



Editorial

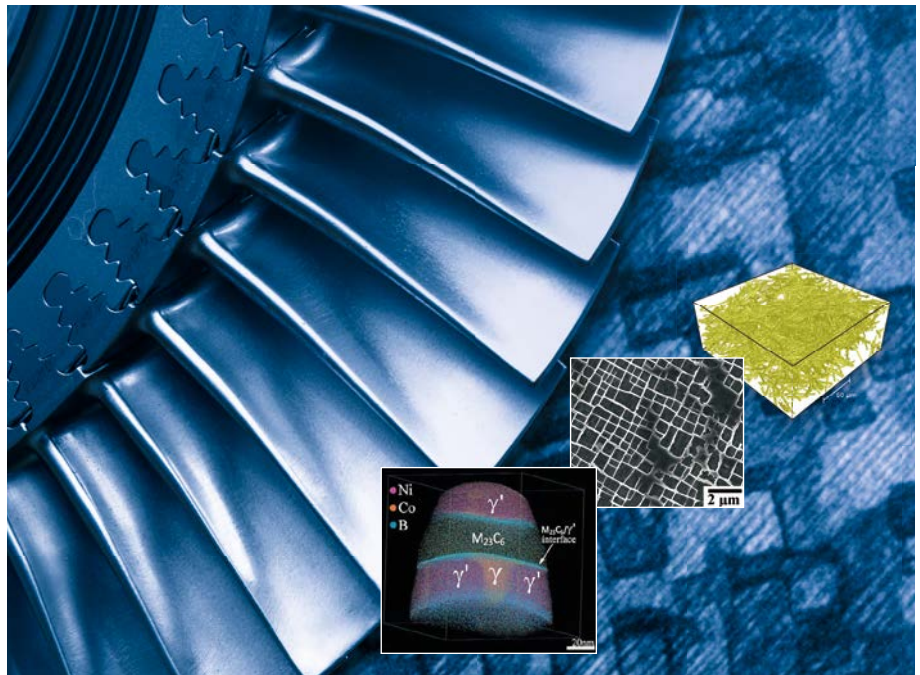


DEAR READER,

The 9th issue of our newsletter series provides information about two new large-scale projects initiated by the Materials Research Department (MRD): the establishment of the new Sonderforschungsbereich-Transregio 103 on Superalloys and the successful application for a new research building, ZGH, which will focus on interface-dominated high performance engineering materials. Furthermore, this newsletter delivers insights into five exemplary research projects which are carried out by MRD scientists. These contributions highlight chemistry-, physics-, modeling- and engineering-aspects of materials science: From ultrafast optical materials spectroscopy via new materials for solar hydrogen production to characterization of phase transformations by nanoindentation and atomistic simulations.

Yours Sincerely,

Prof. Dr.-Ing. Alfred Ludwig



ZGH: A New Materials Research Building for Interface-Dominated High Performance Engineering Materials

Around 40 million euros were granted from the Joint Science Conference of Germany (Gemeinsame Wissenschaftskonferenz, GWK) in the program „Forschungsbau“ for a new research building with scientific infrastructure at RUB which will develop the next generation of interface-dominated engineering materials.

When ZGH will be finished in 2016 in the area between buildings IA and IB, about 80 scientists will perform their interdisciplinary research work in the ZGH („Zentrum für Grenzflächendominierte Höchstleistungswerkstoffe“: Center for interface-dominated high performance engineering materials) on an effective area of about 2,800 square meters.

The research concept of ZGH is based on the expertise of the materials scientists who are organized in the Materials Research Department (MRD) at the RUB. The scientific projects of ZGH will come from about 20 groups: in addition to RUB

scientists, researchers of the Max Planck institutes of iron and coal research in Düsseldorf and Mülheim/Ruhr, as well as at the Jülich Research Center and the German Aerospace Center are involved. ZGH will extend contacts to leading institutes and the industry in materials science.

Producers and users of high-performance materials will benefit from the expected ZGH materials innovations. A fast transfer of scientific results into industry is envisaged. Several new scientific groups will foster early career researchers. The ZGH will establish itself as an interdisciplinary center which offers the best conditions to foster early scientific independence. Whether turbine blades for airplanes or for power generation, electrical/hybrid drives or fuel cells and catalytic reactors – a long lifetime in harsh environments (e.g. high pressure, high temperature, aggressive surroundings) is the main requirement of

➤ high-performance materials. These materials exhibit high structural integrity and simultaneous multifunctionality. The interfaces of these materials can improve the mechanical properties and create new chemical and/or electronic functions.

Materials design by interface engineering

Metallic, semiconducting and dielectric materials will be investigated with a focus on the scientific understanding and design of interfaces. In three main topics mechanically, chemically and physically dominated high-performance materials will be developed by fundamental understanding and control of interfaces on the atomic scale. Results will be transferred to macroscopic materials. The researchers will design novel materials with new combinations of structure and functions. An intensive interdisciplinary collaboration in the fields modeling, synthesis, processing and characterization of materials is needed. New high-performance materials are essential with regard to energy, mobility and environment in a country which is poor in natural resources.

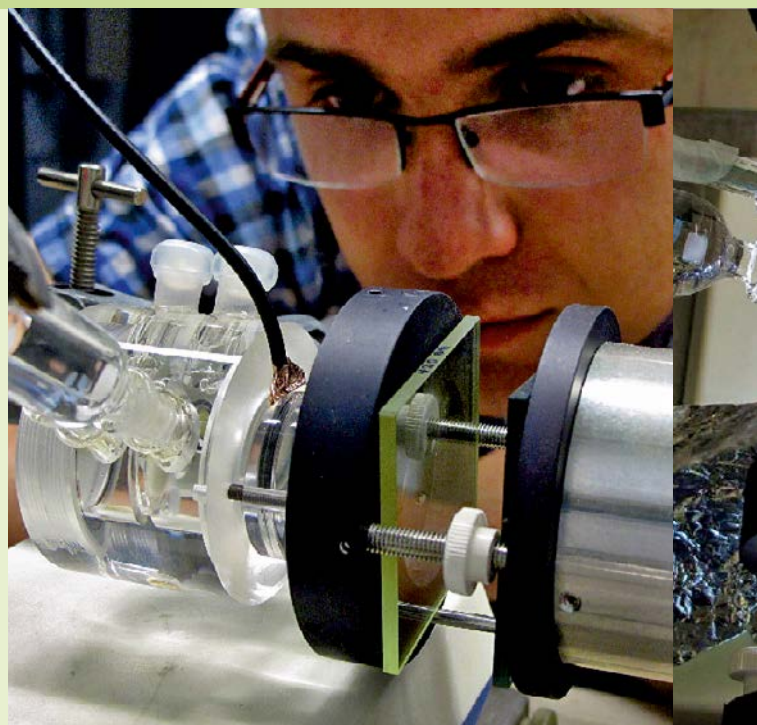
Combination of functional and structural properties

