. Enz

Ultrafine magnetic particles with sizes up to a few tens of nanometers have been subject of intense scientific research for fundamental reasons as well as for a large number of potential applications. The application potential of such particles ranges from areas like information storage, ferrofluids and catalysis to medical diagnostics and drug delivery systems.

Fe/C nanoparticles were synthesized by Chemical Vapor Synthesis (CVS) using a metalorganic precursor. The material is remarkably stable in ambient atmosphere. This material was characterized using methods of X-ray diffraction (XRD), transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), extended X-ray absorption fine structure (EXAFS) studies, SQUID (Superconducting quantum interference device) magnetometry and Mössbauer Spectroscopy. The XRD data (Fig. 1) are dominated by the presence of very broad peaks usually associated with amorphous materials and have in addition a few low intensity crystalline peaks. The relative proportions of these crystalline peaks to that of the broad peaks are marginally different for the two samples we have synthesized so far. Rietveld analysis let us conclude that the bulk of the material (broad reflections) is made of $\alpha$-Fe (bcc) particles where the structural correlation length (grain size) is as small as 0.6 nm. The narrow reflections have been identified as graphite and $\alpha$-Fe as well as $\gamma$-Fe (fcc) with grain sizes of $\sim$10 nm. A size of 3 nm is estimated from transmission electron micrographs. This correlates well with the estimate of 2.9 nm as the (volume weighted) particle size determined from SAXS experiment. Selected area electron diffraction (SAED) of the material provides no evidence of a crystalline structure. The XANES (X-ray absorption near edge structure) spectra (Fig. 2) display identical energies for the first peak at about 7110 eV in both samples and $\alpha$-Fe. Peaks at higher energies are smeared out for the Fe/C nanoparticles. This may be due to a size effect in metal clusters smaller than 1 nm. Therefore, the EXAFS spectrum of batch II has been analyzed by Reverse Monte Carlo simulations (Figs. 3 to 5) using a 1 nm $\alpha$-Fe cluster in an amorphous carbon matrix as model. The resulting Fe-Fe pair distribution function (Fig. 5) shows broadened peaks still resembling the $\alpha$-Fe structure. The major part (batch I: 96%; batch II: 85%) of the Mössbauer signal at 10 K (Fig. 6) is made up of a component that has very broad spectral lines similar in appearance to that of bulk iron based amorphous materials. There is also a substantial low field component to this distribution with a superparamagnetic blocking temperature of about 30 K. Another component with parameters identical to that of bulk $\alpha$-Fe remains even up to temperatures of 100 K. This suggests a much larger superparamagnetic blocking temperature and thereby a larger particle size in accordance with the results of XRD.

A single line attributed to $\gamma$-Fe nanoparticles forms yet another component. All experimental results can be interpreted consistently with amorphous Fe/C nanoparticles with an average diameter of about 3 nm where the nearest neighbour correlations are like that of a randomized bcc structure. This has been observed in the case of certain bulk Fe based metal-metalloid glasses with low metalloid content. These particles are metallic in nature, magnetically extremely soft and highly stable under ambient atmospheric conditions.
Fig. 1: XRD Fe/C Nanoparticles

Fig. 2: Derivative of XANES spectra

Fig. 3: EXAFS spectrum for batch II together with RMC fit

Fig. 4: Pair distribution function as obtained by RMC analysis

Fig. 5: Slice through the RMC model of an \(\alpha\)-Fe cluster in amorphous carbon

Fig. 6: Mössbauer spectra of batch II as a function of temperature
Epitaxial Pr$_2$O$_3$ films on Si as alternative high-$k$ gate materials

S. Gottschalk, H. Hahn, G. Miehe and J. Brötz

The rapid (exponential) progress of computer technology (RAM, clock time) since the 1970s is based on the ability of Silicon semiconductor industry to perform a calculated reduction of the dimensions of the fundamental active device – the metal oxide semiconductor field effect transistor (MOSFET).

As integrated circuit scaling proceeds there is an urgent need for alternative gate dielectrics other than thermally grown Silicon dioxide ($k\approx4$) or oxynitrides ($k\approx9$). For oxide thicknesses below 1.5 nm direct tunneling through ultra thin gate oxides becomes a severe problem, which adversely affects several critical scaling parameters resulting in unacceptable static power consumption and astronomically high power densities (Fig. 1). Therefore the substitution of SiO$_2$ with alternative gate oxides with dielectric constants $k$ significantly higher than that of SiO$_2$ is essentially important in the near future (2006). Common approaches so far included mostly amorphous binary metal (e.g. Al, Ta, Zr, Hf...) oxides and silicates because of their higher crystallization temperature. However, they inhibit the danger of recrystallization and precipitation in post deposition CMOS technology usual processing steps such as dopant activation rapid thermal anneals (RTA). Polycrystalline structures show higher leakage currents since grain boundaries act as preferred tunnel pathways. In the research currently underway worldwide, the concept of epitaxial oxides on Silicon plays only a minor role.

In this work the growth of epitaxial Pr$_2$O$_3$ using molecular beam epitaxy (MBE) is demonstrated. Pr$_2$O$_3$ crystallizes in the hexagonal Lanthanum oxide structure (suitable for epitaxy on Si(111); lattice mismatch 2.3%) and the cubic Fluorite type structure (suitable for epitaxy on Si(100); mismatch 4.6%) with one half of the tetrahedral sites unoccupied for Pr$_2$O$_3$.

Growth on Si (111) at 375°C to 550°C yields single crystal perfect epitaxial films with Si (111) II h-Pr$_2$O$_3$ (0001) orientation as can be seen in XRD and TEM investigations.
Due to the very small lattice mismatch of h-Pr$_2$O$_3$ it is possible to overgrow the oxide with almost defect free epitaxial Si. Furthermore, it is possible to grow multilayer structures as shown in Fig. 2 (a). The electron diffraction of this multilayer system is shown in the inset.

![Fig. 2: TEM micrographs: (a) shows the bright field image of the multilayer system, the corresponding diffraction pattern is given in the inset. HRTEM of the substrate film interface is shown in (b).](image)

It can essentially be interpreted as the superposition of the perfect Si and Pr$_2$O$_3$ lattice. However, the diffraction pattern contains a few weak additional features due to twinning boundaries in the Si as marked in Fig. 2 (a). At this point it is not clear if the formation of these slight imperfections can be avoided by choosing appropriately optimized growth parameters such as growth temperature and deposition rates. The interfaces are very smooth and the films grow nicely in layers with only atomic scale like deviations as verified by AFM measurements (mean roughness < 0.3 nm). Fig. 2 (b) shows the HRTEM micrograph of the interface region. It is clearly visible that the interface is stable in regard to SiO$_2$ formation, which is also verified by XPS measurements. Silicon dioxide formation at the interface is most commonly found in silicon gate oxide interfaces resulting in reduced effective dielectric constant of the whole SiO$_2$/gate oxide stack. In our case the dielectric constant of the as prepared films was determined to be $k \sim 28$ which is in the range of the reported bulk value for Pr$_2$O$_3$.

XRD characterization of a Si/Pr$_2$O$_3$/Si sandwich geometry sample shows the commensurate matching of the Si(111) plane with the hexagonal Pr$_2$O$_3$ basal plane. Phi scans reveal the six-fold in plane symmetry of hexagonal Pr$_2$O$_3$ and the respective three-fold symmetry of Si (111) suggesting a single crystal one domain growth of Pr$_2$O$_3$ and overgrowth of Si respectively since no other Bragg reflections are apparent.

We conclude that Praseodymium oxide is a very promising candidate for future CMOS applications with a dielectric constant $k$ of about 30. As a very promising feature it appears that the oxide can be overgrown epitaxially with Si, which makes it a potential candidate for silicon on insulator (SOI) applications. However, TEM investigations on multilayer systems indicate slight crystal imperfections such as twin boundaries and dislocation lines. Sampling macroscopic dimensions by means of XRD these imperfections can not be detected, yielding only to very sharp single crystal like Bragg reflexes in reciprocal k-space (3-D q-scan measurements). Their impact on electrical performance for semiconductor applications is not clear yet.
Crystallization of Polymer-Derived Silicon Carbonitride at 1873 K under Nitrogen Overpressure

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There are two families of polymer-derived ceramics: silicon oxycarbide (SiOC) and silicon carbonitride (SiCN); both show unusual resistance to crystallization at high temperatures, far greater than the constituents from which they are made. For example, SiCN resists crystallization to a temperature higher than either SiC or Si3N4. One question is whether this behavior is thermodynamically determined or kinetically limited. The slow rates of creep in SiCN, a phenomenon that is also limited by diffusion, suggest that crystallization may be retarded because of extremely low atomic mobility in polymer-derived SiCN. The thermodynamic stability of silicon–nitrogen compounds at high temperatures depends on the nitrogen overpressure. In the case of SiCN, the temperatures where these materials may decompose apparently lie close to the temperatures where they appear to crystallize. The question then arises whether decomposition is a prerequisite for crystallization. The present work, where crystallization and weight change have been studied in tandem, shows that crystallization precedes decomposition. This conclusion is based on two pieces of evidence: (i) when the pressure is increased slightly to prevent decomposition at 1873 K, the material is found to be crystalline, and (ii) the pressure where we see the weight-loss transition is consistent with the thermodynamic equilibrium pressure calculated by assuming the activities of the phases to be equal to those of their crystalline states.

The chemical stability of an amorphous silicon carbonitride ceramic, having the composition 0.57SiC·0.43Si3N4·0.49C, is studied as a function of nitrogen overpressure at 1873 K. The ceramic suffers a weight loss at \( p_{N2} < 3.5 \text{ bar} \) (1 bar = 100 kPa), does not show a weight change from 3.5 to 11 bar, and gains weight above 11 bar. The structure of the ceramic changes with pressure: it is crystalline from 1 to 6 bar, amorphous at ~10 bar, and is crystalline above ~10 bar. The weight-loss transition, at 3.5 bar, is in excellent agreement with the prediction from thermodynamic analysis when the activities of carbon, SiC, and Si3N4 are set equal to those of the crystalline forms; this implies that the material crystallizes before decomposition. The amorphous to crystalline transition that occurs at ~10 bar, and which is accompanied by weight gain, is likely to have taken place by a different mechanism. A nucleation and growth reaction with the atmospheric nitrogen is proposed as the likely mechanism. The supersaturation required to nucleate \( \alpha \)-Si3N4 crystals is calculated to be 30 kJ/mol.
Fig. 1: Experimental and theoretical (thermo-dynamic) prediction for the weight loss and weight gain as function of nitrogen overpressure.
Spinel sialons


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In the system Si-Al-O-N and related multinary systems a large variety of crystalline and vitreous phases is known. These so called sialons are of technological importance, especially for applications as structural ceramics. The "classical" sialons refer to the solid solutions between Al₂O₃, (AlN) and Si₃N₄, known as β-sialons because of their close structural relationship to β-Si₃N₄. In analogy, α-sialons can be derived from α-Si₃N₄, but they also incorporate metal ions like Li, Ca, Y and most rare earth metals. These Si-Al-O-N systems have been extensively studied. Haviar et al. reported their behaviour at high temperature (up to 1800 °C) and high pressure (up to 6 GPa).

In this work we report the synthesis and structure determination of a high pressure sialon phase with spinel structure (space groupFd3m) by conversion of β-Si₂AlON₃ at 13 GPa / 1800°C. Its hardness of 27.5 GPa exceeds the values for β- and α-sialons significantly.

This work extends the recent discovery of binary spinel nitrides, γ-E₃N₄ (E = Si, Ge, Sn), where both octahedral and tetrahedral lattice sites are occupied by cations with a formal charge of +4 ("4-4 spinels"). It was motivated by the observation that β-sialon can be formally derived from β-Si₃N₄ by substituting Si-N pairs by Al-O. Thus, the composition follows the formula Si₃₋ₓAlₓOₓN₄₋ₓ where the β-Si₃N₄ structure is known to exist up to x_max ≈ 2.1. The stoichiometry Al₃O₃N, corresponding to full substitution (x = 3), is said to have spinel structure but in fact has not been observed to the present day. However, at even higher Al-O insertion levels (4.2 ≤ x ≤ 4.7; Al[(3+(x-3)/3)]O₃N[(1-(x-3)/3)], stable spinels containing (vacancy type) defects, the so called γ-alons, are known.[7] Their existence and the discovery of the spinel γ-Si₃N₄ (≡ c-Si₃N₄)[4a,8] prompted us to investigate the possible formation of γ-sialon having Si₃₋ₓAlₓOₓN₄₋ₓ stoichiometry at high pressure.