ZGH will house the latest methods for materials characterization such as aberration-corrected transmission electron microscopy and a three-dimensional atom probe. Furthermore clean room facilities will enable the functionalization of surfaces. These new scientific tools will allow a basic understanding of the atomic structure of materials and the systematic development of new materials. The close combination of scale-bridging experiments and simulation on atomic, microscopic and macroscopic scales characterizes the scientific program of the ZGH.

The research concept of ZGH brings together the worlds of structural and functional materials. New materials will be developed using scale-bridging materials characterization instruments. With the ZGH, an internationally important center emerges, in which materials for harsh environments, material interfaces and the combination of structure and function in new materials will be investigated in a world-wide-unique manner.



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New artificial photosynthetic pathways to fuels and other useful materials

The **Photoactive Materials Group** (www.rub.de/photochem) funded by the NRW government ("NRW-Nachwuchsgruppe") has been established within the Faculty of Chemistry and Biochemistry in July 2010. Our research interests combine synthetic chemistry with aspects of physico-chemical characterization and utilization of novel materials as building blocks for functional photochemical architectures and devices.

From the energetic point of view, practically the whole biosphere is driven by natural photosynthesis, a process in which the energy of sunlight is captured, converted, and stored in high-energy chemical bonds of sugar molecules. The development of photochemical systems capable of **artificial photosynthesis**, mimicking thus the natural photosynthesis by driving, for example, the splitting of water into hydrogen and oxygen, has therefore attracted significant interest. Notably, it is particularly the oxygen-evolving water oxidation reaction which is the major obstacle hampering the efficiency of water-splitting devices. Accordingly, one of the fundamental problems in photoelectrochemical water splitting is the development of *cheap, highly efficient and stable* photoanodes which would drive photooxidation of water into oxygen. Such photoanodes should absorb light in the visible range (wave-



Figure 1: In a home-made photoelectrochemical cell the splitting of water into hydrogen and oxygen occurs under visible light irradiation (wavelength > 420 nm) using a newly developed hybrid photoelectrode.

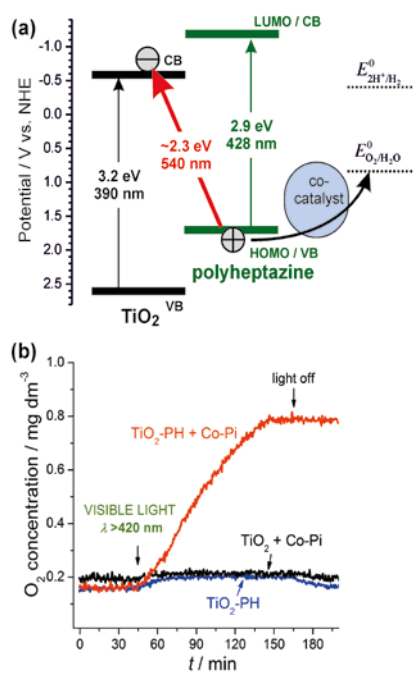


Figure 2: (a) Simplified scheme of the electronic structure of TiO_2 -polyheptazine (TiO_2 -PH) hybrids; (b) TiO_2 -PH hybrid photoanode modified with a CoO_x ("Co-Pi") co-catalyst (red line) exhibits dioxygen evolution under visible light irradiation.

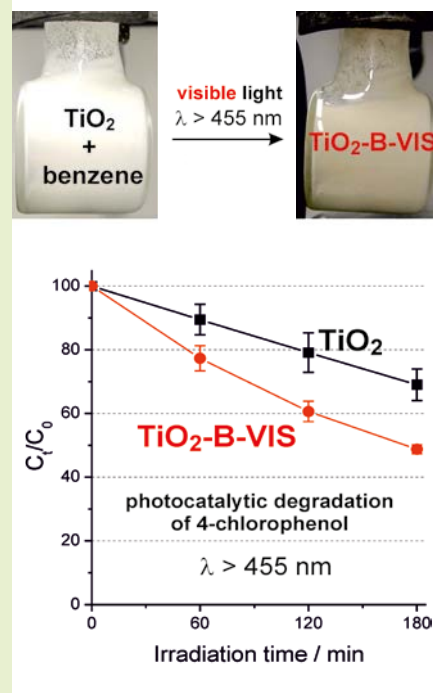


Figure 3: Benzene can be activated by visible light (wavelength > 455 nm) in the presence of TiO_2 , which leads to formation of carbonaceous polymeric deposits on the TiO_2 surface. These photosynthesized surface-modified materials exhibit enhanced activity in photodegradation of phenolic compounds.

length > 400 nm), a major part of solar spectrum. Moreover, they should also have suitable photoelectrochemical (energy of photogenerated charges) and surface catalytic (low overpotential) properties. Low-cost materials fulfilling all these requirements are currently not available. New materials must be developed.