For our experiments we chose a single phase β-sialon starting material with x = 1, (Si₂AlON₃). The composition was verified by X-ray powder diffraction (XRD) using the known dependence of lattice constants on x and electron probe micro analysis (EPMA). Scanning electron microscopy (SEM) revealed grain sizes of 1 - 2 µm. High pressure conversion was carried out using a 6-8 type multi-anvil (MA) apparatus. A β-sialon cylinder (12.5 mg) was inserted into the MA assembly. The applied pressure of 13 GPa was slightly above the value where γ-Si₃N₄ had been synthesised.

While the color of the starting material was white, the recovered sialon had a dark-grey opaque appearance.

The spinel structure was verified using XRD and high resolution transmission electron microscopy (HR-TEM). The diffraction pattern of this sample, with the background subtracted (data set II), is shown, along with its Rietveld difference plot. All reflections can be assigned to a spinel structure. This proves the presence of a single phase material, hereafter named γ-Si₂AlON₃.
Within the spinel structure, the anions are located at \((x,x,x)\) (Wyckoff position 32e), with \(x \equiv x_{(N/O)}\) being the only free parameter. In a spinel with ideal fcc anion lattice, \(x_{(N/O)}\) equals to \(\frac{1}{4}\). A deviation from this value leads to a distorted environment of the octahedral cation site. The parameter \(x_{(N/O)}\) is often referred to as "spinel parameter" \((u)\) and is used to compare anion environments as shown below. In the present case a value of \(x_{(N/O)}^{\Pi} = 0.255\) \((R_{\text{Bragg}} = 4.56)\) was determined from data set II, while data set I yielded \(x_{(N/O)}^I = 0.259\) \((R_{\text{Bragg}} = 6.99)\). From \(a_0^I\) and \(x_{(N/O)}^\Pi\), we calculated the average bond lengths between the tetrahedrally and octahedrally co-ordinated cations and their nearest anionic neighbors, hereafter called \(<\text{tet-N/O}>\) and \(<\text{oct-N/O}>\), respectively. A comparison with the values of \(\gamma\)-Si\(_3\)N\(_4\), reveals that the \(<\text{tet-N/O}>\) is decreased from 1.805 to 1.763 Å, while \(<\text{oct-N/O}>\) is increased from 1.863 to 1.916 Å. The latter is apparently responsible for the lattice expansion from 7.74 to 7.82 Å. Further insertion of Al-O probably causes \(<\text{tet-N/O}>\) to lengthen, since the (ambient pressure) \(\gamma\)-alons reported in literature exhibit \(<\text{tet-N/O}>\) values around 1.8 Å. This phenomenon can be explained assuming preferences of the Si and Al atoms for tetrahedral and octahedral sites, respectively. First, we note that the Si\(_{\text{tet-N}}\) bond length in \(\gamma\)-Si\(_3\)N\(_4\) is larger than that in both \(\alpha\)- and \(\beta\)-Si\(_3\)N\(_4\) in order to match the larger SiN\(_6\) octahedra in the spinel structure of \(\gamma\)-Si\(_3\)N\(_4\). In \(\gamma\)-Si\(_2\)Al\(_2\)O\(_3\), on the other hand, some Si\(_{\text{oct}}\) sites are now replaced by Al\(_{\text{oct}}\) and would allow the Si tetrahedral to shrink down towards its "normal" size. In \(\gamma\)-alons, however, both octahedral and tetrahedral sites are occupied by the bulkier Al ion, thus the tetrahedral bond length increases again. This explanation is consistent with the observed variations of bond length and the expectation from the cation size consideration.

The above discussion suggests that \(\gamma\)-Si\(_2\)Al\(_2\)O\(_3\) is an inverse spinel, with the lower-valent cation preferentially occupying the higher coordinated sites. (The opposite case is called normal spinel.) This is further supported by a comparison to the structural parameters of known spinels: The anion parameters \(u\) of 2-3 and 4-2 spinels (here numbers refer to the valence of cations), when plotted against the ratio between \(<\text{oct-O}>\) and \(<\text{tet-O}>\), are known to follow distinct curves on which the data points for inverse and normal spinels are located at separate sections. In the case of our 4-3 spinel, with \(u = x_{(N/O)} = 0.255\), the calculated data point is found within or close to the section of inverse spinels. The fraction of site occupation, however, could not be determined from the present XRD data. We also should note that the preference of Al for the octahedral site may not always be obeyed, as the actual fraction of site occupation of a spinel-sialon with fixed composition is likely to depend on pressure, temperature and the processing history of the material.

The figure shows an SEM image of Vickers indentations on the ground surface of \(\gamma\)-Si\(_2\)Al\(_2\)O\(_3\). The measures \(2a\) and \(2c\) used for hardness and indentation fracture toughness determination are indicated. The average hardness from 10 indentations at 0.5 kg \((HV_{0.5})\) and 4 indentations at 1.0 kg \((HV_1)\), is as high as 2800 ± 60 \((27.5\) GPa in SI-units). The \(HV_{10}\) values for the single phase \(\alpha\)- and \(\beta\)-sialons are usually 2200 and 1800, respectively. \(HV_{10}\) of \(\gamma\)-alon was reported to be also in the range of 1800. Therefore, \(\gamma\)-sialon appears to be a harder material. Since hardness is known to decrease with the load applied, future experiments using a larger specimen and a higher load (10 kg or more) would be desirable to confirm this observation.
Finally, a fracture toughness of 4.6 MPa·m$^{1/2}$ was determined from the mean indentation crack lengths $<2c>$. This is in the upper range of the toughness values for single phase, fine grain $\alpha$- and $\beta$-sialons, typically from 3 to 4.5.

Fig. 1: SEM-image of HV$_{0.5}$ and HV$_1$ Vickers indentations in $\gamma$-Si$_2$AlON$_3$ with radial cracks extending from their edges. Inset: A HV$_{0.5}$ impression with measurement of indentation diagonal $2a$ and crack length $2c$ indicated.
Due to their fascinating luster, brilliance and iridescent colour effects, pearl luster pigments are used for various industrial purposes. Furthermore, pearl luster pigments can be found in a huge number of end-user applications. Pearlescent pigments may be applied as functional materials, such as optical filters and security printings on bank notes, but also for decorative purposes. The aesthetic and outstanding eye-catching appeal is used in cosmetics, car paints and in packaging materials. For decorative applications the following three points show the great advantages of pearl luster pigments compared with other inorganic pigments. The first point is of course the ability to imitate the brilliance of natural pearls. The second advantage is the illusion of optical depth. The illusion is strengthened by varnishing great areas with paints consisting of pearlescent pigments. The third field is the sensational eye-catching effect. This effect is daily demonstrated by many decorative materials.

The industrial importance of pigments requires further investigations to improve the pearl luster, which is an interference effect. The most important class of pearlescent pigments is based on substrate platelets of about 1 µm thickness (e.g. SiO₂, Al₂O₃) coated with thin films of transparent metal oxides (e.g. TiO₂, Fe₂O₃). The main interest in recent investigations is concentrated on new coating materials. The refractive index of the coating material is of central importance. A high difference in the refractive indices of film and substrate material leads to strong effects and determines the interference colour on a certain viewing angle. Further the sintering properties of the precipitated film are extremely important for the quality of the resulting pearlescent pigment. It is desirable to achieve a condensation of the film without any further crystal grain growth. The ideal pigment consists of a condensed film with a smooth surface without bubbles. Another field of research is the improvement of the interface between substrate and film. The adhesion must be strong enough to achieve a substrate that is completely covered with a condensed film.

In this context the sintering behaviour of pearlescent pigments was investigated at different temperatures by x-ray diffraction (XRD), transmission electron microscopy (TEM), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Fig. 1: Comparison of XRD patterns of a SiO₂-based ZrO₂ pigment at different temperatures. The indices refer to ZrO₂. Left: 650°C, right: 1300°C.
The brilliance and quality of a pearlescent pigment is correlated with structural features such as the average particle size and the roughness of the surface. Both aspects depend on the maximum temperature reached during sintering and on the heating program. As demonstrated by the x-ray diffraction patterns (Fig. 1) and TEM-images (Fig. 2) of a ZrO$_2$/SiO$_2$-pigment, the crystals grow during sintering. Furthermore a variation of standard coating and substrate materials can show the advantages and disadvantages of each combination. After a sequence of variation it is possible to compare the different pearlescent pigments with each other and classify them for a special application field. Hence, future work will continue comparing pearlescent pigments with respect to the influence of structural features on different film and substrate materials.
The catalytic efficiency of Pt-only automotive exhaust catalysts decreases considerably after ageing at high operating temperatures. One of the reasons is the loss of precious metal dispersion due to sintering of Pt clusters. As reported previously, Pt/Pd alloys in oxidative atmospheres sinter much more slowly than pure Pt. However, the catalytic activity of supported Pt/Pd alloy catalysts reveals a slight increase of the CO and propene light-off temperature. The present work investigates the oxidation behavior of Pd in the presence of Pt. Furthermore the alloying after calcination, reduction and thermal ageing treatments commonly used in industry is studied. Finally we propose an explanation for the inhibition of sintering. The structure of the alumina supported bimetallic Pt/Pd diesel oxidation catalyst was studied by extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD) and transmission electron microscopy (TEM) which can be regarded as complementary techniques. Since X-ray diffraction provides information on long-range order for phase identification and average particle size, X-ray absorption methods are sensitive to the local structure on an atomic scale. The combination of these methods offers possibilities for obtaining a more complete structural description and explanation of complex nanodispersed systems.

The 3.5 wt. % Pt/Pd catalyst (Pt:Pd weight ratio 2:1) was prepared using coimpregnation of an alumina support. The results have been compared with those of a pure Pd and pure Pt catalysts.

The X-ray absorption measurements have been performed in transmission geometry at HASYLAB at the "Deutsches Elektronen Synchrotron (DESY)". XANES and EXAFS spectra of the monometallic Pt-, Pd- and the bimetallic Pt/Pd-catalysts were recorded at the Pt L3-edge (11.564 keV) and the Pd K-edge (24.350 keV). The samples were prepared as pellets with 25 wt. % of spectroscopically pure polyethylene as a binding additive. The spectra were measured relative to Pt and Pd foils as reference to allow the exact determination of the absorption edge shift. The X-ray diffraction measurements have been carried out at a Siemens D500 diffractometer using Cu-Kα radiation in Bragg-Brentano geometry.

For data visualization, fitting of the EXAFS functions and calculation of the correlated errors, the software package VIPER was used. Scattering amplitudes and phase shifts of the structure models applied were calculated using the FEFF 8.0 code.

The oxidation behavior of Pd in the presence of Pt differs significantly from that of a Pd-only catalyst. A Pd-only catalyst shows metallic character only after reduction but completely oxidized state was found after calcination as well as after ageing.
On the other hand, after both calcination and thermal ageing under oxidative atmosphere Pd is present in metallic as well as in oxidized state in bimetallic Pt/Pd catalyst (Fig.1). After reduction Pd is completely metallic in form of bimetallic Pt/Pd crystals with statistically occupied crystallographic sites (random alloy). The structural parameters calculated from the EXAFS data allow to propose a model for the distribution of the Pt, Pd and PdO in the aged bimetallic catalyst. According to this model, the metallic phase consists of Pt/Pd-alloyed particles, wherein the Pd-concentration increases towards the cluster surface. The tetragonal PdO phase is present as single crystals that grow at the surface of the Pt/Pd-clusters or as isolated PdO crystals.

Fig. 1: X-ray diffraction patterns and Fourier transforms of the EXAFS spectra for a differently treated bimetallic Pt/Pd catalyst: calcined (Pt/Pd-C), calcined and reduced (Pt/Pd-CR), calcined and thermally aged (Pt/Pd-CT).
Mechanisms of the Hydrogen Reduction of Molybdenum Oxides

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The two stages of the hydrogen reduction of MoO₃ to Mo were investigated in a thermal balance under well defined reaction conditions. Starting with different grain and agglomerate sizes for both stages, the influence of a set of parameters (temperature, local partial pressure of H₂O, gas flow, etc.) on the reaction progress and the final result were studied in detail. Depending on the set of parameters used, different reaction mechanisms like pseudomorphic transformation or chemical vapour transport (CVT) were observed. Taking into account that grains and agglomerates deviate from a spherical shape and a definite grain size, the extent of reaction is well described by standard theoretical gas-solid-reaction models such as the shrinking core model (SCM) or the crackling core model (CCM). Thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area measurements (BET-method) and laser diffraction were used for these studies.

Under all conditions, the first stage shows a reaction path MoO₃ → Mo₄O₁₁ → MoO₂ via chemical vapour transport (CVT). The reaction extent follows the crackling core model. Depending on the local partial pressure of H₂O during reduction, the formed Mo₄O₁₁ and MoO₂ exhibit different size distributions and shapes of the grains.

The extent of reaction of the second stage develops according to the shrinking core model. Depending on the local dew point, two different reaction paths can occur: Pseudomorphic transformation at low dew points and transformation via chemical vapour transport at high dew points.

The shrinking core model, SCM

The shrinking core model by Yagi/Kunii describes a shrinking core of educt, surrounded by a growing layer of product (cf. to fig. 1) during the reaction of a solid particle with gas.

![Shrinking Core Model](Image)

Fig. 1: Schematic drawing of the shrinking core model.

The rate determining step consists of either the chemical reaction at the interface product/educt (reaction controlled) or the diffusion through a layer of the product (diffusion controlled). According to the “classical” theory of the SCM, the transformation of grains follows via a pseudomorphic transformation. In principle, there are two mechanisms for grain transformation:
1. Mechanism of Pseudomorphic Transformation: During the reaction, the reaction interface moves from the grain surface to the core of the grain. The shape of the product remains close to the educt one causing pseudomorphism. Typically, the product shows pores and pore channels.

2. Mechanism of Chemical Vapour Transport: The decomposition of the educt is followed by formation of an intermediate gaseous transport phase. This transport phase is deposited on a nucleus of the product. This way, the grain morphology of the product is generated completely new. The grain size distribution of the product is determined by the conditions of deposition (heterogenous/homogenous nucleation, nucleus growth) from the gas phase. The schematic of a CVT-transformation is shown in figure 3.

Fig. 2: Schematic drawing of a CVT-transformation. $S_1$: educt (solid), $TP_1$: transport phase (gaseous), $S_2$: product (solid).

Results for the first reduction stage $\text{MoO}_3 \rightarrow \text{MoO}_2$

Based on the results of TGA and XRD, SEM was used to search for seeds of nucleation and growth of new phases. Therefore, reduction was interrupted at different states of progress and the powders were examined by SEM to understand spatial and chronological evolutions during the reduction. Some results are shown in the figures 3 to 5.

Reaction mechanism of the first stage of reduction of $\text{MoO}_3$ to $\text{MoO}_2$

The first stage follows the two step version of the crackling core model:

$$
\begin{align*}
\text{MoO}_3,_{\text{nonporous agglomerat}} & \rightarrow_{\alpha=0} \text{MoO}_{4,11},_{\text{grains agglomerat}} & \rightarrow_{\alpha=0,25} \text{MoO}_2,_{\text{grains agglomerat}} \\
\text{MoO}_3,_{\text{agglomerat}} & \text{H}_2 & \rightarrow \text{MoO}_{4,11,11},_{\text{grains agglomerat}} & \rightarrow \text{MoO}_2,_{\text{agglomerat}} & \text{(1)}
\end{align*}
$$

$\alpha$ relates to removal of oxygen. Without exception, the transformation steps take place via a CVT route by generation of a gaseous transport phase:

$$
\begin{align*}
\text{MoO}_3 & \rightarrow_{k_1} TP_1(g) & \rightarrow_{k_2} \text{MoO}_{4,11} & \rightarrow_{k_3} TP_2(g) & \rightarrow_{k_4} \text{MoO}_2
\end{align*}
$$

At otherwise constant conditions (temperature, educt habit) high dew points lower the reaction velocity and stabilize gas phases (longer transport range). Independent of $\text{MoO}_3$ agglomerate and grain size and the desired reduction temperature, $\text{MoO}_{4,11}$ and $\text{MoO}_2$ exhibit a constant habit of grains. $\text{MoO}_{4,11}$-grains are interconnected by massive bridges and they are building agglomerates of a “cauliflower” morphology. During transformation of $\text{MoO}_3$ to $\text{MoO}_{4,11}$ these cauliflower agglomerates grow towards the centre of the initial $\text{MoO}_3$ agglomerate.
Fig. 3: Various states of reduction of a partly reduced MoO$_3$-Climax sample. a) initial MoO$_3$ nonporous; b) Mo$_4$O$_{11}$ porous growing on shrinking core of MoO$_3$; c) Mo$_4$O$_{11}$, porous; d) area of magnification of figure 4

Fig. 4:
Left: magnification of fig. 3, showing Mo$_4$O$_{11}$ on a shrinking core of MoO$_3$-Climax (centre). Right: Mo$_4$O$_{11}$ nucleus on the surface of a MoO$_3$-Climax agglomerate.
The next step is the nucleation of MoO$_2$ on the surface of Mo$_4$O$_{11}$-grains and a consecutive grain growth into the volume of MoO$_2$. Resulting MoO$_2$-grains exhibit a platelet habitus with a height $h$ of 0.1-0.2 $\mu$m and a diameter $d$ of 1-2 $\mu$m. Every transformation to the next oxide phase is oriented from the surface to the centre of the agglomerate. Depending on the extent of reaction and conditions of reduction, several oxide phases can coexist, showing a multilayer structure like onion skins. The habit of agglomerate formation and therefore agglomerate size is kept during the first stage of reduction.

**Results of the second stage of reduction from MoO$_2$ to Mo**

Starting with different grain sizes and grain shapes, MoO$_2$ was reduced to Mo under conditions of extreme dew points. The following sequence of SEM-micrographs proves the existence of the assumed reaction routes: pseudomorphic and CVT transformation.

---

**Fig. 5:**
Left: nucleation of MoO$_2$ in a grain of Mo$_4$O$_{11}$.
Right: growth of platelet-shaped crystals of MoO$_2$ on a Mo$_4$O$_{11}$ agglomerate.
Fig. 7: Reduction of MoO$_2$-standard, sieve fraction (32-45) µm via the pseudomorphic route. 
Left: Initial compact grains of MoO$_2$ (compactness of grains generated by "in situ" sintering of platelets due to overheated reduction during the first stage). 
Right: Close up of grain surface after complete reduction to Mo. The grain shows pore channels. Surface cracks and craters result from stress by tension due to a volume decrease during oxygen removal.

Fig. 8: Reduction of MoO$_2$-standard sieve fraction F7 (355-500) µm via the CVT route under an extremely high dew point. 
Left: surface of agglomerate after complete reduction to Mo, showing the change from MoO$_2$-flakes to octahedral/spherical grains. 
Right: close up of Mo derived by the CVT-route in a powder bed.
Fig. 9: Nucleation and grain growth of Mo via the CVT route.
Left: nucleation (bright dots) and small grains of Mo on MoO$_2$-platelets.
Right: Intersection of a CVT-built Mo layer showing growth of a “skeleton” of Mo grains during the CVT-route. This CVT-layer was built in the centre on the upper side of the W-foil shown in figure 9.

**Reaction mechanism of the second stage of reduction of MoO$_2$ to Mo**

Within the range of the investigated MoO$_2$ agglomerate sizes $d < 1$ mm, no time-dependency for complete reduction was found. The diffusion velocity inside the porous structure of MoO$_2$ agglomerates is sufficiently high to allow a description of kinetics by the shrinking core model.

Depending on the dew point of hydrogen two routes were observed for the transformation of grains:

a) Pseudomorphic transformation:
Up to a maximum adjustable dew point $\tau$(H2) of 20°C under the available experimental conditions a pure pseudomorphic transformation was observed. Therefore, the initial grain shape of MoO$_2$ is kept. Mo powders reduced at extremely low dew points exhibited pyrophoric behaviour. Based on an increase in density during the transformation of MoO$_2$ to Mo, large grains experience tension stresses which lead to craterlike systems of cracks on the grain surface. The outer shape and size of grains and agglomerates are conserved. On a formal basis the pseudomorphic transformation follows the well known equation:

$$ MoO_2 + 2H_2 \rightarrow Mo + 2H_2O \quad (3) $$

b) CVT-transformation of grains:
By hindering H$_2$O to diffuse out of the sample high local dew points were achieved (self created atmosphere). Due to this a pure CVT-transformation of the initial grains was observed ($\tau$(H2) > -40°C). On a formal basis the CVT-transformation follows the following scheme:

$$ MoO_2 \xrightarrow{k_s} TP_3 (g) \xrightarrow{k_e} Mo \quad (4) $$

In contrast to the first stage of reduction, local dew points decisively influence the nucleation and the grain growth of the Mo-phase: Low dew points generate high numbers of nuclei and small grain sizes. High dew points generate low numbers of nuclei and large grain sizes.
The identification of chemicals plays an important role mainly in the fields of automatic filling stations and in recycling of waste chemicals. In both cases the analytical procedure has to be performed non-invasive in the containers. The main advantages for the application of X-rays in identity control are non-destructive analysis of the sample, short analysis time, high depth of information, accuracy of analysis, simple operability, economic efficiency and high sample throughput. The experimental set-up of an energy-dispersive X-ray fluorescence (EDXRF) spectrometer which can be used for samples of very different size is given in Fig. 1. A training set of X-ray spectra (measured fivefold) of 71 chemical compounds was built up. The compounds were divided into four groups: 14 calcium compounds (CaKα/β), 18 potassium compounds (KKα/β), 18 sodium compounds (no fluorescence lines), and 21 organic compounds (no fluorescence lines). In all cases the total spectra were stored (including the Compton- and Rayleigh-scatter lines, characterizing the mean atomic number of the sample). The scatter lines give the possibility to characterize XRF samples which do not produce elemental fluorescence lines.

Chemometric evaluation of the XRF spectra was performed as a combination of conventional methods (e.g. element identification, quantification) and the application of multivariate tools. The methods carrying out this procedure are exploratory methods or unsupervised methods (cluster methods, principle component analysis [PCA], factor
analysis [FA]). They can be used to find groupings of spectra (unsupervised learning). In the final step one has to define prior groups of objects in the training set for classification (supervised learning).

Besides the chemical composition of the samples, the position of the sample, the grain size and the thickness of the package wall influence the XRF spectra.

A library of X-ray spectra (measured fivefold) was built up with the EDXRF set up for non-invasive measurements. Each sample was measured through the package.

To illustrate the influence of the grain size, the spectra of 7 size fractions of SiO₂ were measured fivefold (each with 100 s measurement time) and a principal component analysis (PCA) by singular value decomposition (SVD) was calculated (Fig. 2). This diagram illustrates the significant influence of the grain size on each attempt to separate different chemical compounds.

In order to investigate the influence of the wall thickness on the reliable identification of chemicals, a solid titanium metal sample in PE containers of varying wall thickness (2.5 µm - 2.5 mm) was measured with the non-invasive EDXRF set up.

![Fig. 2: PCA score plot for spectra library illustrate the 7 grain size fraction of SiO₂ for PC2 (2.3%) vs PC1 (82.2%).](image1)

![Fig. 3: PCA score plot for the measurement of a titanium block in varying package wall thickness displayed in a PCA score plot of 16 calcium compounds.](image2)

After calculating a PCA by SVD of these measurements the 8 different spectra of titanium in packages with different wall thickness and 16 calcium compounds were plotted (Fig. 3). Therefore, at first the PCA of the samples with varying wall thickness was calculated. Using the resulting loadings a new PCA was calculated with the spectra of the Ca compounds. The scattering signals region was used as input variable for multivariate analysis. It is shown here that the impact of the packing wall thickness in the interval 2.5 µm - 2.5 mm is large enough to mix up different chemicals by measurements through the packing. However, a slight variation of the packing wall thickness (e.g., 1 ± 0.1 mm) should be acceptable to prevent a misclassification.

The influence of the sample position on the evaluation of measured spectra with PCA by SVD is shown in Fig. 4. The titanium metal sample was measured in a PE packing (usual square reagent packing [thickness ≈ 1 mm] with rounded edges) in different positions (see Fig. 1). The plot of the different sample positions depending on the angle “tube-sample-detector” is displayed in a plot for calcium compounds. Therefore, at first the PCA was calculated for the Ti samples at different positions. Afterwards, using the resulting loadings the PCA was calculated with the Ca compound spectra. Only a slight rotation of 2.5° counter clockwise yields a totally different position in the PCA score plot. Multivariate calibration is a well understood statistical method for extracting latent relationships in analytical data. XRF measurements of chemical compounds without packing and the subsequent multivariate analysis have shown the basic feasibility of forming a chemical
compound classification system based on characteristic X-rays and on coherent and incoherent X-ray scatter radiation. The PCA method using distinct ranges of the spectra as input variables is capable to distinguish between spectra of different chemical compounds measured without packing. In some cases, however, the differences in the mean atomic number are too low or physical and technical parameters play an additional role. In general, the following parameters are important for measurements without packing: mean atomic number, grain size, humidity, and the density of the compound.