Our group has been therefore recently developing photoanodes based on a novel class of visible-light photoactive inorganic/organic **hybrid materials** – TiO_2 modified at the surface with polyheptazine (Figure 1). Notably, the optical absorption edge of the TiO_2 -polyheptazine hybrid is red-shifted into the visible (2.3 eV; ~540 nm) as compared to the bandgaps of both of the single components – TiO_2 (3.2 eV; ~390 nm) and polyheptazine (2.9 eV; ~430 nm). We were able to show that this is due to the formation of an interfacial charge-transfer complex between polyheptazine (donor) and TiO_2 (acceptor)¹. In other words, the direct optical charge transfer leads to photogeneration of separated charges – electrons in TiO_2 and holes in polyheptazine – whereby the energetic position of the latter allows for photooxidation of water, as evidenced by visible light-driven evolution of oxygen on hybrid electrodes modified with IrO_x or CoO_x nanoparticles acting as oxygen evolution co-catalysts²⁻⁴ (Figure 2). Our cur-

rent efforts focus on improving the photoconversion efficiency of such hybrid photoelectrodes through tuning of the properties and interfacing of all the components involved.

Interestingly, we have also recently shown that simple photocatalytic reactions can be utilized also for **photo-synthesis of materials** with enhanced photocatalytic properties (Figure 3). It is well-known that irradiation of TiO_2 by UV light in the presence of benzene leads to brownish coloration of TiO_2 due to formation of stable polymeric products of benzene photo-oxidation. Surprisingly, we observed that even irradiation by *visible* light (wavelength > 455 nm) leads to brown coloration of TiO_2 . Moreover, the thus prepared modified TiO_2 was found to be more active in visible light-induced degradation of 4-chlorophenol (environmental pollutant) than unmodified TiO_2 . Detailed mechanistic investigations have shown that the better photodegradation properties are due to changes of adsorption/desorption properties of TiO_2 modified at the surface with carbonaceous deposits. This study thus presents one of the rare examples in which the modification of TiO_2 for enhanced photoactivity was achieved *via* an artificial photosynthesis route⁵.

The development of artificial systems that can be utilized for harnessing solar

energy to drive useful chemical transformations is one of the key scientific challenges for the 21st century. We believe that heterogeneous photochemistry, acting at the intersection of synthetic chemistry, materials science, and catalysis, is bound to play a major role in this fascinating research field with great promise for real-life applications.

Literature:

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- ² L. Wang, M. Bledowski, A. Ramakrishnan, D. König, A. Ludwig, R. Beranek, *J. Electrochem. Soc.*, **2012**, *159* (7), H616.
- ³ M. Bledowski, L. Wang, A. Ramakrishnan, A.; O.V. Khavryuchenko, A. Bétard, R. Beranek, *ChemPhysChem*, **2012**, *13*, 3018.
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- ⁵ A. Ramakrishnan, S. Neubert, B. Mei, J. Strunk, L. Wang, M. Bledowski, M. Muhler, R. Beranek, *Chem. Commun.*, **2012**, *48*, 8556.

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Optical Spectroscopy for Materials Research

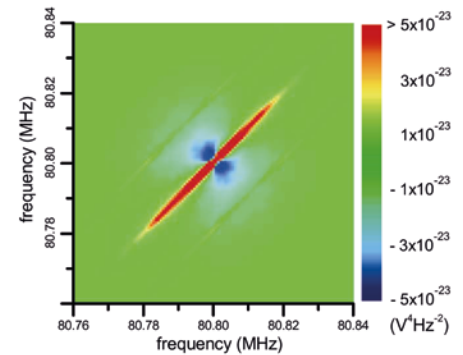
The group Spectroscopy of Condensed Matter at the Department of Physics and Astronomy uses and develops advanced spectroscopic techniques for the fundamental investigation and characterization of materials.

Ultrafast optical spectroscopy is the core activity of our group since its foundation in 2006. The spin dynamics in semiconductors is studied with a temporal resolution down to 100 fs. Semiconductor spin physics is in the focus of intense international research as it might lead to conceptually new electronics (so called spintronics) in the near future when conventional, charge-based electronics will reach its limits of ever increasing miniaturization. Optical methods are perfectly suited for the investigation of spin dynamics as they combine high temporal, energetic and spatial resolution with a high sensitivity to the spin-polarization in a material. We are running a setup for time-resolved Kerr-rotation spectroscopy that has been specifically designed to operate in the blue and ultraviolet spectral range. The group has leading expertise for spin physics in wide-gap semiconductors like GaN. We demonstrated an intrinsic anisotropy of the spin relaxation that is directly linked to the symmetry of the GaN wurtzite crystal structure. A comparison of the spin dynamics in the wurtzite and in the cubic phase of GaN allowed us to highlight the important role played by the symmetry of the crystal lattice. We found world record spin lifetimes at room temperature in cubic GaN. Current and future activities concentrate on the coupled

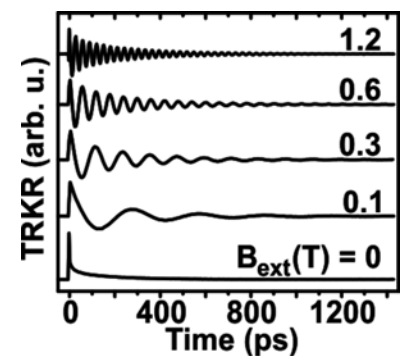
electron-nuclear spin dynamics as well as on the identification of new, promising materials and structures for spintronics.

We further run a setup for time-resolved photoluminescence that allows us to study carrier and spin dynamics with a time resolution of 2 ps, yielding information on important material parameters like, e.g., radiative carrier lifetimes in semiconductors or band-structure parameters like the Landé-g-factor.

Another important activity of the group is the application and development of noise spectroscopy. The systematic investigation of fluctuations in a physical system allows the extraction of important information that cannot be obtained by traditional spectroscopy. The group develops advanced extensions of noise spectroscopy going beyond the usual determination of noise power spectra. We implemented a setup for frequency-resolved two-dimensional correlation spectroscopy with a bandwidth of up to 90 MHz using real-time numerical data processing, including massive-parallel processing on computer graphics cards. This new technique allowed, e.g., the demonstration of purely Gaussian behaviour of $1/f$ resistor noise with unprecedented precision. Currently, we are also working on the application of noise spectroscopy to the study of magnetization



Two-dimensional correlation spectrum of a terrestrial radio signal. The pattern reveals that the frequency modulation (FM) technique was used for signal transmission.