The classification of chemical compounds without packing was not always conclusive. The misclassification risk for the measured test sets is low but not negligible. For a practical application of this type of chemometric XRF spectra evaluation, a decision of its use should be made on the basis of a large number of positive results, thus reducing the statistical uncertainty. In summary, the choice of such an identity control system strongly depends on the demands with respect to the allowable classification risk.

In summary, the correlations between the PC scores and the investigated physical parameters (mean atomic number, $\mu/\rho$, main element concentration) as well as the technical parameters (grain size, packing wall thickness, sample position) for non-invasive measurements through the packing yield a pronounced systematic influence on the position of all spectra in the PC space.

If one knows the relationship between the physical parameters of chemical compounds and the location of their spectra in the PCA data space, it should be possible to anticipate their locations in the space of the library data set, thus predicting the spectra without further measurements. First results were already obtained but have not yet been published.

Fig. 4: PCA score plot for the measurements of samples in varying positions displayed in a PCA score plot for 16 calcium compounds.
Enhancement of the current in a superconductor strip by means of curved superconducting shields

Y. A. Genenko, H. Rauh

The sharp peaking of the current at the edges of superconductor strips is known to cause penetration of magnetic flux leading to a nonlinear electromagnetic response, thereby impairing the performance of superconducting devices such as filters and transmission lines. The usual arrangement which substantially mitigates the inhomogeneity of the sheet current across the width of the strip consists of a superconductor film deposited on an insulated, flat superconducting shield. At small distances between the film and the shield, the edge current peaks decrease, producing an almost homogeneous sheet current distribution. Here, we study the shielding effect in superconducting configurations more elaborate than those commonly employed.

We proceed from a flux-free, current-carrying superconductor strip of thickness \( d \) and width \( w \) within the range \(-w/2 < x < w/2\), intersected symmetrically by the plane \( y = 0\) and extended infinitely in the \( z\)-direction of a cartesian coordinate system \( x, y, z \). The configuration addressed first is thought to include a pair of massive, flat superconducting shields in the Meissner state, occupying the spaces \( y > a \) and \( y < -a \), respectively, their boundaries coinciding with the planes \( y = \pm a\). The requirement that the transverse component of the magnetic field be zero inside the strip yields a homogeneous integral equation for the sheet current distribution which admits an exact analytic solution. The latter is truncated at the distance \( d \) from the edges of the strip, where the sheet current is limited by the threshold value \( J_t \) determined, in turn, by edge barriers protecting the Meissner state against entry of magnetic flux. A variation of the distance between the superconducting shields and the superconductor strip shows that the distribution of the sheet current, \( J_{fs} \), becomes increasingly uniform, the maximum total current growing concomitantly when the shields approach the strip (Fig. 1).

Motivated by the analogy between magnetic and fluid flux, we study next the effect of curved superconducting environments on the distribution of the sheet current in the superconductor strip. Due to compression of magnetic flux, shielding configurations with contraction favour enhancements of the current in the strip. Relating the \( x,y \)-plane to the \( \xi,\eta \)-plane by the method of conformal transformation, we map the boundaries of the flat superconducting shields onto curved surfaces of the same symmetry which may be characterized by their minimum distance to the centre of the strip, \( \delta_0 \), and by their radius of curvature at minimum distance to the centre of the strip, \( \rho_0 \), whilst leaving the superconductor strip unchanged. A variation of the radius of curvature of the tips of the superconducting shields reveals the following trait. The distribution of the sheet current, \( J_{cs} \), which develops a central hump, becomes increasingly dominant when the tips of the shields contract; the maximum total current grows accordingly, such that an enhancement by a factor of about 5 compared with the case of flat shields results for the smallest radius set (Fig. 2).

We comment that, whereas the absolute magnitude of the maximum total current is upward bounded by about \( wJ_t \) for flat shields, values as high as about \( 10wJ_t \) can easily be
attained with curved shields, upon due choice of the geometrical parameters of their boundaries involved.

![Figure 1](image-url)

Fig. 1: Upper part: superconductor strip (bold line) and boundaries of pairs of flat superconducting shields with $a/w = 0.5$ (dotted lines), 0.15 (dashed lines), 0.05 (full lines). Lower part: distribution of the sheet current in the marginal Meissner state for the shielding configurations shown above, when $d/w = 0.001$; the maximum total current adopts the respective values $I_{fs}/wJ_t = 0.112$ (dotted line), 0.161 (dashed line), 0.256 (full line).

Though wholly based on static derivations, our results are deemed to extend to the quasi-static ac regime as well. The enhancement of the total current by means of a pair of curved shields could therefore be favourably exploited in rf microstrip devices, where the currents
are severely limited by their crowding at the edges of the strip. Moreover, the analogy with fluid flow invoked before suggests that an enhancement effect should occur in one-sided curved shielding configurations too.

Fig. 2: Upper part: superconductor strip (bold line) and surfaces of pairs of curved superconducting shields with $\rho_s/w = 1$ (dotted lines), 0.5 (dashed lines), 0.25 (full lines) and $\delta_s/w = 0.05$. Lower part: distribution of the sheet current in the marginal Meissner state for the shielding configurations shown above, when $d/w = 0.001$; the maximum total current adopts the respective values $I_{cs}/J_t = 0.989$ (dotted line), 1.148 (dashed line), 1.261 (full line).
Simulation of grain growth in nanocrystalline nickel induced by ion irradiation

Wolfgang Voegeli, Karsten Albe, Horst Hahn

Nanocrystalline (nc) metals exhibit a number of peculiar materials properties compared to conventional polycrystalline samples because of their small grain sizes and large volume fraction of grain boundaries. Therefore nc-materials are interesting candidates for radiation resistant environments, since grain-boundaries can act as effective sinks for irradiation-induced defects. Experimental studies showed that irradiation induced damage is significantly smaller in nanocrystalline than in polycrystalline samples. The defect evolution in palladium had been studied and a decreasing defect density was reported with decreasing grain size. Moreover, they found a significant increase of the average grain size from 20 to 45 nm in nc-Pd, with a clear dependence on dose and temperature. It is still an open question, however, under which specific conditions ion-induced grain growth occurs.

In the present study we therefore performed computer simulations in order to answer the question, whether grain growth can occur as a direct consequence of the primary state of damage. We used molecular dynamics simulations, which are a powerful and appropriate tool for studying such processes, since collision cascades are confined to relatively small volumes and appear on short time scales. The influence of collision cascades on the microstructure was studied for nanocrystalline samples with 5 nm and 10 nm average grain size, random orientation of the grains and monodisperse size distribution. The model nanocrystalline structures consisted of about 6 x 10^5 atoms for 5 keV cascades corresponding to 16 and 128 grains for the 10 and 5nm grain size samples, respectively. All structures were relaxed in a variable cell MD-simulation at 0 bar and 600K for 15ps and subsequently cooled down to 0K before the cascade was started.

Fig. 1: (a) Initial structure with 5 nm grain size. Atoms on fcc positions are colored grey, all other dark. (b) Cascade volume of a 5 keV recoil after 1 ps. (c) Final structure after cooling down of the cascade.
The PKA is started in grain "1" and directed towards grain "2". Fig. 1 (a) shows the initial structure as obtained after 10 ps relaxation before the collision cascade is started. The thermal spike gets to its maximal extension after approximately 1ps, where the volume compares to that of an individual grain as shown in Fig. 1 (b). During cooling and shrinking of the cascade, atoms at the border of the spike volume are recrystallizing. During this phase, grain "1" in the lower part of the spike can expand over the former grain boundaries into the central grain "2" (see Fig. 1 (c)).

The same simulation result after five cascades is represented by the light grey atoms in Fig. 2 (a). Since the thermal spike occured in approximately the same region in all five cascades, the lower grain "1" was able to expand further into the central grain "2", which lost about half of its volume.

For comparison we carried out an alternative simulation and kept the structure at 1000 K for 1 ns simulation time without initiating a cascade. In this case the thermally induced grain growth after 100 ps is much less than that caused by 5 cascades during the same simulation time, which proves that the ion induced grain growth found in our simulations is not just an artifact of unstable grain boundary structures.
In order to understand the role of the cascade position and volume we have additionally calculated 5 keV cascades in samples of 10 nm grain size, where we found that defect clusters are formed, while the GB positions remained unaffected. After thermal annealing of this structure interstitials were annealed and aggregated at the GB. In contrast grain growth can occur even for the larger 10 nm grains if the cascade volume is located in the area of GBs or triple points. One example is shown in Fig. 3. Here the cascade volume was located close to the triple point "1-2-3". Comparing the initial and final structures, it gets obvious that the triple point has moved towards the center of grain "1" leading to a small shrinkage of the central grain. Obviously, this motion of the triple point is different to that observed in the thermal annealing procedure before.

In conclusion, we have shown that ion-induced grain growth is the dominant process if the spike volume is larger than the grain volume or overlaps the grain boundary area. Shrinkage or growth of grains is accumulated over several events. If the spike volume does not reach the GB area we do not observe ion-induced grain growth. In all cases vacancies and vacancies clusters are formed, while interstitials are accommodated by the grain boundaries.


Ell, Jürgen; Elektronische Struktur gesputterter Silber-Zinkoxid-Schichtsysteme, Surface Science in cooperation with ISE Freiburg, May 2002.


Faulhaber, Sabine; *Precursors for Ternary Wide Band-Gap Semiconductors Based on Gallium Nitride*, Dispersive Solids, Materials Department of the University of California, Santa Barbara, USA, October 2002.

Gies, Astrid; *Synthèse et caractérisation de couches minces d'oxide de vanadium pour une utilisation comme électrode positive dans des microbatteries au lithium*, Structure Research, June 2002.


Kriegsmann, Arne; *Effects of Particle Reinforcement on the Recrystallization of Al-Zr Alloys*, Physical Metallurgy, October 2002.


Kraft, Gunther; *Chemisch-analytische Charakterisierung von unterschiedlich behandelten Gußeisenoberflächen* (Analytical Characterization of variously treated surfaces of cast iron), Chemical Analytics, November 2002.


Roth, Sebastian; Evaluierung von Aerosolmassenspektrometrie-Messungen im CVS-Verfahren, Thin Films, July 2002.


**PhD Theses**


Beerbom, Martin; *Hochaufgelöste Photoelektronenspektroskopie zur Untersuchung nassche-mischer und elektrochemischer Prozessschritte an GaAs-Oberflächen*, Surface Science, February 2002.


Njeh, Anouar; *Caractéristique structurales et élastiques des couches minces Ag/Si et Cu/Si*, Faculté des Sciences, Université Sfax (Tunesien), Structure Research, July 2002.

Roth, Christina; *Structural and electrochemical characterization of carbon-supported Pt-Ru and Pt-Ru-W catalysts for application in polymer-membrane fuel cells*, Structure Research, June 2002.


Wahl, Claudia; Charakterisierung innerer Grenzflächen in mikrokristallinem SiO₂ mit Transmissionselektronenmikroskopie, Structure Research, February 2002.

Habilitations

Lupascu, Doru: Fatigue of Ferroelectric Lead Zirconate Titanate and Related Issues, Ceramics Group, June 2002.


Junior-Professorship in Materials Modelling

Albe, Karsten; Materialmodellierung und Computersimulation: Rückblicke, Einblicke, Ausblicke, November 2002.

Patents

Kinski, I.; Riedel, R.; Winkler, H.; Anselmann, R.; Verfahren zur Herstellung von Nitriden, Merck KGaA, german patent registration, submitted 24.04.02.

In the solar system, Earth is a 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 the 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 CO₂-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 trace gases, 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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Prof. Dr. Pedro Depetris, Univ. of Cordoba, Argentina

### Research Projects (funded)

Kempe & Rosendahl: Speleothemes and Pleistocene climate in Central Europe (DFG)

Rosendahl: Interdisciplinary project HIMAP in the Alpine Martell Valley, Italy

The project HIMAP (Hinteres Martelltal Projekt) involves different disciplines (geology, hydrogeology, hydrochemistry, hydrology, glaciology, climatology, engineering geology, sedimentology and socio-economic sciences) of the Technical University of Darmstadt (National Park Stilfser Joch/Italie)
Rosendahl: Absolute chronology of tufa dams in the Seeburg Valley/Swabian Alb (City of Bad Urach)

Publications


Hydrogeology

Hydrogeology is dealing with groundwater under natural conditions as well as under the influence of man, e.g. sealing of terrains, contaminated sites or agriculture. Equally important parts are the hydraulics, balance and quality and protection of groundwater. Hydrogeologists are working in the field, in the laboratory and with EDV. With this the hydrogeology delivers essential contributions to evaluation and management of water resources. There are important connections to the fields of engineering geology, sedimentology, environmental science and civil engineering, as well as to the conservation of nature.

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Dipl.-Geol. Katy Unger
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graduate students of Civil Engineering Kai Bergerin Matthias Gebhardt

Research Projects


Stable nitrogen isotopes as an indicator for the origin of nitrate in the groundwater of the Otzberg area.

Water quality problems in connection to irrigation in the Ebro area, Spain
Publications


Engineering Geology

Engineering Geology uses geoscientific methods for the solution of tasks in planning and execution of building measures. This contains investigations for the attitude of sediments and rocks as building ground or building material and for geological processes influencing these characteristics. Engineering geology is consequently a link between geosciences and engineering sciences. For the engineering geology, problems in technical environmental conservation are of increasing importance.

The department of engineering geology is equipped with modern, computer controlled test appliances and carries out investigations of soils and rocks, corresponding to valid standards. The equipment contains triaxial- and box shear-testing machines, permeameter, swell- and shrink-testing machines, compression-permeability-machines and a strength test apparatus of the company CONTROLLS. For the determination of strength- and deformation-characteristics of rocks, a modern, computer based testing system of the company FORM+TEST Riedlingen was installed.

Research fields are the determination of soil physical characteristics of loose soils, stress-strain-behaviour of soils and rocks, swelling analysis of the „Messel oil shale“, slope stabilities in the „Martelltal“ and the special geotechnical characteristics of rubble-recycling-materials and slags from waste incineration facilities.

These works are often carried out in partnership with industry.

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Research Projects


Geotechnical characteristics of rubble-recycling-materials and tests of slags from waste incineration facilities for the use of these components as dike-building-materials (Dt. Bundesstiftung Umwelt, Industry 2002-2004)

Stability of slopes in the UNESCO-world heritage Messel pit

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 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. 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.

In 2002, a georadar equipment has been established as a specific method for near-surface investigations. First results in the exploration of soils, rocks, and river dikes could be achieved on various test sites in SW Germany (see also research reports). The sedimentary geology group hosted the international SEDIMENT 2002 meeting from 29th to 31th May in Darmstadt with 250 participants who came from ten different European countries, from the USA, and Canada.

Staff Members

<table>
<thead>
<tr>
<th>Head</th>
<th>Prof. Dr. Matthias Hinderer</th>
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<tr>
<td>Research Associates</td>
<td>Dr. Annette Götz</td>
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<td>Dr. Jens Hornung</td>
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<td>Katrin Ruckwied</td>
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<td>Nils Lenhard</td>
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Research Projects

Computer-aided global analysis of modern denudation rates in small to medium-sized drainage basins (river loads, reservoir siltation, lake sedimentation) (DFG since 2001)

Sediment budget of Pliocene and Quaternary unconsolidated deposits of the Rheingletscher area, Swiss midlands and the Upper Rhein Graben (DFG since 2002)

Sedimentology and palynofacies of the Upper Cretaceous (Vocontian Basin. SE France) (DFG 2000-2002)

Comparison of Pangaeanean landlocked successions (Upper Triassic): lithofacies make up, reservoir architecture and depositional controls

Fluvial to lacustrine-deltaic sedimentation at southern Junggar-Basin (Triassic, NW-China)

Structural clarification of river dikes at Main and Rhine (SW-Germany) using ground penetrating radar (together with Engineering Geology, Regierungspräsidium)

Early volcanism in central Mexico: implications from the volcaniclastic Tepotztlan formation

Publications

Abel, T.; Hinderer, M.; Sauter, M.; Karst genesis of the Swabian Alb, South Germany, since the Pliocene in Climate Changes - The Karst Record II, A second meeting on karst and palaeoclimatic reconstruction; Czech Republic, Poland and Slovakia, July 27 - August 9, 2000, Geologica Polonica 52 (2002) 43-54.


**Editors:**


Georesources and geohazards

The Georesources and Geohazards Division has been established at Darmstadt University of Technology in 2001. It teaches phenomena and risk management of geohazards (earthquakes, volcanic eruptions, subrosion etc.) and georesources (groundwater, mineral resources, soils), the geology of raw materials, photogeology, and techniques of geographical information systems (GIS). Focus is put on the description of the complex geoscientific interrelationships between different land use forms and possible land use. To be able to specify the uncertainty of possible hazards, risk analysis methods are used. Additionally, emphasis is put on the problem of taking land use decisions implying the development and evaluation of interdisciplinary decision systems.

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Research Projects

Investigation of the architecture of a terrestrial subsidence basin of Plio-/Pleistocene age (Hanau-Seligenstadt Basin) with a sequence stratigraphic approach and regionalization and evaluation of its georesources supported by a geographical information system. One aim of the project is to set up an atlas of the georesources of the investigated area.

Development of GIS-based risk-assessment and decision methodologies for sustainable land- and resource use decisions and evaluation of geohazards associated with different land use scenarios. Regions, where the developed tools and procedures will be tested or evaluated respectively are in the Hanau-Seligenstadt Basin. Furthermore contacts to potential partners in Brazil and Spain are established.
Publications


Geomaterials Science

Geomaterials science investigates composition, microstructure, properties, behaviour and formation conditions of minerals, rocks, melts and fluids. This demands an extensive characterisation of geomaterials and experiments on their behaviour with respect to pressure, temperature, deformation and chemical environment. Of special importance is the factor time, i.e., the question how fast the reactions and processes occur. The time scale covers the range from microseconds to the geologic time scale up to millions of years. Geomaterials science is the materials science of geosciences.

The research program of the Division Geomaterials Science of the Institute of Applied Geosciences is dedicated to the crystal chemistry of the constituents of rocks and materials. We are studying the real structure, phase transformations and deformational behaviour of crystals, predominantly by methods of transmission electron microscopy. Research topics of the last 10 years were: microstructure and properties of high tech ceramics; weathering and corrosion of natural building materials; cooling history of volcanic rocks deduced from the microstructure; microstructure and mineral reactions of metamorphic rocks; formation conditions, thermic and deformational history of meteorites; electronic states and coordination number of crystalline and amorphous phases, especially the quantitative determination of the ratio Fe$^{2+}$/Fe$^{3+}$.

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Research Projects

Intergrowths between amphiboles, talc and chlorite in a metamorphosed ultramafic rock of the KTB pilot hole, Bavaria (DFG)

TEM study on eclogites from the Tauern window, Eastern Alps: the microstructure as result and indicator of metamorphic processes (DFG)
Crystal chemistry and microstructures of Fe$_2$SiO$_4$ – Fe$_3$O$_4$ spinelloids (DFG)
Synthesis and Characterization of Mixed-Valence Barium Titanates

Oxygen Vacancies in Perovskite and Related Structures: Implications for the Lower Mantle

Oxidation state of iron in hydrous mantle phases: Implications for subduction and mantle oxygen fugacity

An interface clusters mixture model for the structure of amorphous silicon monoxide

Strong magnetic linear dichroism in Fe $L_{23}$ and O $K$ electron energy-loss near-edge spectra of antiferromagnetic hematite $\alpha$-Fe$_2$O$_3$

Publications


Technical Petrology

The scientific and educational field of technical petrology is based on fundamental knowledge in magmatic, metamorphic (greenschist facies to ultra-metamorphism) and low-temperature petrology (studies in diagenesis and sub-greenschist facies metamorphism) but also in sediment petrography. The principal effort is concentrated on the characterization and classification of magmatic, sedimentary and metamorphic rocks. 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, and in material sciences. The determination of the genetic history and evolution of rocks through time and space gives, e.g., information for ore and hydrocarbon exploration and the basics on the study of rock and ore deposits for prospection and exploitation interests. To understand mineralization, recrystallisation and petrogenesis of rocks an important effort is focused on tectono-thermal research, tectonophysics and structural geology (from the kilometre to nanometre scale). 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 in our department will be centred on low-temperature petrology with strong relations to applied mineralogy and sedimentology, two other fields of principal interest at the TU Darmstadt.

Technical petrology covers a broad field of studies: - on diagenesis with application in bore hole and geothermal exploration, on clay and carbonaceous materials related with problems in tunnel constructions, - on applied organic and clay petrology (exploration of hydrocarbons), - on rock-water interactions of fluids, contaminated fluids and weathering depending on petrologic variations, - on maceral analysis of coals, - on sorption properties of carbonaceous and clay materials, - on the determination of nano- and microstructures of mixed-layering (rock swelling capacity) and graphitisation structures (refractory quality), - on the improvement of forward numerical geothermal, and maturity, and basin-analysis models (studies on hydrocarbon and fluid migration), - on kinetic models to describe illite aggradations, and smectite-illite reaction progress, and the coalification of macerals, - or on the synthesis of graphite structures and organic matter maturity related to technical aspects, - on recognizing of soot and carbon black in filtering installations or the thermal resistance of organic particles 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 mesoscopic and macroscopic 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 condition are very common. Therefore a broad analytical spectrum must be applied. In general microscopy and basically XRD studies have to be combined with DTA, TGA, isotopic geochemistry, and gas chromatography. Due to the small size, also fluid inclusion studies, AEM, TEM, HRTEM, Raman spectroscopy, EELS and XAS give important hints to low temperature petrologic researches. These techniques have to be used in the same way in a natural or synthetic system.
The main research interests of the study group of R. Ferreiro Mählmann (head of the group since August 2002) are concentrated in the petrologic and petrographic study of tectono-metamorphic orogenic terrains (Alps, Carpathians, Andes). More specifically research is concentrated on diagenesis and low-temperature metamorphism, dealing primarily with pelites and rocks rich in organic matter. Of special interest is the application of different analytical techniques in the study of the metamorphism of organic matter. Here the principal interest is focussed on the study of vitrinite and bituminite macerals, important constituents of coals and the main source for oil and gas formation and economic reservoirs. In low-grade metamorphic studies mineral-disequilibrium is a frequent factor and is documented through the irregularity of the alteration processes of mineral and organic matter reactions. The research is focussed on the application of field-petrology and mineralogical laboratory methods to problems related to equilibrium and disequilibrium conditions between different organic and inorganic parameters. To find a general solution for these kinds of problems field data are combined with empirical deductions and with the results of temperature-time-pressure experiments. The results are used to establish kinetically based models that offer a better constraint of temperatures. Used kinetic models are introduced in commercial forward-modelling packages to get numerical approaches. These models allow the answer to several complex tectono-metamorphic questions (e.g. amount of tectonic load, erosion and exhumation, deformation-metamorphism relations, heat flow history, paleo-geothermal gradients, basin reconstruction, orogenic history). They also provide information related to coal, oil and gas formation, hydrocarbon migration, the potential of hydrocarbon formation, the metamorphic and meteoric fluid flow mechanics and to hydrothermal path-ways in the studied rocks.

The research of the study group of D. Scheuvens and E. Stein (now at University Gießen) focuses on the deformation and metamorphism of crystalline rocks. We try to combine structural, petrological and geochronological data to reconstruct P-T-deformation-time paths of metamorphic and plutonic rocks in order to unravel the orogenic evolution in parts of mountain belts. Our data result both from field and laboratory work with emphasis on micro-structural observations.

The main project of D. Scheuvens is located in the Campo crystalline complex (southern part of the central Alps). The major aim of the project is to discriminate between pre-Alpine and eo-Alpine tectono-metamorphic events to get a better understanding of the orogenic processes that were active during Cretaceous stacking and exhumation in this part of the Alpine belt.

The current project of E. Stein investigates the interplay of plutonism, deformation and metamorphism in the eastern part of the `zone axiale´ of the Montagne Noire (southern France), a classical geological region to study the burial and exhumation of rocks.

A further small project of D. Scheuvens and E. Stein mainly deals with the structural evolution of the eastern part of the Frankensteiner intrusives (northern Odenwald) and its contact aureole from high-grade to brittle conditions.