Spin oscillation in bulk GaN monitored by time-resolved Kerr-rotation spectroscopy for increasing external magnetic field.

dynamics in metallic structures using optical ultrafast spin noise spectroscopy and inductive Barkhausen jump spectroscopy.

As a new research line, a setup for the direct determination of temperature changes ΔT in ferroic thin films due to the magnetocaloric effect is established. The direct determination of ΔT is of great importance for the identification of new materials for effective and energy-saving ferroic cooling. The quest for new materials will be conducted in close collaboration with the group of Prof. Dr. Alfred Ludwig who provides thin film material libraries of candidate materials with continuously varying composition. Materials will be further characterized by static magneto-optical Kerr-effect (MOKE) measurements, where we work on ultimate, shot-noise limited sensitivity by, e.g., developing dedicated ultra-low-noise laser systems.



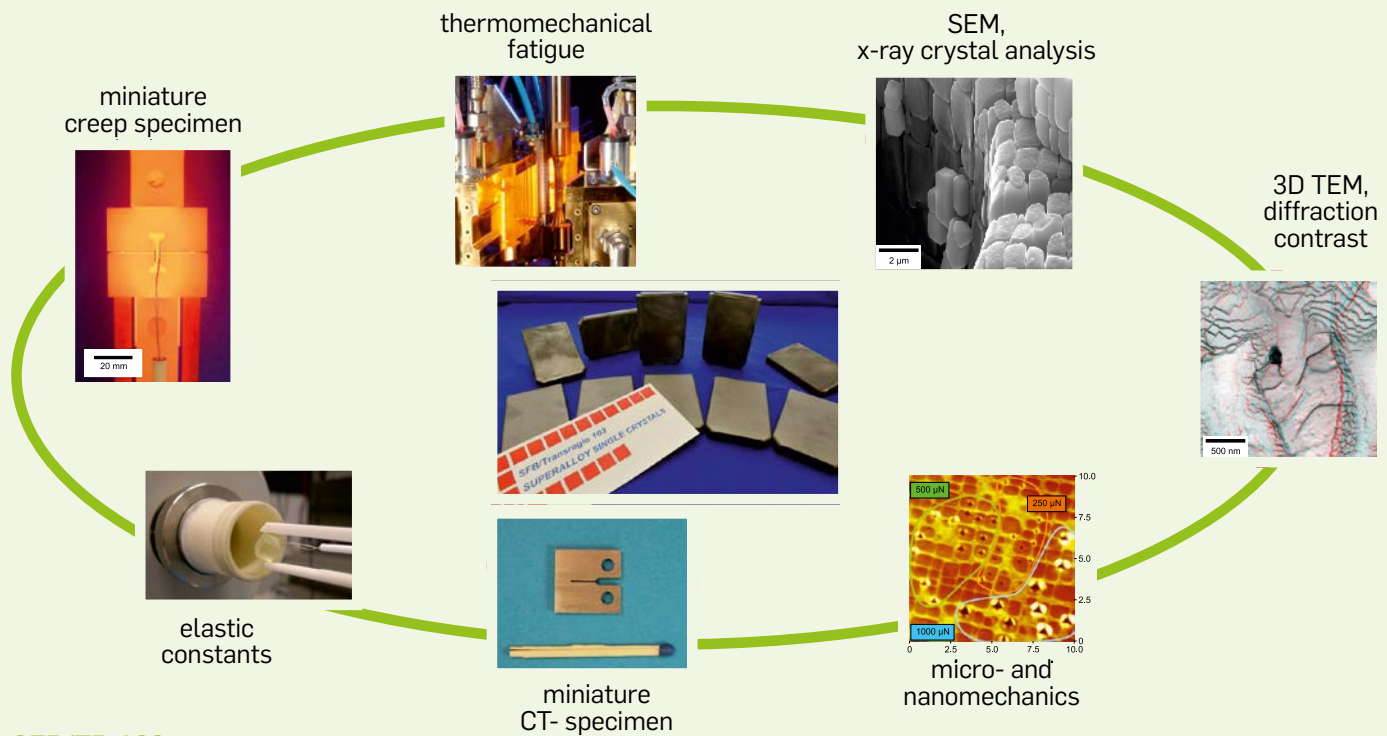
The laser setup for ultra-fast Kerr-Rotation spectroscopy on wide-bandgap semiconductors. Photo by Jens Sundheim.



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SFB/TR 103:

From Atoms to Turbine Blades – A Scientific Approach for the Development of Next Generation of Single Crystal Super Alloys

Single crystal Ni-base superalloys are key materials for turbine blades in modern gas turbines for aero engines and power plants. International mobility and global energy supply rely on this class of high temperature materials. The focus of research in the first 4 year funding period of SFB/Transregio 103 is to clarify open questions related to processing of superalloy single crystals, to the stability of microstructures at high temperatures and to elementary deformation and damage mechanisms.

These new materials demand at first a basic understanding of all aspects of alloy design and performance. This comprises the role of heterogeneities, both on a large scale (dendritic and interdendritic regions) and small scale (γ/γ' -microstructure). It is important to understand how microstructural and atomistic parameters affect thermodynamic equilibria, the evolution of microstructure during processing and high temperature deformation. It includes the exact role of alloying elements, especially d-shell elements. The focus lies on creep deformation mechanisms, microstructural stability (nucleation and growth of new phases, coarsening of the γ/γ' -microstructure), castability (porosity, parameters of the dendritic structure), and surface integrity (oxidation and coatings). More detailed knowledge of materials

properties and elementary processes will be gained through mechanical measurements like e.g. miniaturized creep and fatigue as well as characterization methods like aberration-corrected TEM and 3DAP.

Methods like single crystalline solidification in a cooling bath with an ionic liquid, additive processing using selective electron beam melting, heat treatments under hydrostatic pressure, and coating technologies help to establish specific nano- and microstructures with a better homogeneity.

On the theoretical side materials modeling is applied to materials processing as well as high temperature behaviour – bridging all scales, from atomistic (ab-initio-methods, molecular dynamics) to mesoscopic (discrete dislocation modeling and thermodynamic/kinetic modeling of microstructural evolution) and macroscopic (physically sound constitutive equations).