Two events during 2002 have to be mentioned in addition: i.) R. Ferreiro Mählmann participated with S.Th. Schmidt (Genève) as guest editors of the special issue “Diagenesis and Low-Grade Metamorphism” in the Swiss Bulletin of Mineralogy and Petrology. ii.) Organization as co-convener in Nice (EGS-AGU-EUG Joint Assembly 2003) of the session “Processes at low temperatures: advances in studies of disequilibrium systems”. 107
Staff Members

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Research Projects

Petrostructural and P-T-t-d evolution of the austroalpine Campo crystalline Complex - northern Italy (DFG, cooperation with University Vienna, A and GFZ Potsdam, D)

The pattern of diagenesis and metamorphism recognized by vitrinite reflectance and illite-crystallinity mapping in the Grison Alps of Switzerland (DFG, SNF, cooperation with University Frankfurt a. M., D)

Map of the Alpine metamorphism in the Alps. CMGM subcommission of metamorphic maps

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 Bern, CH and Departement für Zivilschutz, Bern, CH)

Experimental study on the pressure dependence of organic matter, specifically vitrinite reflectance (SNF, USGS, cooperation with University Stanford, USA and USGS high pressure laboratory, Menlo Park, USA)

Laboratory study of vitrinite maturation rate as a function of temperature, time, starting material, aqueous fluid pressure, and oxygen fugacity (PRFACS, cooperation with University Stanford, USA)

Very low grade metamorphism studies in Chile, France, New Caledonia, and Romania (SNF, CEEC/NIS, August Collin Fond, cooperation with University Gießen, D; University Basel, CH; University Genève, CH; Geological Survey of Romania, RO and University of Chile, Santiago de Chile, CL)
Combustion, DTA-TGA, TEM, Raman-spectroscopic, C-isotopic and microscopic studies of carbonaceous material in a metamorphic profile from diagenesis to amphibolite facies (SNF, August Collin Fond, cooperation with University Basel, CH and C.R.E.G.U. Nancy, F)

Effects of tectonic shear strain on phyllosilicates and organic matter (SNF, OTKA Hungary, August Collin Fond, cooperation with University Budapest, HU)

Deformation, fluid flow and mineral reactions along the Glarus overthrust and along the extensional Turba Mylonite Zone, eastern Swiss Alps, Switzerland (cooperation with University Basel, CH; University Genève, CH; University Budapest, HU; Johns Hopkins University Baltimore, USA and C.N.R.S., Marseille, F)

Maturity modelling in nappe tectonic settings, comparison and evaluation of different empiric, numerical, and kinetic based maturity modelling techniques through petrologic calibrations

Alpine metamorphism, specifically low temperature petrologic studies in the Central Alps (cooperation with University Basel, CH, University Vienna, A, University Salzburg, A and GFZ Potsdam, D)

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

**Publications**


Scheuvens, D.: Metamorphism and microstructures along a high-temperature metamorphic field gradient: the north-eastern boundary of the Královský hvozd unit (Bohemian Massif, Czech Republic), J. metamorphic Geol. **20** (2002) 413-428.


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) and National Institute of Occupational Health in Oslo (Norway).

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

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Research Projects

Environmental scanning electron microscopical studies of the hygroscopic behaviour of individual aerosol particles
Exposure to aerosol particles in urban areas (Graduiertenkolleg “Spurenanalytik von Elementspezies: Methodenentwicklungen und Anwendungen, Universität Mainz)

Source apportionment of rural and urban aerosols

Optical properties of complex aerosol particles derived from transmission electron microscopy (MPI für Chemie, Abteilung Biogeochemie, Mainz)

Environmental scanning electron microscopical studies of ice-forming nuclei

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

Publications


Popular Science Publications

Institute of Geography
Human Geography
Urban Geography and Regional Research

Among topics investigated by Urban Geography are factors affecting the functional types of cities and settlements (historical and present), internal spatial structure (e.g. functions and development of the Central Business District, social problem areas), urban systems and networks, localisation and hierarchy of commercial centers, regional expansion (suburbanization) and spheres of influence. In our Institute the regional focuses of studies are the Rhine-Main-area, France and South-Africa.

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Research Projects

Retail trade development, city marketing and regional marketing in South Hessen

Urban development in France: New towns and technopoles

Effects of military conversion on urban and socio-geographic structures

Tourism in the Western Cape Province (South Africa), development and geographical effects
Publications


The Pleistocene climate history of Central Europe is characterized by a high variability, higher than in most other regions of Earth. This is due to the influence of the North Atlantic and its leading role in amplifying Glacial/Interglacial cycles and its interaction with the major transient continental ice masses. Some authors suggest that the glacially important Dansgaard/Oeschger Cycles are induced by internal periodic instabilities of the North Atlantic. Layers of coarse lithoclastics, which occur in North Atlantic sediments (so-called Heinrich layers) are witnesses of periodic wide-spread collapses of the Laurentian ice shield with severe climatic consequences for the climate in Europe. Also, the sudden terminations of the glacial periods can only be caused by short-term changes in the Earth System, such as the onset of the deep ocean circulation in the North Atlantic. The climatic record of the past several hundred thousand years has been recovered in a high resolution from ice cores both from Greenland and Antarctica, showing that the Northern Hemisphere is imposing its climate variability unto that of the southern hemisphere, albeit with attenuated amplitudes.

Historically, geological records from continental Europe were therefore leading in identifying past climate changes, such as is documented in the names of the Interglacial and post-Glacial climate periods of the last glaciation cycle. Further back, however, this record is largely blank (perhaps with the exception of glacial loess covers and isolated paleolimnic records) and the paleoclimatologist needs to recur to the isotopic chronology established from continous marine sediment and ice cores.

Caves, however, provide a protected environment, where continental high resolution records can be found. Specifically the growth of speleothems provides a record which has largely been unread in Europe. This has many reasons. Some of them are methodologically and others are inherent to the cave environment and the speleothems themselves. Also, not many geologist are familiar with the potential of cave speleothems and only few have first hand access to these resources.

Methodologically it was first necessary to develop a dating technique, which could look beyond the time range of the $^{14}$C determination. After initially using U/Th spectrometry, the development of U/Th TIMS dating now allows to use smaller samples and to obtain more precise dates, even for those time ranges, which so far were the realm of the $^{14}$C technique.

The environmental reasons for being so slow in uncovering the cave-based climate record are several. The first is accessibility of the record. Many caves are protected under natural preservation regulations. Others lack sinter, or are only accessible to divers and even if they occur in quarries, where sampling could be conducted, this is often forbidden by the quarry owners or news of the resource reach the university teams too late. But the most discouraging fact is: the sinter in Central European caves appears to be a large jumble of broken masses, all encased in an impenetrable layer of Postglacial and Holocene sinter. This situation is unlike the situation in caves from more southern latitudes, where the stalagmites have apparently grown throughout much longer time periods and appear to be larger and less damaged.
We are convinced that this broken nature of the sinter record is itself a climate record and that it is related to the large and frequent climatic changes in Europe itself, i.e. it has been caused by the wide-spread occurrence of ice in caves under glacial and permafrost conditions. We therefore have essentially a punctuated record, consisting of continuous interglacial and interstadial sections separated by glacial hiatuses. The climate record in Central European caves will therefore need to be pieced together from many individual observations. This is a task which will take many years.

The project "Sinter and Paleoclimate in Central Europe during the Pleistocene" was started in 1999 and continued in 2002.
Alkalinity pump and carbonate precipitation: a comparison of the crater lakes of Kauhako Hawai‘i, Satonda, Indonesia and Niuafo‘ou, Tonga

Stephan Kempe

The present ocean is aerobic and the difference in alkalinity between surface and bottom waters is largely governed by enzymatic precipitation of CaCO₃ near the surface and dissolution of sinking CaCO₃ at depth fueled by a CO₂ release through heterotrophic respiration. In the geologic past the ocean was, however, anaerobic for long periods and the alkalinity was governed by sulfate reduction at depth and enzymatic as well as biologically induced CaCO₃ deposition in highly carbonate supersaturated shallow waters. This system of alkalinity regulation was called “alkalinity pump” (Kempe & Kazmierczak, 1994). The alkalinity pump can be studied in the Black Sea (Kempe, 1990) and in sulfate containing, isolated and deep and therefore stratified water bodies. We studied three craters filled with lakes at sea level for their structure, hydrochemistry and associated carbonates. Two of them, Satonda Crater Lake, Indonesia (64 m deep) and Kaukako Crater Lake, Moloka‘i, Hawai‘i (>250 m deep) are filled with infiltrated sea water, while the Lake on Niuafo‘ou, Tonga, (121 m deep) is filled with water derived from precipitation. All three lakes are stratified and anaerobic at depth. The bottom waters have very high to moderate alkalinites, generated by bacterial sulfate reduction. The associated surface waters have also increased alkalinites, i.e. values higher than in the present ocean. Correspondingly the pH and the saturation index of calcite and aragonite in the surface layers are higher than in the present ocean (i.e. in excess of 8.4 pH and 0.8 SI, respectively). CaCO₃ precipitation consequently is governed by extracellular permineralization of (mostly cyanobacterial) biofilms (manifested as massive microbialites in case of Satonda and Niuafo‘ou and carbonate crusts in case of Kauhako) and not by intracellular, enzymatic biomineralization (as an exception red algae occur in Satonda and one species of gastropod occurs in each of the lakes, as well as ostracods). Alkalinity increases during sulfate reduction caused by the generation of bicarbonate from respired organic matter. This bicarbonate therefore carries a negative carbon isotope signature.
Figure 1 compares the three lakes with regard to their \( \delta^{13}C \) depth profiles, Satonda shows the largest excursions with depth. This negative signature also mixes into the surface layer and causes the resulting carbonates to be lighter in carbon than present marine carbonates. Overturning oceans therefore could cause negative isotopic excursions in the associated shallow water carbonates. This is exactly what is documented for all of the large mass extinction events, suggesting the importance of the alkalinity pump for evolution and for the history of the ocean.
Erosional Caves on Mauna Kea, Hawai‘i

Stephan Kempe

In 2000 and 2001, two large (each ca. 1000 m long) cave systems have been surveyed by a team of the TU Darmstadt on the eastern, heavily eroded flank of Mauna Kea: The Pa‘auhau Civil Defense Cave and the Kukaiau Cave (ThatCave/ThisCave System): Both caves occur in the Hamakua Volcanic Series, the oldest Mauna Kea rocks exposed (ca. 250-60 ka BP). They are the first substantial cave systems documented for lavas of this volcano and the first caves on Hawai‘i showing extensive morphological signs of water erosion.

The Pa‘auhau Civil Defense Cave is a lava tube in origin. This is attested by the presence of the typical morphological elements of a lava tube like secondary ceilings, linings, base sheets, stalactites and lava falls. Nevertheless the cave was heavily modified by a stream which entered uphill and traversed much, but not all, of the cave. It left waterfall walls, polished walls, floors and ceilings, scallops, waterfall ponds, gravel, rounded blocks and mud.

Kukaiau Cave is a still active water cave in which a creek sinks. Its waters resurface in a parallel valley (stream piracy) about 100 m deeper. 200 m above the stream exit, a sump is situated, which has been explored in June 2002 by the author for the first time (see pictures below). Kukaiau Cave is developed in a variety of different volcanic rocks (see schematic geological longitudinal section) and is mostly erosional in origin. The observations sustaining this conclusion include: missing lava tube inventories, characteristics of the hydraulic profile, presence of a base layer (a red paleosol) along which the major section of the upper cave seems to have developed, occurrence of allophane and halloysite which have impregnated the primary porosity causing a locally perched water table, and the geology of the rock in which part of the cave is developed.

The finding of water erosional caves in lavas of Hawai‘i offers a new view on deep seated water courses in volcanic edifices.
Sump Section: A, natural rock dam maintaining water level in Echo Lake; B) Echo Lake, which separates the upper and lower part of the cave and was penetrated in June 2002 for the first time; C) Chute above Echo Lake, here gravel is moved uphill when the cave floods; D) view down the last chute, when the cave floods, the water upwells from here into the vadose, lower section of the cave under a pressure of up to 6 bar.
Groundwater in high-density areas, e.g. big cities and industrialized areas, is often contaminated with organic and inorganic compounds. Emission sources (housing areas, industrial areas, roads, sewers, gas stations, etc.) are usually located close to the water users, hence, the flow path of a groundwater contaminant to potential receptors (e.g. wells) is short (with respect to time and distance). The delineation of an existing contaminant plume using groundwater wells is very difficult as well, because of the many potential emission sources and the probability of overlapping plumes. Moreover, the usually dense setup of buildings, roads, pipelines, etc. makes it almost impossible to install a (good practice) sampling well network. Thus, recognition and quantification of contaminated sites in a city need more integrative approaches. The current project investigates the quality of urban groundwater and the mass transfer of typical urban contaminants along the flow path under the city of Darmstadt using a mass balance concept.