New alloys should also reflect the availability of strategic elements, e.g. less Re, more Ru, W, Mo, Ge. In addition to Ni-based superalloys, a special effort will be made to explore the high temperature properties of Co-based single crystal super alloys with γ/γ' -microstructures. The results will contribute to improvements in high temperature design and refurbishment strategies.



Within SFB/TR 103, RUB and the Friedrich-Alexander-Universität Erlangen-Nürnberg are the main collaborative partners. They join forces with MPIE Düsseldorf, DLR Cologne, and FZ Jülich. The scientific contributions in SFB/TR 103 come from different areas of expertise, like materials science and engineering, solid state physics and chemistry, scale bridging materials modeling and processing and manufacturing technology. With this innovative approach, SFB/TR 103 researchers aim to make an impact in a key technology, which is important from an economic and scientific point of view. In May 2012, all members and researchers came together during the first interaction week in Erlangen.

On May 21–24, 2012, all members and researchers came together during the first interaction week in Erlangen. The week started with a one day school on basics of Ni-based superalloys (R. Rettig, project B1), on Co-based superalloys (S. Neumeier, project B3) and on thermodynamic and kinetic approaches including CALPHAD



The members of SFB/Transregio 103 at the interaction week in Erlangen, May 2012.
Photo by Kerstin Gebhardt.

➤ (S. Fries, project C6). The participants from the Ruhr-Universität Bochum, the DLR Köln, the FZ Jülich and the MPIE had a guided tour through the research facilities of the material scientists at the Friedrich-Alexander Universität Erlangen. The following days were dedicated to individual project presentations. On Wednesday afternoon, the members of the Scientific and Technical Advisory Board joined the meeting (T. Pollock – UC SB, M. Mills – OSU, R. Reed – University of Birmingham, J. Gabel - MTU, O. Lüsebrink – Siemens AG and T. Wagner – Doncasters). M. Mills gave an overview lecture on dislocation mechanisms which govern the high temperature deformation of single crystal super alloys. Then the STAB members could interact with the individual SFB/Transregio 103 projects during a poster show. On Thursday, G. Eggeler (RUB co-ordinator, mechanical properties), R. Singer (FAU co-ordinator, processing of single crystal Ni-base super alloys), M. Göken (new aspects of single crystal Co-base super alloys), E. Spiecker (characterization), and R. Drautz (modelling) presented overviews of interdisciplinary work in SFB/TR 103. After these overview talks the STAB members retreated to discuss what was presented and to work out recommendations for further work. In parallel, the SFB/TR 103 members had the first general assembly. After a working lunch, M. Mills, the STAB spokesman, communicated the STAB recommendations to the SFB/Transregio 103 members. There were encouraging comments and recommendations with respect to the focus of the work. In the afternoon, all participants of the meeting enjoyed an evening on the “Erlanger Bergkirchweih”.

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Metal oxide photocatalysts for solar hydrogen production

Photocatalysis with semiconductor materials is a very promising method to utilize solar energy for sustainable energy conversion and fuel generation. In the last decades, mixed metal oxides came more and more into the focus of attention as the variety of elemental combinations is promising to realize a plenitude of novel photocatalysts for hydrogen formation but also environmental remediation.

To achieve economically attractive H₂ production from splitting of water, the development of photocatalysts active with visible light accounting for around 43 % of the electromagnetic radiation on the planet's surface is indispensable. However, visible light photoactivity still remains a key challenge since most of the

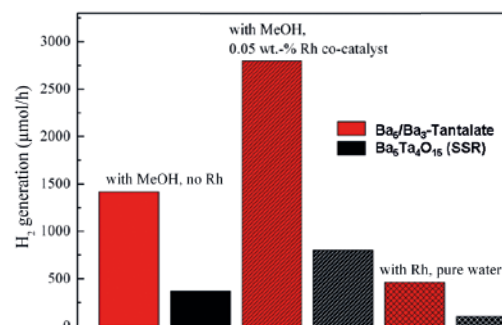


Figure 2: Hydrogen evolution with barium tantalates from 10% MeOH/water suspensions with and without deposited Rh co-catalyst as well as from pure water (with Rh co-catalyst); Ba₅Ta₄O₁₅ prepared via solid state reaction (black) is compared to Ba₅Ta₄O₁₅/Ba₃Ta₅O₁₅ composite obtained via the sol-gel citrate route (red).

The picture right shows the double-walled inner irradiation-type quartz reactor with Hg mid-pressure immersion lamp developed by G.W. Busser and M. Muhler being used for the photocatalytic hydrogen evolution.

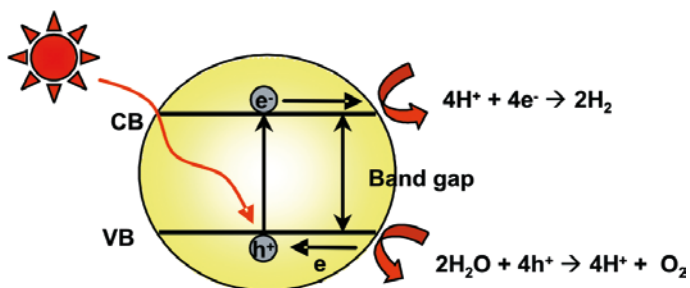
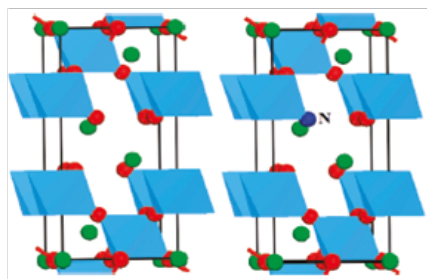


Figure 1: Simple scheme showing the photocatalytic water splitting process,



Structural models for undoped and N-doped $\text{Ba}_5\text{Ta}_4\text{O}_{15}$



Simple beaker glass reaction in the sol-gel based synthesis route.

active photocatalysts have wide intrinsic band gaps > 3 eV. Narrowing the band gap into the visible light region (< 2.8 eV) is therefore an important issue.

Especially mixed-oxide photocatalysts with e. g. layered perovskite structure have been found promising materials to reach this goal because they exhibit open crystal structures for effective band engineering by gas phase doping, and the network of corner-sharing octahedra in particular is a pre-condition for high photocatalytic activity.