Several sampling campaigns of the shallow groundwater were carried out from winter 1999 to summer 2002 in the area of the city (urban and rural). The groundwater monitoring wells (GMWs) were classed into 3 control planes (upstream-, city-, and downstream-plane, see Fig. 1) perpendicular to the main groundwater flow. Inorganic (cations, anions, several anthropogenic elements) and organic parameters (such as PAH, BTEX) were analyzed using standard methods.

To quantify the groundwater contamination in the high-density area of the city of Darmstadt (highly industrialized, 140,000 inhabitants), we established a hydrogeological model of the area of Darmstadt using all relevant data such as geological profiles from borings, groundwater recharge (considering precipitation, surface sealing, etc.) and discharge (surface, industrial, etc.). The hydrogeological data was processed as a 3-D-model with the commercially available code Visual Modflow. Based on this model, 6 budget zone planes with up to 6 subzones were defined within the model area (Fig. 1) and the water budget for each of the 27 resulting zones was calculated. The water budget and the concentrations of the contaminants were used to calculate mass fluxes and mass balances for each contaminant.

The analysis of the hydrogeological data shows that groundwater flow in the subsurface of the city is generally from East to West, though alteration of flow direction could be detected in several budget zones. Since there is no mentionable contaminant source upstream, it was assumed that all contamination to be found resulted from urban input. Accordingly, the GMWs in the upstream-plane show normal geogenetic background values for all relevant naturally occurring inorganic species. Organic compounds which are typical for urban environments could only be found in traces in many samples, and may stem from atmospheric input. Concentrations increase in the city-plane, directly influenced by emissions from sewer leakage, road traffic, gas stations, etc. Inorganic and organic contaminants (such as chloride, phosphate, sodium, potassium, PAHs, fuel related contaminants, etc.) could be found in various concentrations in the urban groundwater, sometimes reaching the water regulations of the State Hessia. In the downstream-plane, usually a drop of concentrations can be observed.

Fig. 2 shows the calculated fluxes of chloride in the various budget zones. For the non-reactive chloride, a positive budget (pale-grey areas) could be calculated in 5 subzones, mainly in the area with the densest population. As there is no geogenic source for chloride in the study area, chloride from urban sources must be reaching groundwater in relevant masses. All other subzones show negative budgets (dark-grey areas in Fig. 2), which can be explained with dilution phenomena respectively diving of the contaminant plumes below the sampled depth due to recharge. In general, the zones down-stream of the city show negative mass balances.
Fig 1: Model area (dashed line) with groundwater monitoring wells (GMWs) and the defined 27 budget zones/subzones; general groundwater flow from E to W.

Fig 2: Calculated mass fluxes for chloride; general groundwater flow from E to W; numbers in bold italics represent the mass balance for each budget zone.
Recycling materials for river dike construction

H. Vogel

Large quantities of natural materials like sand, gravel or clay are necessary for construction and remediation of river dikes. Until today, large quantities of these materials get extracted in the immediate vicinity of the dikes construction site. This procedure has far-reaching negative effects on the ecosystem near the river on the one hand and on the hydraulic conditions in the underground on the other hand. In the German Industrial Standard DIN 19712 for river dikes, amongst other things, secondary raw materials (slags, rubble materials, ...) are suitable – but not applied until today - for use in construction of river dikes. First chemical, mineralogical and geotechnical investigations have shown, that an at least partly replacement of natural building material by secondary raw materials will be possible. For testing these new materials in reality, a test-dike will be built and long term studies will clarify, if the secondary materials will be suitable for use in river dike construction. Main topics of the investigations are the geotechnical suitability and the possible influence of the recycling materials on the environment.
Sediment budget of Pliocene and Quaternary unconsolidated deposits of the Rhine Glacier Area, Swiss Midlands and the Upper Rhine Graben

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The Pliocene and Quaternary unconsolidated rocks of the Alpenrhein valley / Bodensee amphitheatre, Hochrhein, Swabian terrace landscape, Swiss Midlands and the Upper Rhine Graben together with its Alpine drainage areas represent an almost closed denudation-accumulation system. Based on a newly developed combined stratigraphy valid in all five landsystems and an extensive data base (e.g. drillings, outcrop studies, mapping, seismics, pollen analysis) the sediment volumes of a minimum of four glacial megacycles will be quantified in a project within the ICDP framework by using an electronical data base and GIS techniques. New insights are expected into the morphodynamic response of the Alps to climate change and the interplay with their uplift, the mechanisms of the growth and decay of Alpine foreland glaciers and the morphogenesis of the Alpine foreland inclusive changes in the drainage pattern. The sediment volumes will be compared with heavy mineral distributions and dating results to identify sediment sources in the Alps and shifts of the glacial and fluvial drainage systems over time. This linkage will also allow for a control of the number and magnitude of glacier advances into the Alpine foreland and the Quaternary denudation history of the Alps. A great number of scientific and commercial drillings have been analysed and put together in a sequence stratigraphic framework. The regional interconnection of these point data is based on the identification of discontinuity surfaces which define the sediment volumes of the various glacial megacycles. Until now, we quantified three megacycles (MEG, Riss, Würm) in Upper Swabia and the Upper Rhine Graben with the stratigraphic base level concept. To control the results of our litho- and eventstratigraphic approach, we will use palynological and heavy mineral investigations. Further, we started to collect samples for OSL and TIMS U/Th dating.

All data will be handled in a digital database and analysed by GIS techniques. The results and the methodological framework of the project will have implications not only for the climate-driven evolution of the Quaternary rocks in Southern Germany but also for their use as raw materials and aquifers.
Cross section through the Quaternary and Pliocene sediments of the Alps-Upper Swabia- Hochrhein-Upper Rhine Graben. In the Alpine valleys, only deposits of the Last Glaciation are conserved. Also in Upper Swabia, sediments of the Last Glaciation dominate. Basin fills of the Penultimate Glaciation and the Most Extensive Glaciation are only preserved in a distal position. These basin fills are external terminated by the dedicated end morains. The Hochrhein, in first line, is dominated by sediment bypass. So we only find river terraces. The Upper Rhine Graben is the main sediment trap and here we find the eroded material of previous Upper Swabian basin fills. We connect these areas with an sequence- and event stratigraphic approach and therefore link bounding discontinuities in Upper Swabia with bounding continuities in the Upper Rhine Graben.
Structural clarification of river dikes at Main and Rhine (SW-Germany) using ground penetrating radar

J. Hornung, H. Vogel, T. Schiedek, M. Hinderer

Dikes along rivers are a common way to protect urban as well as agricultural areas from floods. Along the Southwest German rivers Rhine and Main construction of dikes started in medieval times and every generation improved the existing dikes, increased their height, repaired broken ones and added new ones. All these activities are not or insufficiently documented which makes it difficult to decide whether a dike is safe, need to be renewed or completely reconstructed.

To investigate the internal structure of a dike non-penetrative methods should be preferentially used to avoid obvious or hidden damages. Ground penetrating radar is a method to overcome this serious problem. Electromagnetic radiation is send into the subsurface and deflected at boundaries where the electrical properties change (conductivity and dielectricity). Lithologically this may reflect changes in grain size, sediment composition, mineralogy or water saturation. We used a SIR 2000 ground penetrating radar from GSSI with shielded bistatic 100 MHz and 200 MHz antennas. For structural clarification the 100 MHz center frequency revealed the best results. It could be shown that the separation of the transmitter and the receiver has a significant influence on the quality of the data.

At several locations of the Rhine river (Biebesheim) and the Main river (Offenbach) about 3 km of radar lines were measured. The data showed structural inhomogeneities within the dike such as intercalated layers (feature of construction), construction stages with outpinching wedge shaped dike-bodies, failure structures, possibly effects of piping or ancient breakthroughs. The intensity of amplitudes could be used to estimate qualitatively the clay content of the construction material or to detect wet zones. The observations were calibrated and proved by drillings. In the subsurface at the landward or riverward side of the dikes ancient drainage channels, sand filled river beds and other structural inhomogeneities could be detected which may represent potential flow paths undermining the dikes during flood periods.

It could be shown that ground penetrating radar represents a good tool for structural clarification of the dike, its fore- or backyard and if properly calibrated for characterisation of construction material. Security inspection drillings are regularly undertaken in remote areas every km, in areas of specific interest every 0.1 km (directly on the dike). Radar investigations are a quick, cost-efficient and reliable tool to detect dike-conditions either for closing the lack of data between drill locations or to better place and minimize drillings.
With the help of ground penetrating radar structural inhomogeneities such as piping, different materials, faults or failure structures could be interpreted in river dikes and in its subsurface, so less observation drillings could be placed at more important locations.
Dehydration reactions of (OH)- and/or (H$_2$O)-bearing minerals are common metamorphic processes occurring, for example, during the subduction of crustal lithologies into the upper mantle. A large number of hydrous, rock-forming minerals such as amphibole, chlorite, and mica contain brucite-like structural components. Brucite is therefore a model compound for the study of the structural break-down resulting from dehydration of such rock-forming minerals. Brucite Mg(OH)$_2$ crystallises in the sheet-like CdI$_2$-structure, where the hydroxyls form a hexagonal close-packed array and the Mg ions occupy octahedral interstices between alternate sheets. The O-H bonds are exclusively parallel to the crystallographic $c$ axis. Viewed in a direction perpendicular to the $c$ axis, the hydroxyls form planes alternately above and below that of the Mg ions. Adjacent hydroxide planes are held together by weak interactions between hydroxyls. In brucite, the O ions are threefold coordinated by Mg ions. Dehydration of brucite at elevated temperatures results in the formation of cubic periclase MgO. Periclase adopts the NaCl-structure with Mg and O both present in octahedral coordination. In contrast to brucite, the oxygens in periclase approach a cubic close packing. Therefore, dehydration of brucite and the resulting formation of periclase must be accompanied by a rearrangement of the packing sequence of oxygen layers.

In situ study the dehydration of brucite and to monitor the crystal structural evolution from brucite to periclase, we used a combination of transmission electron microscopy (TEM) techniques involving selected area electron diffraction, electron energy-loss spectroscopy and conventional and high-resolution TEM techniques. CTEM shows the immediate onset of decomposition and mobilization of water under the electron-irradiated area. The dehydration starts at the rim of hexagonal brucite platelets and proceeds towards the core. Dehydration is accompanied by a morphological shrinkage of 5% and 10–20% in the crystallographic $a$- and $c$-directions, respectively. The volume contraction occurs first in the rim and then takes place in the center of grains. Low-loss EEL spectroscopy suggests, however, a change in the local mass thickness of 50–55% parallel to the $c$-direction. Based on these observations, the porosity in the dehydrated material was estimated to be 37.5–50%. HRTEM shows that the decomposition product MgO is composed of numerous, tiny crystallites and voids. Electron diffraction reveals a topotactic relationship between original brucite and the resulting decomposition product with [0001]$_{\text{Bru}}$ // [111]$_{\text{MgO}}$ and [11$ar{2}$0]$_{\text{Bru}}$ // [1$ar{1}$0]$_{\text{MgO}}$. In the time course of dehydration, the originally sharp diffraction spots of brucite become diffuse and lens-shaped, whereby the shape of spots may reflect the shape and limited long-range order of resulting MgO crystallites. Since the porosity of the dehydrated material is only slightly smaller than the maximum theoretical porosity of 54%, we conclude that only a small fraction of the voids is transported out of the aggregates.