Such mixed metal oxide photocatalysts are synthesized in our group by a sol-gel based citrate route.

For example, layered $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ photocatalysts are traditionally synthesized by solid state reaction (SSR). The introduced

novel sol-gel synthesis route using EDTA (ethylene diamine tetraacetic acid) and citric acid as complexing reagents allows lower synthesis temperatures and shorter reaction times. The resulting powders exhibit smaller particle sizes (~ 50 nm) and higher surface areas, typical prerequisites for high photocatalytic activity.

Band gap engineering via anion doping with nitrogen is performed, for example, on layered perovskite photocatalysts $\text{A}_5\text{M}_4\text{O}_{15}$ ($\text{A} = \text{Sr}, \text{Ba}; \text{M} = \text{Ta}, \text{Nb}$). Like e. g. N- and S-doped CsTaWO_6 , these layered perovskites can produce H_2 without any co-catalyst.

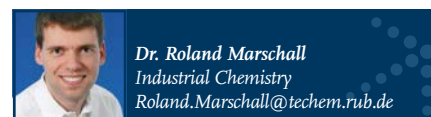
By variation of the educt concentrations in the sol-gel preparation besides of pure $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ also composites containing $\text{Ba}_3\text{Ta}_5\text{O}_{15}$ as a second phase can easily be formed. The presence of $\text{Ba}_3\text{Ta}_5\text{O}_{15}$ has a profound effect on the H_2 generation, which increases drastically for this $\text{Ba}_5\text{Ta}_4\text{O}_{15}/\text{Ba}_3\text{Ta}_5\text{O}_{15}$ nanocomposite in comparison to the pure $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ materials. By addition of only very small amounts of 0.025 wt-% Rh co-catalyst, deposited on the barium tantalate nanocomposites by stepwise photoreduction using Na_3RhCl_6 , the pure $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ generates about 800 $\mu\text{mol/h}$ hydrogen from methanol-containing water; whereas the $\text{Ba}_5\text{Ta}_4\text{O}_{15}/\text{Ba}_3\text{Ta}_5\text{O}_{15}$ nanocomposite, forms almost 2800 $\mu\text{mol/h}$.

$\text{Ba}_5\text{Ta}_4\text{O}_{15}$ exhibits a wide band gap of 4.5 eV, allowing only the absorption of UV light. Already the presence of $\text{Ba}_3\text{Ta}_5\text{O}_{15}$ decreases the band gap by about 0.7 eV. By treatment with NH_3 an effective incorporation of nitrogen into the layered perovskite materials was observed, leading to orange materials with a band gap of only 2.5 eV ensuring absorbance well in the visible light region.

In addition, yttrium and bismuth titanate pyrochlores are optimized in our group, and tested in photocatalytic H_2 production with photodeposited Pt or Rh nanoparticles as co-catalysts. The activity of $\text{Y}_2\text{Ti}_2\text{O}_7$ is greatly enhanced by an excess of 10% titanium, initiating some structural cation interchange and minimization of lattice distortions. The band gap energy of the yttrium titanate is decreased by replacing some or all of the yttrium ions by bismuth. Whereas stoichiometric YBiTi_2O_7 and $\text{Bi}_2\text{Ti}_2\text{O}_7$ are almost inactive, the introduction of high titanium excess of up to 40% results in good H_2 production rates.

Investigating structure-activity correlations in photocatalysis will help to understand mechanisms and will lead to an optimum tuning of ternary and quaternary oxide structures for solar fuel generation. Formation of nanocomposites will help to improve the charge separation in photocatalytic systems.

To generate directly pure H_2 without subsequent energy-demanding cleaning processes, additionally two-compartment cells employing proton-conducting composite membranes are developed and continuously improved.



Structural phase transformations in solids:

Insight from long time-scale atomistic simulations

Structural phase transformations in solids are a key aspect in materials science. Phase transformations determine to a large extent the microstructure and thus the macroscopic properties of a wide range of technologically important materials. Only little is known on the atomistic level about the fundamental mechanisms underlying structural phase transformations, mainly due to the complexity of the problem and the involved time-scales.

In atomistic simulations the atoms are represented by individual particles that interact with each other. A widely used approach to investigate the time evolution in such systems are molecular dynamics (MD) simulations. In classical MD simulations the particles move according to Newton's equation of motion, which can be integrated, if for each particle its velocity as well as position and the resulting forces between the particles are known. Naturally, different atomistic processes can take place on very different time-scale. In metal solids e.g., lattice vibrations have a typical vibrational period of a few hundred femtoseconds whereas diffusion between neighbouring atomic sites occurs on a micro- to millisecond time-scale. Thus, an atom will vibrate around its equilibrium position about a billion times until it diffuses to the next site. Compared to atomic vibrations diffusion processes can be considered as *rare events* (cf. Fig. 1).

To obtain reliable dynamical trajectories of an atomic system MD simulations have to resolve the fastest motion in a system, which are typically the vibrations. On the other hand, the long-time dynamical behaviour is often determined by the rare events. Due to the significant separation of time-scales between the fast vibrations and the rare events it becomes impossible to study the evolution of the system on extended time-scales using MD simulations. One approach to overcome this rare-event problem is to coarse-grain the dynamics. If the dynamics of the rare events can be properly described based on the underlying fast kinetics, then the system can be simulated up to very long time-scales. A stochastic trajectory of rare events is created within *kinetic Monte Carlo* (kMC) simulations. At each time step of the kMC simulation all possible

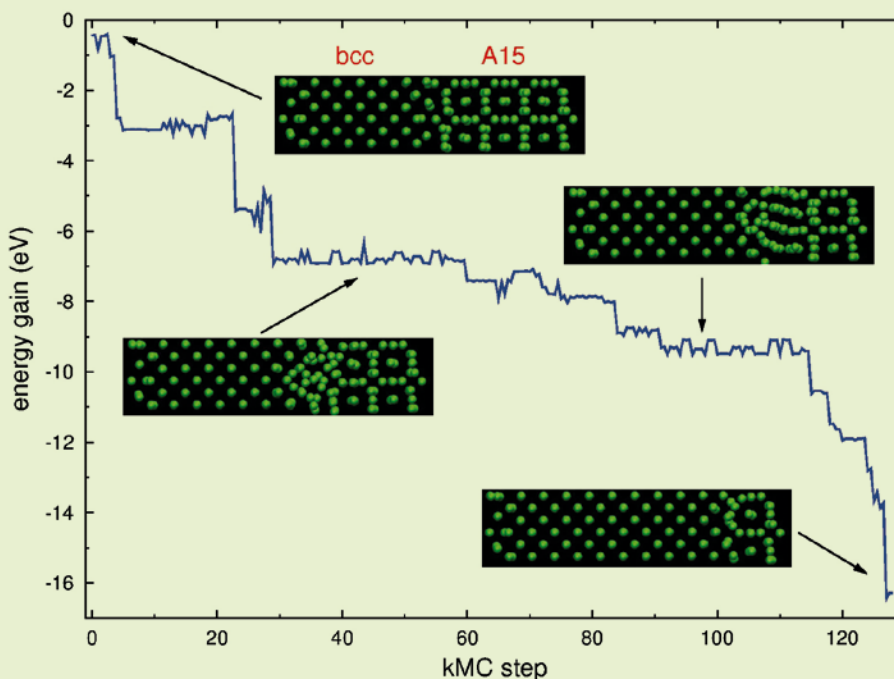


Figure 2: Energy profile of an adaptive kinetic Monte Carlo trajectory showing the solid-solid phase transformation from A15 to bcc in molybdenum. The transformation proceeds via concerted multi-atom processes. Since the bcc-phase is energetically more stable than the A15-phase a considerable energy gain is observed during the transformation.

rare events and their corresponding probabilities to occur have to be determined to evolve the system. For simple processes, as nearest-neighbour diffusion on a lattice, a list of possible rare events and their probabilities can be generated a priori. For more complex systems, as solid-solid phase transformations, involving concerted multi-atom processes the rare events are often unknown and have to be identified on-the-fly. This can be achieved within an *adaptive* kMC approach, where possible rare-event processes are discovered gradually during the simulation.

Snapshots from a trajectory of a solid-solid phase transformation in molybdenum obtained from an adaptive kMC simulation are shown in Fig. 2. Initially

half of the simulation cell is in a body-centred cubic (bcc) structure (left side) and the other half in a topologically close-packed (TCP) A15 structure (right side). During the simulation the A15-phase transforms into the energetically more stable bcc-phase. The growth of the bcc-phase leads to a significant energy gain in the system, which is reflected in the energy profile along the akMC trajectory. The snapshots show that during the transformation quite complex atomic rearrangements take place at the interface between the bcc- and A15-phase, with each rare-event process involving a considerable number of atoms. In this rather small simulation cell the bcc-phase grows layer-by-layer via a number of processes with reasonable energy barriers.

The analysis of such simulations of phase transformations in solids can provide invaluable information on e.g. transformation mechanisms, nucleation, interface mobilities, the effect of strain as well as composition and the importance of point and extended defects. This detailed insight on the atomistic level can then be used as the basis for the development of advanced strategies in modern materials design.

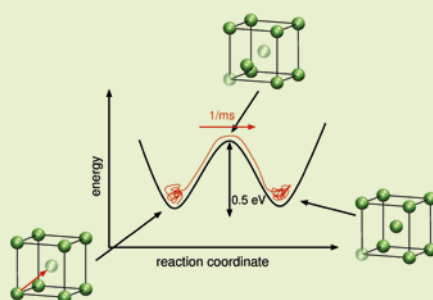


Figure 1: Schematic representation of the energy profile of a nearest-neighbour diffusion process in a solid. Within molecular dynamics simulations the atoms vibrate around their equilibrium position about a billion times before they move from one site to the next. Compared to the vibrations diffusion processes can be considered as *rare events*.



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Atomistic simulation of the kinetics of phase transformations
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Characterization of the local martensitic phase transformation behaviour of NiTi shape memory alloys using nanoindentation

NiTi shape memory alloys (SMA) exhibit a reversible martensitic phase transformation, which can be stress- or temperature-induced. This phase transformation is associated with strains in the order of 8%. Due to these special mechanical properties NiTi SMA are used in various engineering and medical applications, e.g. micro-actuators, stents, or orthodontic wires. Most medical applications make use of the mechanical shape memory effect (pseudoelasticity, PE), where mechanical loading of the austenite (B2) results in the stress-induced formation of martensite (B19'). During unloading, the reverse transformation occurs.

Due to applications of NiTi in miniaturized technical systems, the characterization of the local mechanical behaviour, especially the phase transformation behaviour, is essential for the development and application of these components. To account for the understanding of the mechanical properties and the deforma-

tion mechanisms of NiTi SMA on the micro scale, we perform nanoindentation with definite indentation parameters and investigate the microstructural changes.

Fig. 1a shows an experimental load displacement curve from nanoindentation (spherical indenter tip $R = 5 \mu\text{m}$, maximum load $P_{\text{max}} = 10 \text{ mN}$) of a PE NiTi. This load displacement curve exhibits a typical PE hysteresis and large recovery during unloading. To better quantify and compare the pseudoelastic recovery during nanoindentation, we calculate the remnant depth ratio (RDR) from the remnant depth h_{rem} and the maximum depth h_{max} : $\text{RDR} = h_{\text{rem}} / h_{\text{max}}$. Small RDR values characterize large recovery due to a pronounced reverse phase transformation during unloading. The calculated RDR for this experiment is around 10%. Post-mortem microstructural analysis of the cross section of the corresponding indent is shown in Fig. 1b. The transmission electron microscopy (TEM) image exhibits a full austenitic microstruc-