The analysis of the energy-loss near-edge structure (ELNES) and the extended energy-loss fine structure (EXELFS) of the O K edge for threefold-coordinated oxygen in brucite and sixfold-coordinated oxygen in periclase is reported to yield highly accurate information on the local atomic environment of the oxygen atoms, especially the coordination numbers and Debye-Waller factors. A time-dependent or rather electron irradiation-dependent series of O K-edge ELNES spectra measured on the synthetic brucite powder reveals the distinct effect of electron irradiation-induced decomposition and dehydration (Fig. 1), where the spectral features change from the first spectrum, acquired after 10 seconds, to the O K ELNES, acquired after 70 s irradiation time, which is very similar to the O K edge of periclase. In Fig. 2, the magnitude of the Fourier-transform of $|\text{FT} (\chi k^3) |$, known as the radial distribution function...
(RDF) of the O K-edge EXELFS, is presented for intermediately and completely dehydrated states and compared to the RDF of periclase. All RDFs display a very intense peak at a modified radial distance $R' = 0.175$ nm corresponding to the first coordination shell consisting of Mg ions around the excited O ion. The intensity of the first shell peak, however, is changing dramatically by more than a factor of 2 from nearly “fresh” brucite to the dehydrated phase, because it is directly related to the O coordination number $N$ and the Debye-Waller factor. Based on irradiation-induced changes in the coordination number, Debye-Waller factor and the morphological contraction, the water loss was quantified in order to examine reaction kinetics according to the Avrami equation. The rate of the isothermal heterogeneous solid-state decomposition reaction of brucite $\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}$ is interpreted as a complex three-stage process: (i) In the first step, the decomposition reaction proceeds via an interface-controlled process, starting at the rim of brucite, whereby water escapes through the basal plane. (ii) The dehydrated lattice collapses then at the rim, whereas the core region is still hydrated. To further dehydrate the grain, the voids have to interconnect and rearrange in the form of a network slowing down the decomposition reaction resulting in a diffusion-controlled process. (iii) Finally, the pores are interconnected and reach the surface. The dehydration accelerates and is again an interface-controlled process. Results on this subject may provide fundamental information on the mobilisation of water in rocks.

![Fig. 1: O K-ELNES spectra from a damage sequence from fresh (irradiation time $t = 10$ s) to dehydrated (irradiation time $t = 70$ s) brucite compared to periclase.](image1)

![Fig. 2: Magnitude of the Fourier-transform of $|\text{FT}(\chi k^2)|$, the radial distribution function for the O K edges of a dehydration sequence of brucite and of periclase. The irradiation times and the corresponding coordination numbers $N$ are described. All first coordination shell peaks are located at modified radial distances of $R' = 0.175$ nm. Some of the spectra have been shifted for clarity, but are all plotted on the same intensity scale.](image2)
Laboratory Study Of Vitrinite Maturation Rate As A Function Of Temperature, Time, Starting Material, Aqueous Fluid Pressure, And Oxygen Fugacity — Corroboration Of Prior Work

Rafael Ferreiro Mählmann and Gary W. Ernst
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Kinetic investigations were performed on disaggregated samples of angiosperm and gymnosperm xylite (mainly pure huminite fragments) at 2.0 kbar aqueous fluid pressure and oxygen fugacity defined by hematite-magnetite and magnetite + quartz-fayalite buffers. Individual experiments lasted from 5 to 204 days. The rates of vitrinite reflectance (VR) increase were evaluated at 200, 250, 300, and 400 °C isotherms; experimentally determined, approximately steady-state values for the mean %Rr are 0.54, 0.74, 1.10, and 2.25, respectively. For geological lengths of time, appropriate values of %Rr = K0t0.076 (where K0 is a function of temperature, and t is in days). The overall activation energy describing the kinetics of devolatilization reactions responsible for increase in VR measured in our experiments is 21.8 ± 0.3 kJ/mol. Combined with earlier published rate studies conducted by our group we conclude that the rate of vitrinite maturation is virtually unaffected by oxidation state, “wet” versus “dry” conditions, and nature of the starting lignitic material (conifers, hardwood). To a small extent, elevated lithostatic pressure retards the rate of increase in VR. Different, nonsystematic trends are observed for the resinite-exudatinite-bituminite present in the lignite material and in low temperature and short runs. Strong disequilibrium was recognized in short runs of the 200 and 250 °C isotherms. These new run data demonstrate that VR is chiefly a function of temperature and time. In support of earlier field, theoretical, and laboratory studies, for all but geologically insignificant time intervals, vitrinite reflectance is an appropriate proxy for host-rock burial temperature.
Temperature Determination Between 50 And 270 °C Through Fluid Inclusion Microthermometry And Vitrinite Reflectance Values In The External Parts Of The Central Alps

Josef Mullis*, Monika Wolf** and Rafael Ferreiro Mählmann

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Fluid inclusion homogenization temperatures in prismatic and synkinematically grown fibre quartz from 40 Alpine fissures in external parts of the Central Alps were compared with the vitrinite maturation rank determined by vitrinite reflectance \%R_I / R_{max} of the surrounding rocks. As the measured higher hydrocarbon- (HHC) and methane-bearing water-rich fluid inclusions are related to water-bearing higher hydrocarbon- and methane-rich fluid inclusions controlled by fluid immiscibility, their homogenization temperatures reveal entrapping temperatures. Earliest prismatic (without decrepitated fluid inclusions) and fibrous quartz growth in diagenetic and low-grade metamorphic rocks occur close to the maximum heating temperatures. The homogenization temperatures of higher hydrocarbon-bearing water-rich fluid inclusions can be used as a geothermometer between 50 and 200 °C, and corroborating prior work for methane-saturated water-rich fluids to the upper limit of the methane stability = 270 °C.

The process of vitrinite maturation is irreversible and the level of organic maturity is basically the product of temperature and time; pressure has a minor influence. Based on experimental data, numerical kinetic models and maturity inversion techniques it is possible to derive thermal histories from vitrinite reflectance data in sedimentary basins and also in orogenic belts as recently demonstrated for some Helvetic units. Thus determined diagenetic to metamorphic temperatures, calibrated through fluid inclusion microthermometry give a much higher direct control to maturity models used.

In the temperature range from 50 to 270 °C, the following relationship between fluid inclusion homogenization temperatures and vitrinite reflectance for an orogenic belt like the external parts of the Central Alps has been established:

150 °C \ VR = 1.3 ± 0.2 % End of the oil window; oil/wet gas,

200 °C \ VR = 2.4 ± 0.4 % Transition: Higher hydrocarbon zone/methane zone (\geq 99 mol\% CH_4 of hydrocarbons),

240 °C \ VR = 3.8 ± 0.5 % Transition: Diagenetic/low-grade anchizone

270 °C \ VR = 6.0 ± 0.8 % Transition: Low-grade anchizone/high-grade anchizone. End of the methane stability (gas window).
Retail trade development, city marketing and regional-marketing in South Hessen

T. Blau, S. Gutberlet, T. Lindstaedt, H.-D. May

In the last years new forms of retail developed and thereby new hierarchies of locations. One main task is to analyse new sites and types of shops in the Rhine-Main-Region (e.g. shopping centers, factory outlet centers, stations, airport).

Emphasis of the first research was Frankfurt Airport as a new location of retailing. This airport is the location for a wide range of offers of retail and services to the consumer. In their composition, the offers resemble the arrangement of a conventional shopping center. It was determined that today there are 188 shops at the airport, which are visited not exclusively by passengers, but also by persons from the periphery.

Our interview in August 2001 led to the result that the most frequently used areas are the shops and restaurants. We determined that the meaning of the retail trade at the airport is very important (see Fig. 1).

As already found out, the airport is a competitive location to the inner city of Frankfurt. We were able to show that with the airport a new coverage emphasis developed in the Rhine-Main-Region. This new location is standing in competition to the inner cities of the surrounding large towns.

As further new locations we currently examine new kinds of associations of special stores outside the inner cities, for example the one in Sprendlingen or, respectively, factory outlet centers.

Other main topics are the fluctuations of retail and the advancing structural changes in selected cities in the Rhine-Main-Region. There have already been studies about the inner city of Darmstadt (Gutberlet, 2002). In the following map, one of the first results of this investigation is shown.

Fig. 1: Most frequently used areas at the airport
Source: Blau 2002
It is obvious that within three years, from 1999 to 2002, several fluctuations occurred, mainly due to non integrated retail, especially “green lawns”. This could be proven by an interview series with the concerned shop owners in the inner city of Darmstadt. Within the fluctuations, an increase of “textilisation” and “filialisation” could be witnessed.

The comparison of the liquidation of shops relating to the individual branches derives differentiated information concerning the fluctuation. Particularly the clothing industry exhibits a strong fluctuation: 18 openings are confronted with 14 close-downs. Within the range, in the branches household goods, garden needs and furniture 14 openings and 19 close-downs as well as in the category leisure articles 15 openings and close-downs could be observed. However, fluctuation in the other branches is relatively strong as well. Only the categories textiles, shoes, hotels, cinema, pleasure and electronics show only few changes.

Another focus of the project is to investigate if city marketing is an adequate modern instrument for an integrated development to secure or to increase the attractivity of the inner city. The diverging concepts of city management in different cities of the Rhine-Main-Region will be compared and examined in regard to whether they prefer an individual city marketing to assert themselves against the surrounding competition or whether they work together with the aim to improve the regional image of the Rhine-Main-Region.

Another main topic of this project focusses on regional marketing. This part of the project is just in an initial stage, in preparation for the exploration work.
The growing tendencies of globalisation concerning the economy force a tougher competition, inducing the regions to enter into a kind of business rivalry. Single communities are not able to stand this fierce competition beyond regional networks. Great importance is placed on the cooperation of communities in organized regions or superior associations.

Particular cases are the organisation of intermediate regions between agglomerations just as regions which are overlapping several counties. As a first area for the investigations the zone between the agglomerations of Rhine-Main and Rhine-Neckar has been selected. Here different regional organized units are established, such as: Rhine-Neckar-Triangle, Regional Planning Association Rhine-Neckar, Region Starkenburg, Planning Association Agglomeration Frankfurt-Rhine-Main, IHK Forum Rhine-Main, Metropolitana, or the various terms of the Bergstrasse. These regional delimitations are in some cases overlapping.

The concepts and strategies in regional-marketing of those delimitations are analysed at the moment. As a next step, the components image, regional identity and acceptance of regions will be under review about their usability in a regional concept for this intermediate zone.
Military Conversion on Urban and Socio-geographic Structures
Direct and Indirect Effects on Communities in Rhineland-Palatinate

D. Basmer, H.-D. May

The research project aims to determine the direct and indirect effects of military conversion of former military sites using case studies in Rhineland-Palatinate. On one hand, the project focuses on impacts of troop reductions on capacity utilization of urban infrastructure as well as on supply and the configuration of central places. On the other hand, socio-geographic changes are analysed by monitoring the influx of new population groups on former military property.

Contrary to the common opinion the research literature, first mappings and socio-empirical surveys of retailers in Bad Sobernheim indicate only low structural effects. Retail has adapted to the change in consumer demand flexibly and very fast.

The conversion-related change in social structure was analysed in the case study of Sohren, located in close proximity to the former US-Airbase Hahn. Ethnic German migrants from Russia were settled in the former US military housing space and make up to about 35% of the 3,600 inhabitants of Sohren.

The current analysis of a representative interview of 200 households by means of a standardized questionnaire produced first intermediate results. Significant differences were found in food supply. Ethnic German migrants visit mainly super- and consumer markets, while the long-time residents more often buy in smaller grocery shops (fig. 1).

Furthermore, differences were found in recreation behaviour (fig. 2). The long-time residents place higher esteem on clubs as important parts in recreational activities and social life within the community. In contrast, ethnic German migrants seldom take part in this offer. The results of this housing survey in Sohren show that conversion-related changes in behavior and demands of the different social groups were found. In addition, integration problems were demonstrated.
Geographical studies of tourism in the Western Cape Province (Republic South Africa) since the end of apartheid

I. J. Demhardt

The project analyses the increasing impact of tourism on the economy as well as the change of landscapes and urban spaces. It explores this development on various levels of investigation engaging questionnaire surveys and functional mappings.

The macro level identifies main international and national factors regulating the recent tourism development as influence of (post-)apartheid, rapid urbanisation and third world demographic patterns with special consideration to AIDS and crime. Against this, backdrop structures of national administration and the tourism industry are analysed and the ruling patterns of domestic and foreign demand established.

A first in regional tourism research in South Africa is the in-depth investigation of the Western Cape Province as meso level. For that area relevant physical and human factors were identified and the role of Cape Town as provincial capital and primate city of tourism for the whole of South Africa was evaluated. Furthermore recent tendencies in provincial tourism development, tourism administration, strategic potentials as well as the domestic and foreign patterns of demand are explained.

On micro level, case studies were undertaken to investigate the highly variable and rapidly changing local tourism profiles on both supply and demand sides of the tourism industry. Four rural settlements (Franschhoek, Stellenbosch, Montagu and Clanwilliam with Wupperthal) were identified covering the whole range from outright mono-structures down to initial stages of tourism development.
Diploma Theses


M.A. Theses


Kosub, M.; Das Image der Region Nordhessen als Standortfaktor der Wirtschaftsförderung – Wie sieht das Image der Region aus und welche Rolle spielt dabei die Bezeichnung „Nordhessen“?, Urban Geography and Regional Research, August 2002.


**PhD Theses**