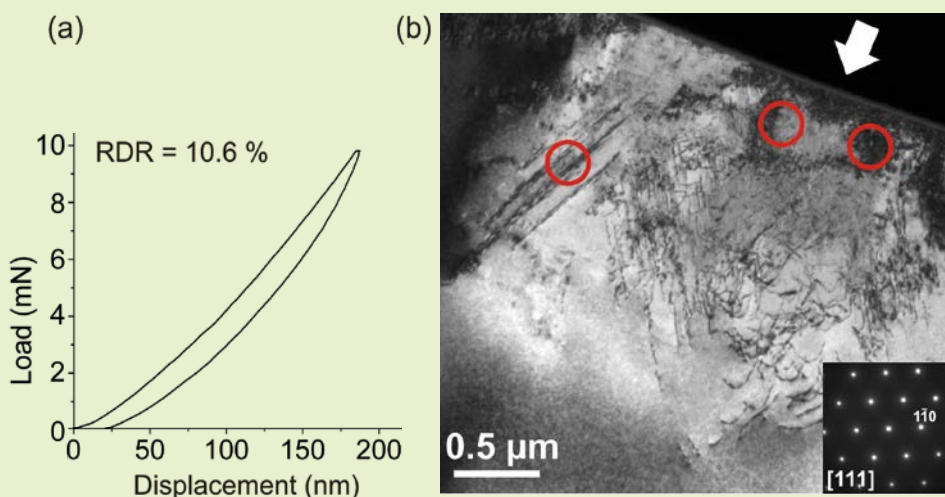


Figure 1: Nanoindentation of a pseudoelastic NiTi SMA. (a) Experimental load displacement curve from indentation in a pseudoelastic NiTi¹. (b) Corresponding post-mortem TEM bright field image of the cross section of the remnant indent¹.

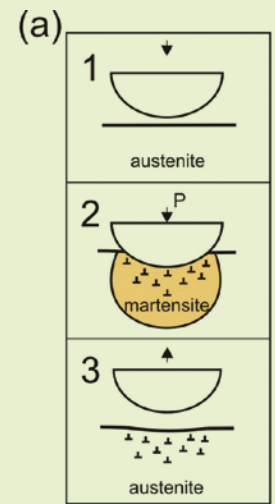
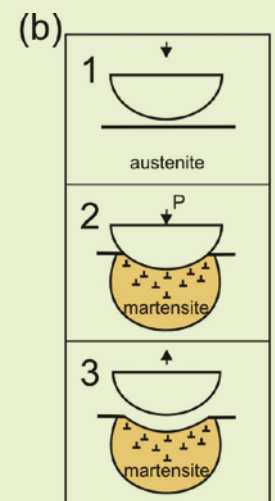


Figure 2: (a) Schematic drawing of the microstructural evolution during nanoindentation of a PE NiTi. (b) Schematic drawing of the microstructural evolution during nanoindentation of a NiTi SMA, where the stress-induced martensite is stable after unloading.



ture with a high dislocation density, especially close to the previous indentation (marked by a white arrow). The red circles indicate regions where diffraction patterns were made. One representative pattern is shown in the inset, exhibiting only spots of the B2 structure. This indicates that during unloading the complete reverse phase transformation to austenite occurs, which is characterized in the load displacement curves by the large recovery during unloading.

During nanoindentation of a PE NiTi, stress-induced martensite and dislocations form during loading, Fig. 2 a. The stress-induced martensite usually completely disappears during unloading (Fig. 2 a), which makes the characterization of the microstructural features of the martensite formation challenging. To observe the stress-induced martensite and to characterize the elementary processes of deformation, we selected a NiTi SMA exhibiting specific phase transformation behaviour.

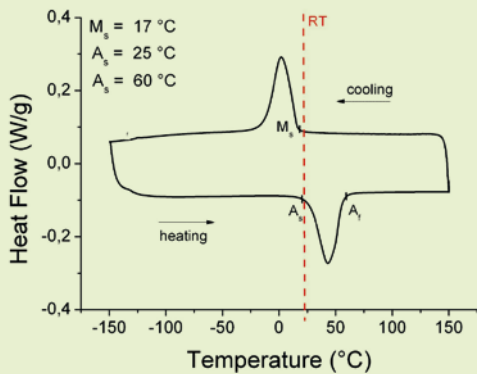


Figure 3: Heat flow temperature diagram for the specific NiTi SMA, which allows the direct observation of stress-induced martensite in post-mortem investigations.

The selected alloy should perform a stress-induced transformation from austenite to martensite during loading and this stress-induced martensite should be thermally stable and remain during unloading (Fig. 2 b) so that it can be investigated post-mortem in TEM. In cooperation with the Processing Group (Dr.-Ing. J. Frenzel and Dipl.-Ing. B. Maaß) at the chair for materials science and engineering, a NiTi alloy with these particular functional properties was produced. Fig. 3 shows a heat flow temperature diagram from differential scanning calorimetry measurements where the specific transformation temperatures can be identified. Our alloy shows a single step phase transformation during cooling and heating with martensite and austenite start temperatures of $M_s = 17\text{ °C}$ and $A_s = 25\text{ °C}$. This means that nanoindentation of this specific NiTi SMA at room temperature results in a stress-induced phase transformation during loading and during unloading the stress-induced martensite is stable. Investigations using this alloy can therefore for the first time provide direct TEM evidence for the formation of stress-induced martensite during nanoindentation. Experiments are currently running.

¹⁾ J. Pfetzling, M. F.-X. Wagner, T. Simon, A. Schaefer, C. Somsen, G. Eggeler, Proc. of ESOMAT 2009, DOI: 10.1051/esomat/200906027.



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Short News

ERC Advanced Grant for SMARTMET

The European Research Council grants about 3 Mio. euros for “SMARTMET – intelligent metals“, where J. Neugebauer and D. Raabe plan a systematic development of new intelligent metal alloys which are needed e.g. for cars, turbines, and biomedical materials. Smallest crystalline changes determine the properties of these materials. The investigations will be theoretical at one side, experimental on the other side: i.e. a combined theoretical-experimental approach is pursued. Neugebauer’s department “Computational Materials Design” will forecast properties of new alloys. The aim is to find hard and ductile alloys by combining stable and instable phases in one material. Under harsh conditions, e.g. a crash, the instable phase becomes stable. These predicted alloys will be fabricated in Raabe’s department “Microstructure Physics and Alloy Design” and analyzed down to the atomic scale.



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